



Nano-engineered Solutions for Sustainable Environmental Cleanup

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Abstract

Nanotechnology, with its distinctive characteristics and versatile applications, demonstrates considerable potential in detecting, removing, and degrading pollutants such as heavy metals, organic compounds, and microplastics. The utilization of nanotechnology for environmental remediation presents a promising and innovative approach to tackle the growing environmental challenges. This review article offers a thorough examination of recent advancements in nanotechnology and its application in addressing various types of environmental pollutants and highlights the potential of nanomaterials, such as metal-based nanoparticles, carbon nanotubes, and nanofibrous membranes, in various remediation processes. The article investigates the underlying mechanisms of nanomaterials in pollutant adsorption and degradation, highlighting the significance of their high surface-to-volume ratio, enhanced reactivity, and customizable surface properties. Nanoadsorbents demonstrate high adsorption capacities and selectivity for the removal of pollutants from water and soil. Nanofiltration membranes offer precise separation capabilities for the removal of contaminants from water sources. Photocatalysis using nanomaterials shows promise for air pollution remediation. Additionally, the development of nanosensors enables real-time monitoring and detection of pollutants. Overall, nanotechnology offers innovative and efficient solutions for addressing environmental pollution.

Keywords Nanotechnology · Nano-remediation · Nano-adsorption · Nanotubes · Nano-sensor · Photocatalysis

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1 Introduction

Environmental pollution is the introduction of harmful elements or contaminants into the natural surroundings, causing unfavorable alterations [168]. These pollutants can manifest in different ways, including chemical substances or various forms of energy like noise, heat, or light [158]. The main categories of environmental pollution encompass air pollution, water pollution, and soil pollution. The rapid development of human civilization in the late nineteenth century occurred as a result of the industrial revolution. However, the increase in urbanization and industrialization over the years has degraded the quality of the environment [15]. As a consequence of traditional disposal practices of industrial waste materials, there has been an increase in the toxicity of groundwater and air which in turn is affecting both human health and wildlife [106]. Due to all such malpractices, human society in the twenty-first century is facing major environmental issues such as global climate change and pollution which can pose a great threat to human health and the ecosystem.

Air pollution is primarily caused by the release of harmful substances into the atmosphere, largely resulting from human activities such as the combustion of fossil fuels for

electricity, transportation, and industrial processes [22]. This contamination can lead to respiratory illnesses and other health issues in humans, adversely affect animals, damage crops, and contribute to climate change [211]. Recent statistics indicate that even a slight increase of 1 $\mu\text{g}/\text{m}^3$ in PM_{2.5} particles can lead to a 15% rise in the COVID-19 mortality rate [61]. Water pollution, on the other hand, transpires when detrimental substances like chemicals or microorganisms contaminate a body of water, compromising its quality and rendering it hazardous to both humans and the environment [106]. The commercial production of chemicals raises concerns about their potential to pollute oceans and other water bodies. Ensuring clean water sources is a critical global issue in contemporary times. The World Health Organization (WHO) reports that a staggering 844 million individuals lack access to safe drinking water, and out of these, 159 million depend on surface water [11]. Soil pollution arises from the introduction of artificial chemicals or modifications to the natural soil environment. It commonly results from industrial practices, the use of agricultural chemicals, or improper waste disposal [10]. This contamination poses risks to living organisms within the soil and has detrimental effects on plants, setting off a cascade of consequences that impact entire food chains [8].

The exacerbation of air, water, and soil pollution leads to various problems. For instance, the presence of airborne fine particulate matters (PMs) raises the risk of acute and chronic respiratory diseases, heart disease, stroke, and lung cancer. According to world health statistics, drinking water pollution was responsible for almost 900,000 deaths related to diarrhea globally in 2016, with over 470,000 of those deaths being children. Soil pollution from heavy metals and persistent organic pollutants (POPs) poses health hazards, causing concerns about metal poisoning or endocrine-disrupting effects, particularly affecting developmental processes during early life stages [92]. Environmental pollution, often unnoticed but culpable, requires more attention in understanding the origins of stubborn human diseases. WHO estimates that roughly 24% of deaths are linked to environmental factors, encompassing hazardous biological, physical, and chemical elements in the environment. Biohazard factors in the environment fall under the category of traditional environmental hazards [124], which include pathogenic bacteria, viruses, and parasites. The infamous COVID-19 pandemic, caused by the emergence of the COVID-19 virus in late 2019, has swept across the globe, inflicting a devastating impact on global public health. As of May 1, 2021, the World Health Organization (WHO) reported that the COVID-19 pandemic had affected over 153 million individuals and led to more than 3.2 million fatalities [240].

A diverse range of materials can be utilized for environmental remediation, leading to numerous approaches available for this purpose. The complexity of pollutant mixtures,

their high volatility, and low reactivity make their capture and degradation challenging. In light of this, recent research has been concentrating on the application of nanomaterials to create innovative environmental remediation technologies. Nanotechnology involves the creation and manipulation of materials at the nanometer scale, achieved by either enlarging single-atom assemblies or refining and reducing bulk materials [141]. Currently, nanotechnologies are widely acknowledged for their potential to offer benefits across various domains, such as medical research, water purification, environmental remediation, communication and information technology, and the development of stronger and lighter materials [40]. The application of nanotechnology shows promise in improving environmental conditions in the air, water, and soil. Nanotechnology enables the creation of innovative advanced materials used in more effective techniques for treating water and wastewater. These methods encompass various applications like membranes, materials for adsorption, nano catalysts, modified surfaces, protective coatings, and chemical agents [39]. It has the potential to aid in the development of innovative cleanup techniques through improved detection and sensing of contaminants. Understanding the creation and growth dynamics of nanoparticles is essential to effectively prevent pollutants and reduce emissions [131]. However, while nanotechnology can enhance environmental quality, it also introduces the possibility of new environmental hazards [51, 205].

2 Strategies of Nanotechnology for Environmental Remediation

Nanotechnology has a number of potential environmental benefits for controlling soil, water, and air pollution. The major ways of environmental remediation by nanotechnology are adsorption by nano adsorptive materials, filtration by nano filters, photocatalysis, and sensing and detection.

2.1 Adsorption

Adsorption is one of the most basic and important techniques that are used for environmental remediation [139]. Adsorption is a surface phenomenon where the contaminants are adsorbed on the surface of the material with the help of some physical and chemical forces [123] (Fig. 1). The substance that is adsorbed on the surface is called adsorbate, and the substance on to which it is adsorbed is called adsorbent. Various parameters on which adsorption phenomena depends are temperature, pH, size and surface morphology, adsorbent dose, adsorbate concentration and structure, etc. [96].

Nanomaterial used for adsorption is called nanoadsorbent. A larger surface-to-volume ratio and more active

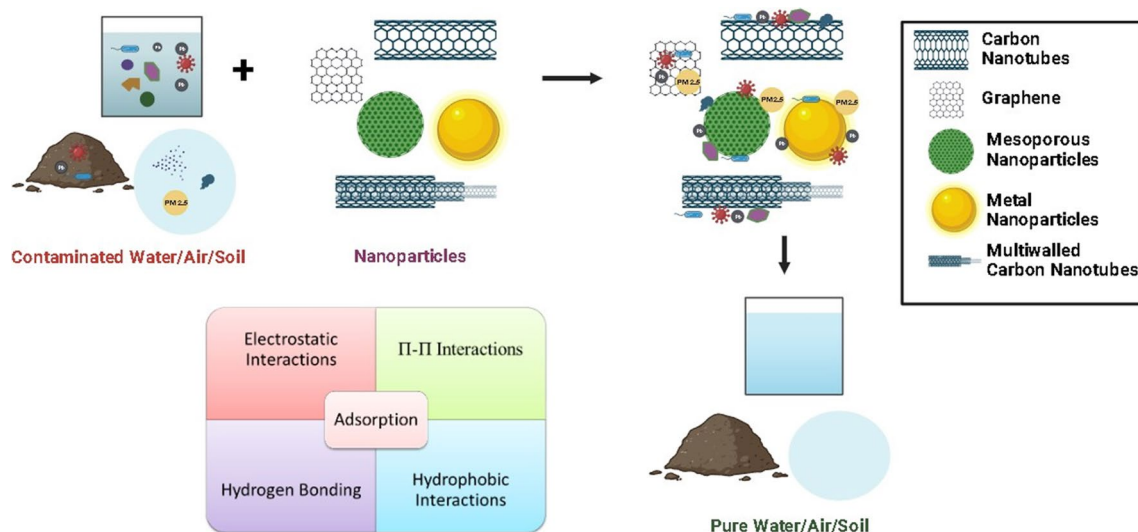


Fig. 1 Nanomaterial-based adsorption for tackling pollutants

sites makes the nanoparticles suitable for environmental remediation through an adsorption mechanism [218]. Nanoadsorbents have nanoscale pores, high selectivity, high permeability, good mechanical stability, and good thermal stability [9]. The adsorption of pollutants is achieved by various forces like forming ionic bonds, covalent bonds, hydrophobic interactions, hydrogen bonds, and van der Waal forces [148].

Generally, there are three steps involved in the process of adsorption [63]:

- (1) The transport of the pollutant from the bulk solution to the surface of the adsorbent
- (2) Adsorption on the particle surface
- (3) Transport within the adsorbent particle

Nanoadsorbents are of two types.

2.1.1 Metal-Based Nanoadsorbents

Different metals (nano silver, nano gold) and metal oxides (MnO_2 , TiO_2 , iron oxides, MgO , ZnO) are used for the removal of pollutants from water, soil, and air, but the majority of the studies have been dedicated to the removal of contaminations like heavy metals and chlorinated organic pollutants from water (Table 1). Metal and metal oxides are very efficient adsorbents with advantages such as fast kinetics and high adsorption capacity [191]. Metal oxides are widely used due to their high surface area which is the most desired characteristic for an adsorbent, specific affinity, and minimal environmental impact [67]. Because of their low solubility and no involvement in the formation of

secondary pollutants, these metal oxides are widely used for the removal of heavy metal ions and dyes from water [191].

Iron Nanoparticles Iron and iron oxide nanomaterials are considered a good option for environmental remediation because of their simplicity and resourcefulness. Three forms of iron oxide can be used as adsorbents, out of which two are magnetic forms: (1) magnetite, (Fe_3O_4), (2) maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and one non-magnetic form hematite ($\alpha\text{-Fe}_2\text{O}_3$) [140, 165].

The applications of magnetic nanoparticles, magnetite, and maghemite have received a great attention as nanoadsorbents due to their unique physical and chemical properties which makes them better adsorbents than the traditional ones [82, 111, 217]. The main advantage of using magnetic adsorbents is that they can be easily removed from the system after adsorption by using simple magnets [138]. The magnetic nanomaterial is covered with the help of some coating material such as silica, metals, metal oxide, surfactants, metal sulfide, and organic molecules to prevent them from oxidation and other chemical degradations which can lower their capacity to work [108]. The most commonly used coating is of silica. These silica coatings improve the chemical stability of these magnetic nanomaterials [258]. These magnetic nanomaterials can be functionalized with different chemical groups to enhance their adsorption capacity. The functional groups can be tightly bonded to the silica coating. For example, an amino-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ is used to adsorb heavy metal ions such as Pb(II) , Cd(II) , and Cu(II) . The increase in adsorption capacity is due to the formation of a complex between the amino group of adsorbents and the metal ions [88, 198]. Thiol-modified $\text{Fe}_3\text{O}_4@$

Table 1 Pollutants adsorbed by metal-based nanomaterials

Sr. no	Adsorbent	Adsorbate	Reference
1	FeNPs	As(III), As(V)	[247]
2	Amino-functionalized Fe ₃ O ₄ @SiO ₂	Cd(II), Cr(II)	[88]
3	Thiol-modified Fe ₃ O ₄	Hg(II), Pb(II)	[73]
4	Humic acid-coated Fe ₃ O ₄	Hg(II), Cd(II), Cu(II), Pb(II)	[262]
5	γ-Fe ₂ O ₃	Pb(II), Sb(III)	[70]
6	Porous Fe ₂ O ₃	Pb(II), CR(II)	[136]
7	Fe ₂ O ₃	As	[38]
8	AgNPs	Cu ²⁺	[18]
9	AgNPs	Hg ²⁺	[186]
10	AgNPs	Cd ²⁺	[17]
11	AgNPs	Co ²⁺ , Pb ²⁺	[27]
12	TiO ₂	Pb ²⁺	[65]
13	TiO ₂	Cd ²⁺	[197]
14	TiO ₂	Cd ²⁺ , Cu ²⁺ , Pb ²⁺	[84]
15	TiO ₂	Cd ²⁺ , Pb ²⁺ , \	[28]
16	TiO ₂	Pb ²⁺	[193]
17	Fe ₃ O ₄ @SiO ₂	Congo red	[233]
18	Humic acid-modified Fe ₃ O ₄	Rhodamine B	[109]
19	Sodium dodecyl sulfate-modified Fe ₃ O ₄	Methyl violet	[110]
20	Fe ₃ O ₄ @PDA	Methylene blue	[259]
21	Fe ₃ O ₄ @C	Methyl orange	[259]
22	γ-Fe ₂ O ₃	Acid Red 27, Acid Orange 52	[113]
23	α-Fe ₂ O ₃ nanorods	Congo red	[145]
24	AgNps	Rhodamine B	[29]
25	AgNPs	Reactive turquoise blue dye	[35]
26	AgNPs	Malachite green	[59]
27	AgNps	Naphthalene	[1]
28	AgNps	Tetracycline, levofloxacin, benzylpenicillin	[83]
29	Sulfosalicylic acid-modified TiO ₂	Methylene blue	[154]
30	TiO ₂	Rhodamine B	[221]

SiO₂ is found to adsorb heavy metal mercury (Hg) and lead (Pb). The strong interaction between thiol group and Hg leads to efficient adsorption [73, 262] developed humic acid-coated Fe₃O₄ nanoparticles for the removal of heavy metal ions Hg(II), Pb(II), Cd(II), and Cu(II). Humic acid-modified Fe₃O₄ can be used to adsorb a dye named rhodamine B which is a fluorescent dye and is highly toxic [109]. Sodium dodecyl sulfate-modified Fe₃O₄ can be used for removal of methyl violet dye. Sodium dodecyl sulfate is an anionic surfactant that can produce a negative surface on the nanoparticle and enhance the adsorption of cationic dyes [110]. When the adsorption capacity of polydopamine-coated Fe₃O₄ (Fe₃O₄@PDA) and carbon-coated Fe₃O₄ (Fe₃O₄@C) was compared, it was found that Fe₃O₄@PDA adsorb methylene blue more efficiently and Fe₃O₄@C adsorb methyl orange due to the electrostatic interaction between the adsorbate and the adsorbent [259].

Porous Fe₂O₃ nanoparticles can be used for the adsorption of various heavy metals and organic compounds from contaminated water [244]. Pb(II) and Cr(II) can be adsorbed on the porous Fe₂O₃ nanoparticles [136]. According to Li et al. [136], the cationic metal ions are adsorbed on the nanoparticles with the help of chemical bonding between the oxygen ion of the porous Fe₂O₃ surface and the cationic metal ion. The anionic metal ion adsorption is facilitated by ion exchange and electrostatic interactions and organic contaminants by surface complexation.

Magnetic ion exchange resins (MIEX^R) can be used for the removal of various pollutants such as natural organic matter, antibiotics, micropollutants, and dyes from water. Magnetic ion exchange resin is added to the water treatment plant in the form of beads. These resin beads have magnetic properties, small size, and high surface area that make them a good adsorbent.

Silver Nanoparticles Silver nanoparticles are used efficiently for the removal of various contaminants from soil, water, and air because of their low toxicity, antimicrobial activity, small size, and large surface area [74, 216]. Silver nanoparticles (AgNPs) can adsorb various heavy metals, for example Cu^{2+} [18], Hg^{2+} [212], Cd^{2+} [17], Co^{2+} , and Pb^{2+} [27], different harmful dyes such as rhodamine B [29], reactive black, reactive navy blue, remazol brilliant blue R [87], and malachite green [59, 81], other organic pollutants like phenol [25] and naphthalene [1], and antibiotics like tetracycline, levofloxacin, and benzylpenicillin [83].

TiO₂ Nanoparticles Titanium oxide (TiO₂) has been extensively studied for waste treatment and air purification because of its low toxicity, low cost, semiconducting behavior, and photocatalytic activity [156, 219]. The crystalline form of TiO₂ is more photoactive than its amorphous form, and the amorphous form is used effectively for adsorption in non-photocatalytic processes because of its small particle size, disordered surface structure, and high surface area [213]. TiO₂ nanoparticles adsorb various inorganic and organic contaminants from water which are given in the Table 1. TiO₂ is also used for sewage water treatment by adsorption of heavy metals such as cadmium [197], lead, and copper [84]. TiO₂ NPs adsorb heavy metals from soil also. For example, TiO₂ nanomaterials were used for removal of harmful heavy metal Pb(II) from the soil through an integrated remediation approach using TiO₂ nanomaterial and plant root-associated bacteria [65]. These nanomaterials can be surface-modified to increase their adsorption efficiency. For example, TiO₂ nanomaterial surface modified with sulfosalicylic acid is used to efficiently remove methylene blue [154].

2.1.2 Carbon-Based Nanoadsorbents

The use of nanoscale carbon has many advantages over the conventional materials because of the much larger surface area and structural and electronic properties that can make them powerful adsorbents. The advantages of these materials in environmental remediation are due to their great capacity to adsorb a wide range of pollutants (Table 2), fast kinetics, and good surface area [94]. Carbon possesses mutable hybridization states. This mutable hybridization along with structural arrangements possessed by carbon materials makes them a better remediation tool than metal-based nanomaterial [100]. These mutable hybridization states make it possible for carbon nanomaterial to obtain different systematic configurations such as carbon nanotubes (single walled and multi-walled) and graphene [94].

Carbon nanotubes (CNTs) are cylindrical molecules consisting of rolled-up sheets of single single-layer carbon

atoms (graphene) [80]. Carbon nanotubes are of two types: single-walled with a diameter of less than 1 nm or multiwall that consists of several concentric interlinked nanotubes, with a diameter reaching more than 100 nm. These nanotubes have ultra-high strength, low-weight material that possesses highly conductive electrical and thermal properties which makes them highly attractive for different applications [69]. Nowadays, carbon nanotubes are emerging as potential adsorbents because of their well-defined cylindrical hollow structure, large surface area, high aspect ratios, hydrophobic walls, and easily modified surfaces [222].

The sites at which adsorption can take place on CNTs are as follows: (1) external surface of CNTs, (2) internal surface of CNTs, (3) interstitial pathway between individual nanotube sheets, and (4) external groove sites [188].

The adsorption characteristics of the carbon nanotubes can be altered by the introduction of the desired functional group on its surface according to the nature of the adsorbate. For example, the oxidation of CNTs with the help of NaOCl, HNO₃, and KMnO₄ increases the adsorption of divalent metal ions [85, 181]. Based on the method of synthesis of nanotubes, these can have different functional groups such as $-\text{OH}$, $-\text{C}=\text{O}$, and $-\text{COOH}$ which makes it polar and help in the removal of polar pollutants. These CNTs can be used for the remediation of water by adsorption of heavy metals. Metal ions can be adsorbed by carbon nanotubes by electrostatic attraction and chemical bonding. Different heavy metals that can be removed with the help of CNTs are Cu^{2+} , Pb^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} [2, 85, 133, 194, 204], chromium (VI) [19, 101, 207], arsenic [76], and mercury [78]. Carbon nanotubes are also capable of adsorbing dyes from water such as methylene blue and Safranin O [246]. Yadav et al. [246] observed that the adsorption of the dyes was affected by changes in temperature, and 30 °C was noted as the optimum temperature. Some other dyes that can be adsorbed with the help of carbon nanotubes are Direct Yellow 86 (DY 86), Direct Red 224 (DR 224) (both used in fabric and paper coloring) [122], reactive blue, reactive yellow (used for dyeing natural fibers), and Acid Red 183 (applied in wool and leather color) [66, 68, 235]. An order in the adsorption of dyes from water with the help of carbon nanotubes is also reported, single single-walled carbon nanotubes have a higher adsorption capacity than multiwalled carbon nanotubes, and functionalized and carbon nanotubes composite have a better adsorption capacity than carbon nanotubes [66].

Organic pollutants such as polar and non-polar organic compounds can also be adsorbed from the environment with the help of CNTs. According to Díaz-Flores et al. [72], adsorption capacity of CNTs increases in order non-polar aliphatic < nonpolar aromatic < nitro aromatics, and within nitro aromatics, the adsorption affinity increases

Table 2 Pollutants adsorbed by carbon-based nanomaterials

Sr. no	Adsorbent	Adsorbate	Reference
1	HNO ₃ -treated MWCNTs	Pb ²⁺	[85]
2	Oxidized MWCNTs	Cr(VI)	[207]
3	Acidified MWCNTs	Cr(VI)	[101]
5	MWCNTs	Cd ²⁺ , Pb ²⁺ , Cu ²⁺ , Zn ²⁺	[2, 75]
6	Oxidized CNTs	Cd ²⁺ , Zn ²⁺ , Pb ²⁺ , Ni ²⁺ , Cu ²⁺	[85, 181]
7	MWCNTs coated with iron oxide	As	[3]
8	MWCNTs	Hg(II)	[195]
9	CNTs	Methylene blue and Safranin O	[68]
10	CNTs	Direct Yellow 86, Direct Red 224	[122]
11	MWCNTs	Reactive Blue4, Acid red 183	[235]
12	CNTs	Naphthalene, Phenanthrene	[226]
13	SWCNTs	Organic vapors	[239]
14	CNTs	Trihalomethanes	[58]
15	Pristine graphene	Toluene	[115, 116]
16	Fe-doped graphene	CO, CO ₂ , SO ₂ , H ₂ S	[62]
17	Graphene-coated iron oxide	Pb ²⁺ and As ³⁺	[114]
18	Calcined graphene	Cr(VI)	[214]
19	MOF graphene	Ni(II)	[178]
20	N-doped graphene oxide	Congo red dye	[249]
21	Magnetic β-cyclodextrin-graphene oxide	Malachite green	[227]
22	Graphene oxide	Methylene blue	[152]
23	Reduced graphene Oxide	Methylene blue and methylene orange	[152]
24	Graphene oxide	Phenolic compounds	[47]
25	Activated Graphene nanosheets (KOH treated)	p-nitrotoluene, naphthalene, phenanthrene	[229, 234]
26	Reduced graphene oxide	1-Naphthol	[13]
27	Hexadecylamine graphene quantum dots (hexadecyl-GQDs)	Phenanthrene	[119]

with number of nitro functional groups. Polycyclic aromatic hydrocarbons (generally produced when coal, oil, gas, wood, garbage, and tobacco are burned) such as naphthalene and phenanthrene can be adsorbed at CNTs [226]. Organic vapors such as toluene, methyl ethyl ketones, hexane, and cyclohexane can be adsorbed at SWCNTs in an order of toluene > methyl ethyl ketone > hexane > cyclohexane [58, 239].

Graphene is a single layer of carbon atoms that is organized in a hexagonal lattice and has several environmental applications [121]. Graphene is incredible flexibility but have a tensile strength more than 200 times to steel and ultra-light in weight. Graphene has very wide surface area so is used as an efficient nanoadsorbent [173, 174].

Another form of graphene used for nanoadsorption of pollutants is graphene oxide which is an extension of carbon material that has two-dimensional structures and is produced by the oxidation of graphite layer by chemical methods. Graphene family nanomaterials comprise different types of nanomaterials like graphene oxide (GO), reduced graphene oxide (rGO), pristine graphene (pGr), few layer graphene (FLG), and multilayer graphene (MLG) [173, 174]. These

graphene or graphene oxides can be functionalized with carboxyl, hydroxyl, carbonyl, and epoxide groups to increase their adsorption capacity [128]. Because of this wide range of functional groups, graphene fits to an ideal option for adsorption. These nanomaterials remove the contaminants through pi–pi interactions and electrostatic interactions [236]). Reduced graphene oxide has higher hydrophobicity and larger Pi conjugated area compared to GO, leading to a higher affinity of rGO than GO to hydrophobic compounds and aromatic compounds [55]. The graphene oxide itself can work straightforward on the adsorbate and absorb the pollutants at very impressive levels [228, 230].

This graphene can be used for the removal of various pollutants from air water and soil. For example, pristine graphene is used for the removal of volatile organic compounds like toluene from air at low concentration of about 30 ppm. The adsorption of toluene on pristine graphene is because of the pi–pi interactions between pristine graphene surface and toluene molecule [115, 116]. According to [115, 116], the efficiency of pristine graphene for the removal of toluene is about 98%. Fe-doped graphene is used for the

efficient removal of various harmful gases like CO, CO₂, SO₂, and H₂S. But the CO₂ interaction turns unstable onto Fe-graphene by co-adsorption of O₂ in the presence of O₂ in the environment [62]. Graphene can adsorb various heavy metal pollutants from water; for example, graphene-coated iron oxide (GCIO) is used for the adsorption of lead Pb²⁺ and arsenic As³⁺ ions from aqueous solution. According to Khare et al. [114], the maximum removal of the Pb²⁺ ion achieved was 97.62%, and that of As³⁺ was 86.62%. Other heavy metal ions that can be removed with the help of graphene are chromium Cr(VI) by adsorption on calcined graphene [214], Ni(II) adsorption on metal–organic framework-graphene (MOF-Graphene) [178], and Hg²⁺ removal by functionalized graphene oxide, a poly (allyl acetoacetate)-grafted graphene oxide with an efficiency of 95% within 2 min [5]. The adsorption capacity of graphene and its compounds can be used for the removal of various dyes. Congo red dye, an azo dye that is used to dye cotton and has very negative effects at very low concentration, can be adsorbed by N-doped graphene oxide [249], adsorption of malachite green, used to dye silk paper and leather and is considered as carcinogenic, mutagenic and can cause respiratory toxicity using magnetic β-cyclodextrin-graphene oxide nanocomposite [227]. When the adsorption of cationic dye (methylene blue, MB) and anionic dye (methylene orange, MO) was compared on adsorbent graphene oxide, GO and reduced graphene oxide, rGO by Minitha et al. [152]. It was found that reduced graphene oxide showed high adsorption capacity toward both MB and MO and graphene oxide efficiently adsorbed MB as compared to MO. The reason behind this was found that the interactions between cationic dye and graphene oxide are facilitated by oxygen functional group, and adsorption is through electrostatic interaction whereas interaction of cationic and anionic dye with reduced graphene is facilitated by oxygen functional group and vacancy defect, and the adsorption is via electrostatic interaction and pi–pi interactions. Various organic pollutants are removed with the help of graphene family–based nano-adsorption such as phenolic compounds like phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and bisphenol A (BPA). Their adsorption involves electrostatic interaction, pi–pi interaction, and hydrogen bonding between the adsorbate and graphene oxide. GO has the highest adsorption affinity for phenol because of formation of the hydrogen bond [47].

To increase the adsorption capacity of graphene, nanosheet wrinkles or folds can be introduced. For examples wrinkles and folds were introduced by thermally treating the graphene nanosheets (GNS) with KOH to produce activated graphene nanosheets (AGN). This increased the surface area and micropore volume of AGN as compared to GNS. When the adsorption capacity was compared, the adsorption of organic contaminants p-nitrotoluene, naphthalene, and phenanthrene was greatly enhanced at AGN as compared to

GNS. Small molecules also showed higher adsorption due to increased pore volume on the surface of graphene [229].

2.2 Nanofiltration

Nanofiltration is the separation process by membranes of nano pore size. It is a pressure-driven process located between ultrafiltration and reverse osmosis and usually operated at a trans membrane pressure of 5 to 40 bar [16]. Filtration by membrane technologies is reliable because of efficient removal of contaminants without production of any harmful by-product. The basic principle on which membranes work is the use of semipermeable membranes that can remove the pollutants [189] (Fig. 2). Membrane technologies are mostly used for the purification of water because of low energy consumption and highly precise separation. Basically, these membranes are permeable to water and less permeable to solutes [149]. The conventional separation methods like reverse osmosis, ultrafiltration, and microfiltration are being used widely overall the world. But these methods remove all the solute, and nanofiltration membranes remove only selective solutes and can retain the important ones [171]. Advantages of using nanomaterial-based membranes are higher selectivity, more energy efficiency, high reactivity, and faster reaction rates. These nanomaterial-based nanomembranes can separate the inorganic contaminants like heavy metal and organic contaminants from water [242] (Table 3). One more advantage of using nanomaterial-based membranes is that nanomaterials have some extra properties like chemical degradation, photocatalysis, and antimicrobial activities [248].

Nanofiltration membranes can be classified in two categories based on the material they are made up of carbon nanomaterial–based filtration membranes or metal and metal oxide nanomaterial–based filtration membranes.

Nanomaterial-based filtration membranes can remove the hardness of water and organic matter from water [48]. Hardness of water is a major issue generally caused by bivalent ions such as calcium Ca²⁺ ions and magnesium Mg²⁺ ions. Nanofiltration membranes can remove these divalent ions with high degree of efficiency. For example, a nanofiltration membrane fabricated with polyethyleneimine (PEI) three channel capillary ultrafiltration membrane modified with piperazine grafted MWCNT-OH was found to have a high rejection rate (>97%) toward divalent ions (Ca²⁺ and Mg²⁺) but a low rejection rate (<70%) toward the monovalent ions (Na⁺ and Li⁺). So, these membranes exhibit good ability for water softening and separation of Mg²⁺ and Li⁺ ions from mixed salt solutions [253].

The efficiency of the membranes can be increased by adding some specific compounds; for example, a monomer, trimesoyl-[4,4-dimethyl-5(4H)-azolactone] (TMDMA), was used as a secondary reaction molecule in semi-aromatic

Fig. 2 Nanofiltration in pollutant cleanup

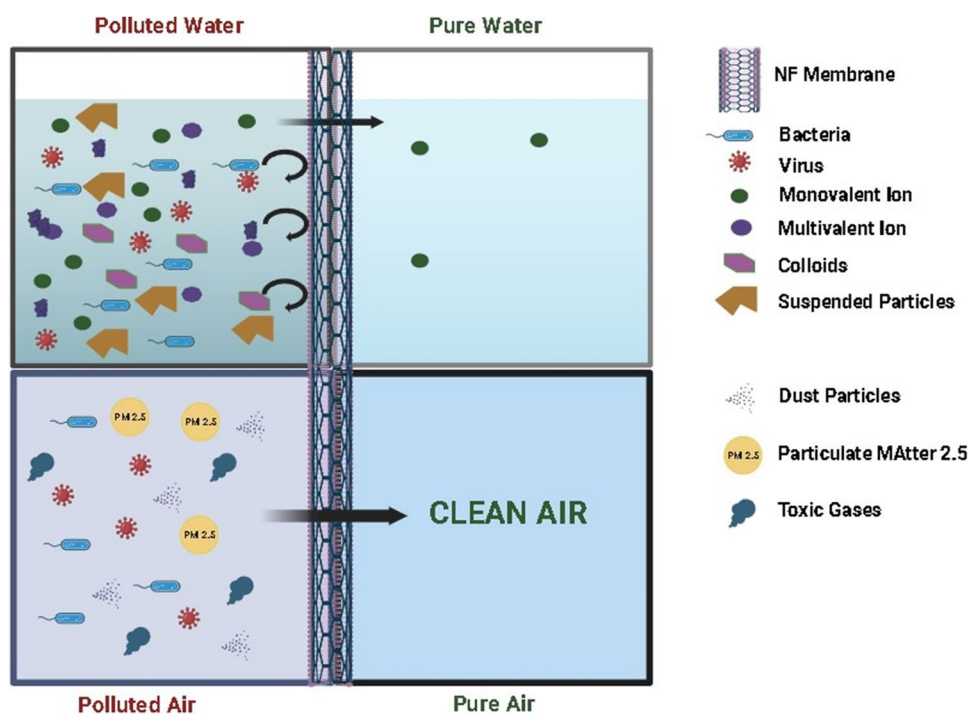


Table 3 Efficient nanomaterials for targeted pollutant capture

Sr. no	Nanomaterial	Contaminant filtered	Reference
1	Carbon nanomaterial	Zn^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+}	[220]
2	MWCNTs	Zn^{2+}	[14]
3	MWCNT-OH/polyethyleneimine	Hardness of water (Ca^{2+} , Mg^{2+} ions)	[253]
4	SiO_2	Na_2SO_4 , $MgSO_4$, $MgCl_2$, $NaCl$	[206]
5	Chitosan	Nitrate	[89]
6	Branched Polyethyleneimine (bPEI) and poly (acrylic acid)/ tungsten oxide/polyacrylonitrile PAA/ WO_3 /PAN composite	Oil water separation	[142]
7	Reduced-graphene oxide/carbon nanotubes	Methyl orange	[56, 107]
8	Hydrolysed aluminum	Bisphenol A	[232]
9	Polyacrylonitrile	$PM_{2.5}$	[180]
10	Graphene oxide/polyacrylonitrile composite	$PM_{2.5}$	[132]
11	Cerium oxide (CeO_2)	<i>Escherichia coli</i>	[125]

polyamide nanofiltration membrane. This compound narrowed the pore size and decreased the surface charge which in turn increased the rejection rate of Mg^{2+} and Ca^{2+} ions [251].

Nanofiltration membranes can remove the heavy metal ions from the water by physical absorption or by chemical interactions like hydrogen bonding or by polymerization. For example, heavy metal ions Zn^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+} were removed by using carbon nanomaterial synthesized from carbon, and hyper-branched polyethyleneimine HPEI was used as a crosslinking agent. The efficiency of rejection of heavy metal ions was found to be around 95% with a rejection sequence of $Zn^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Pb^{2+}$

[220]. Functionalized carbon nanotubes are a great option for removal of heavy metals like zn^{2+} ions by complexation reaction. The functionalized carbon nanotubes were found to have a rejection capacity of about 98% toward Zn^{2+} ions [14]. A nanofiltration membrane using SiO_2 nanoparticles was fabricated with poly (amidoamine) dendrimer and trimesoyl chloride (TMC). Nano SiO_2 improved the thermal stability, hydrophobicity, and membrane permeation properties without any loss to the rejection capacity. The order of salt rejection rate noticed was $Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$ [263].

The nanofiltration membranes work by size exclusion, by sieving, or by interacting electrostatically with the molecules

[77]. In case of uncharged molecules, separation occurs by the sieving method, and in case of ionic molecule separation, filtration is done by both electrostatic interactions and size exclusion [203]. The surface and pore charge play a significant role in separation of solutes from the water.

Nanofiltration membranes are commonly used for the filtration of natural organic matter from water which is a key component of the water [200]. Natural organic matter affects the quality of water as carrier of metals and hydrophobic organic compounds and contributes to the undesirable taste, color, and odor problems [150]. The natural organic matter like humic acid and fulvic acid can be efficiently removed with the help of nanofiltration membranes [153]. For the removal of hydrophobic organic matter, hydrophilic nanofiltration membranes are used. The membranes can remove the hydrophobic organic matter more efficiently at higher pH, i.e., a high rejection rate at higher pH and a low rejection rate at lower pH [250]. The nanofiltration membranes have smaller pores that can reject the organic contaminants that otherwise will pass through ultrafiltration membranes. Nanofiltration membranes can effectively filter the biological contaminants. Cerium oxide (CeO_2) nanoparticle-embedded polyamide filtration membrane was found to effectively reduce the attack of bacteria *Escherichia coli* when compared to the pure polyamide membrane [125].

Most major problem in operation of nanofiltration system is fouling of the membranes. Fouling is the irreversible deposition of the retained particles, macromolecules, colloids, and salts on the membrane surface or within the pores of the membrane [144]. Fouling is often caused by the colloidal particles and natural organic matter. This fouling can reduce the quality and quantity of the filtered water and increases the cost of treatment [261]. When concentration of the ionic salt increase in the solution more than its solubility, they start forming precipitates and cause damage to the membrane by plugging of the pores [175]. Inorganic foulants involved in nanofiltration membrane fouling are often carbonates, phosphates, and sulfates of divalent metal ions [137]. Natural organic matter also causes the fouling of the membrane by various mechanisms like adsorption, gel formation, precipitation, and interactions with multivalent ions or by reacting with the membrane polymers [199]. The natural organic matter acts as feed for the microorganism, hence increasing their concentration and ultimately leading to membrane fouling by the accumulation of microorganisms on the surface of the membrane [176]. The colloidal particles lead to the membrane fouling by the process of cake formation by accumulation of colloidal particles on the membrane surface [31].

To prevent the membrane fouling, several preventive measures can be taken as pre-treatment such as pre-coagulation, adsorption, and oxidation of water to be treated is suggested that can optimize the pH and ionic strength of the

feed solution. This results in low salt precipitation and less membrane fouling [250]. Selection of the membrane with optimum pore size can result in the reduced fouling. Cleaning of the membrane is helpful in the reduction of fouling. Cleaning involves the addition of some chelating agents to feed solution like EDTA which can decompose aggregates which foul the membrane by depositing on it [238].

One of the major problems is oil water separation from oil-contaminated waste water because the tiny oil droplets are very disadvantageous to environment and is very difficult to treat [86]. The traditional filtration methods can make the water adequate for the discharge, but the water is inappropriate for reuse [172]. This can be solved with the help of nanofiltration membranes as these can remove most of the water from the emulsion and make it recyclable in a cost-effective manner. Compared to traditional treatment methods, membrane technology presents benefits such as efficient oil removal, a compact design, reduced reliance on chemical additives, and consistent effluent quality [161]. The filtering material can be hydrophobic and lipophilic that can separate oil or hydrophilic and lyophobic that can separate water from the oil water mixture, or it can be controllable material [44]. When the oil water separation capability of nanofiltration and ultrafiltration membranes was compared, it was found that nanofiltration membranes can provide better separation than ultrafiltration membranes without sacrificing flux and recovery percentage [179].

Air pollution has raised a great concern to the public health. One major factor that contributes to the air pollution is particulate matter $\text{PM}_{2.5}$. $\text{PM}_{2.5}$ are the tiny particles or droplets having size $2.5 \mu\text{m}$ or less [132, 234]. Because of the small size, these particles can get deep into lungs and can cause various respiratory disorders like lung cancer and asthma. This particulate matter can get indoor from outdoor and is hazardous to human health, and this needs to be prevented [135]. Nanofibrous membranes are a great option for it. Nanofibers have the effective diameter for fine filtration. Hot gas filters were created using a structure consisting of a polyimide nanofiber membrane situated between layers of woven carbon fabrics, with the aim of capturing fine particles at the $\text{PM}_{2.5}$ level. These polyimide (PI) nanofibers, averaging 190 nm in diameter, were electro spun onto carbon fabric supports to form the filtration layers. Performance tests for filtration demonstrated an impressive maximum efficiency of 99.99% in capturing $\text{PM}_{2.5}$ particles.

Various polymers are being used for fabrication of nanofibrous membranes. Among various methods of nanofibrous membranes, electro spinning is the one which is used mostly. Most commonly used polymer is polyacrylonitrile (PAN) as it is easy to electro spun, commercially available, thermally stable, and tolerant to many solvents. Nanofibrous membrane fabricated using polyacrylonitrile

(PAN) showed very high air dust filtration of more than 99.99% in between $PM_{0.3}$ and $PM_{2.5}$ [180]. Graphene oxide/polyacrylonitrile composite fabricated nanofibrous membranes also showed an efficiency of 99.97% toward $PM_{2.5}$ removal from air [132].

Now, with the help of technology, smart nanofibrous membranes are being prepared. These smart nanofibrous membranes have self-healing properties; i.e., they can repair the damage even in the presence of water which increases their durability and the efficiency to remove the contaminants [43, 256]. These membranes are fabricated by layer-by-layer assembly. Layer-by-layer assembly of the polymer increases the strength and toughness of the membrane. Ma et al. [142] fabricated a multifunctional membrane using branched poly (ethylenimine) (bPEI) and poly (acrylic acid) (PAA)/tungsten oxide (WO_3)/polyacrylonitrile PAA/ WO_3 /PAN composite by combination of blow spinning and layer-by-layer method. The membrane ensured good oil water separation and had water enabled self-healing properties. These kinds of smart membranes have significant potential for remediation of wastewater.

2.3 Photocatalysis

A chemical reaction can be sped up through a process known as photocatalysis in which a material or photocatalyst uses light energy [243]. In the realm of environmental remediation, where it is applied to the cleansing and detoxification of various pollutants, this phenomenon has attracted considerable interest [50]. Due to their special characteristics, nanoparticles, particularly semiconductor nanoparticles, have demonstrated considerable promise as photocatalyst for environmental remediation [90]. When nanoparticles are used as photocatalyst, they are usually composed of a semiconductor material such as titanium dioxide (TiO_2), zinc oxide (ZnO), or cadmium sulfide (CdS) [147]. These semiconductors have a band gap energy which is the energy difference between the valence band (where electrons are bound to atoms) and the conduction band (where electrons can move freely) [102]. When photons with the energy equal to or greater than the band gap energy are absorbed by the nanoparticle, electron-hole pairs are generated. The excited electrons and holes have high reactivity and can participate in redox reactions with the environmental contaminants [210]. The main benefits of these photocatalysts lie in their cost-effectiveness, stability, potent oxidation capabilities, and non-toxic nature [191]. The detailed process of photocatalysis by nanoparticles for environmental remediation involves a series of steps, including light absorption, charge generation and separation, redox reactions, pollutant adsorption, and degradation. Let's delve deeper into each step:

2.3.1 Light Absorption and Generation of Electron Hole Pair

The process begins when the nanoparticles absorb photons from a light source. Semiconductor nanoparticles have a unique electronic structure characterized by energy levels or bands. The valence band is the highest energy band where electrons are bound to atoms, while the conduction band is the next higher energy band where electrons are free to flow. The energy difference between these two bands is known as the band gap energy [102]. When a semiconductor nanoparticle is exposed to light, it interacts with photons. Photons carry energy that is directly related to their frequency or wavelength. The minimal energy needed to excite an electron in the valence band to the conduction band depends on the nanoparticle's band gap energy. Only photons with energy equal to or greater than the band gap energy can induce such an electron transition [190]. When a photon with adequate energy strikes the semiconductor nanoparticle, it is absorbed, and its energy is transferred to an electron in the valence band. This energy raises the electron's energy level, moving it up to the conduction band. As a result, an electron-hole pair is created: an electron is now in the conduction band, while a positively charged hole is left behind in the valence band [210].

2.3.2 Charge Generation and Separation

The movement of an electron to the conduction band and the formation of a hole in the valence band create an exciton. To efficiently utilize the electron and hole for photocatalytic processes, it is crucial to prevent their recombination [118]. Recombination happens when the electron and the hole annihilate each other, resulting in the releasing of their energy as heat. Efficient charge separation involves spatially separating the electron and hole within the nanoparticle. The efficiency of this step is vital for the overall photocatalytic process, as recombination of the electron-hole pair (which is a competing process) leads to the loss of photocatalytic activity [252].

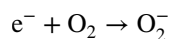
2.3.3 Redox Reaction

After the photo-generated electrons and holes are separated, they can engage in redox reactions with species that have been adsorbed to the surface of nanoparticles or in the environment [143]. The breakdown of pollutants depends heavily on these interactions [32]. The common redox reactions consist of:

- (A) Reduction reactions: Photo-generated electrons can take part in reduction reactions, in which they donate some of their excess energy to an adsorbate species.

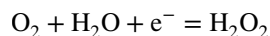
This causes the production of reactive oxygen species (ROS). Some common reduction reactions are:

- (a) Oxygen reduction: Oxygen molecules (O_2) that are dissolved in the surrounding environment can react with photo-generated electrons to create superoxide radicals (O_2^-) or other ROS. This reaction can be represented as:



The superoxide radicals (O_2^-) can further react with water or other species to generate hydroxyl radicals ($\cdot OH$) or other ROS, which are highly reactive and can oxidize organic contaminants [64, 139].

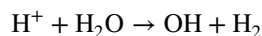
- (b) Production of hydrogen peroxide: In the presence of water, photo-generated electrons can reduce molecule oxygen to make hydrogen peroxide (H_2O_2):



Hydrogen peroxide is a strong oxidizing agent and can contribute to the degradation of pollutants by generating hydroxyl radicals ($\cdot OH$) [192].

- (B) Oxidation reactions: Photo-generated holes are capable of taking part in reactions of oxidation in which they absorb electrons from adsorbed species or water molecules, producing the extremely reactive hydroxyl radicals ($\cdot OH$). Typical oxidation processes include:

- (a) Organic pollutant oxidation: Photo-generated holes can directly oxidize organic contaminants that have been deposited on the surface of nanoparticles. The process involves the transfer of a hole to the adsorbed pollutant that results in the formation of a radical cation ($\cdot +$). Further reactions with water or other species can eventually lead to the production of hydroxyl radicals ($\cdot OH$) and the degradation of the pollutant.
- (b) Water oxidation: Photo-generated holes can interact with the water molecules adsorbed on the nanoparticle surface, leading to the formation of hydroxyl radicals ($\cdot OH$):



Hydroxyl radicals are powerful oxidizing agents and play a vital role in the degradation of various organic pollutants [209].

- (C) Other redox reactions

Depending on the particular nanoparticle and surrounding circumstances, photo-generated electrons and holes can take part in other redox reactions in addition to those indicated above:

- (a) Direct electron transfer: Photo-generated electrons can directly transfer to adsorbed species, leading to their reduction. For instance, the photo-generated electrons can decrease environmental oxidized substances like metal ions.
- (b) Hole scavenging: Photo-generated holes may react with electron donors or scavengers present in the environment. This can happen as a result of interactions with inorganic or organic substances, essentially stopping the electrons from recombining with them and extending the lifetime of the charge carriers.

Highly reactive species like hydroxyl radicals ($\cdot OH$), superoxide radicals (O_2^-), and other ROS are produced as a result of the redox processes started by the photo-generated electrons and holes. These species can target and breakdown organic contaminants that are present in the environment because they have powerful oxidizing or reducing abilities [139, 209] (Fig. 3).

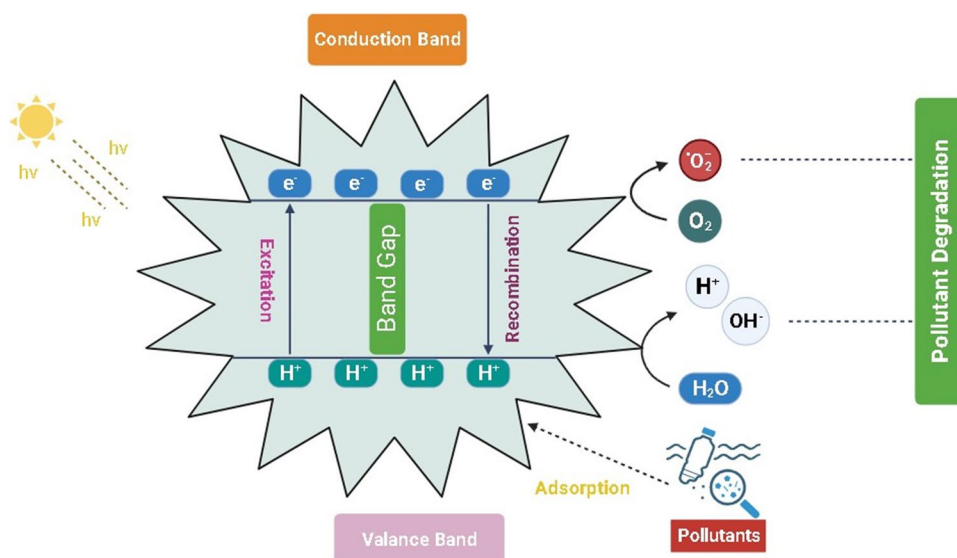
2.3.4 Adsorption of Pollutants

The surface of nanoparticles serves as a site for adsorption of environmental pollutants. Through a variety of interactions, such as electrostatic forces, hydrogen bonds, or van der Waals interactions, the contaminants may bind to the nanoparticle's surface. The adsorption step facilitates the interaction between the pollutant molecules and the reactive species generated by the photocatalyst, improving the degradation efficiency.

2.3.5 Degradation of Pollutants

After being adsorbed, the pollutants interact with the reactive species (ROS) produced during the photo catalytic reaction, which causes the molecules to degrade or convert [209]. The contaminants' chemical bonds are attacked by the reactive species, which causes the pollutants to disintegrate into less harmful, less complex metabolites. Until the pollutant is completely mineralized into carbon dioxide, water, and other safe chemicals, this degradation process continues.

Fig. 3 Nano-photocatalysis for pollutant degradation



2.3.6 Regeneration of the Catalyst

Following the degradation process, the nanoparticle photocatalyst can be renewed for more photocatalytic cycles [185].

A number of metal oxides (including TiO_2 , ZnO , Ag_2O , MoO_3 , ZrO_2 , WO_3 , $-Fe_2O_3$, SnO_2 , and $SrTiO_3$) and metal chalcogenides (including ZnS , CdS , $CdSe$, WS_2 , and MoS_2) can be utilized as photocatalyst [33, 146].

TiO_2 -based photocatalytic oxidation has been widely used to degrade organic pigments due to its stability, affordability, and optical absorption in the ultraviolet (UV) spectrum [98]. However, due to its wide band gap (3.2 eV), TiO_2 's inactivity in visible light severely hampered its large-scale deployment, which is often rectified via band gap engineering [134]. For instance, Khan et al. [112] changed commercial TiO_2 NPs using an electron beam treatment to make them active in the visible light. In addition to this, a number of additional strategies have also been tested to improve the photocatalytic performance of TiO_2 in the visible range. These strategies include doping with the transition metals and plating noble metal ions (Ag, Au, etc.) on the TiO_2 surface [23]. For example, nitrogen doping of TiO_2 fibers by Calisir et al. [45] utilizing polyvinylpyrrolidone as a carrier polymer and nitrogen source considerably increased the sample's ability to absorb light in the visible range when it was created. The green synthesis of narrow-band-gap and visible-light-active TiO_2 NPs utilizing biodegradable components such as plant extracts, microbes, and enzymes is gaining popularity due to its simplicity, affordability, eco-friendliness, and low toxicity [12]. These narrow band gap Ti_2 nanoparticles are a potential to degrade various dyes, volatile organic compounds (VOC), antibiotic, and other organic contaminants [12, 26, 42, 49, 52, 117, 127, 177].

Certain modifications are done to enhance the productivity of titanium nanoparticles. For instance, Mohammadi and Mousavi [155] modified TiO_2 nanoparticles with glycine and β -cyclodextrin and prepared TiO_2 -Gly- β CD photocatalyst for degradation of organic dyes methylene blue (MB) and methyl orange (MO). Results suggested that compared to pure TiO_2 , TiO_2 -Gly- β CD photocatalyst showed a higher degradation rate. Sulfur and nitrogen-doped- TiO_2 nanoparticles were synthesized by Jafari et al. [103] and were found to efficiently photo degrade naphthalene ($C_{10}H_8$) from aqueous environment. Photocatalysis involving TiO_2 proves effective in eliminating NO_x from the car emissions, a growing concern for the urban pollution [184]. By blending the colloidal- TiO_2 solution with cement, the resulting oxidation of nitrogen oxides generates nitric acid, which subsequently reacts with the cement to create calcium nitrate. This compound can be readily washed away by rainwater. Japan has extensively tested this innovative "photo-road technology" for over decades [130].

A significant scientific progress in the area of photocatalysis has been seen in recent years due to the special and very advantageous features of ZnO nanoparticles. ZnO nanoparticles are known to compete favorably with TiO_2 and modified TiO_2 in the visible light-driven photocatalytic destruction of organic contaminants due to their low cost, nontoxicity, and environmental friendliness. In fact, it has been claimed that ZnO exhibits a wider range of solar response in the visible light spectrum than TiO_2 [170]. ZnO is a type II-IV semiconductor with the potential to be used in photocatalytic processes due to its broad band gap of 3.37 eV, high exciton binding energy of 60 meV, efficient UV absorbance, and good chemical stability [129, 201]. The photocatalytic activity of ZnO nanoparticles (NPs) made using the sol-gel process was reported by Chen et al.

[57]. The degradation of Congo red, orange, and DB38 azo dyes was used to test the photocatalytic activity of ZnO NPs, the results showed that the removal rate of azo dyes improved with higher dose of catalyst and decreased the initial concentration of azo dyes. A suitable architecture and structure that reduce the loss of photogenerated electron loss during excitation state and increase photon absorption are necessary for the highly efficient performance of ZnO photocatalyst in heterogeneous photocatalysis reaction. Numerous strategies have been investigated with the goal of improving ZnO's photocatalytic abilities when exposed to visible light. Doping ZnO with metals and metal ions is one of these, and it has grown in popularity among scientists. With less competitive electron-hole recombination, this method has been found to improve photocatalytic properties when compared to undoped ZnO [30, 34].

When ZnO is doped with Fe^{3+} , Ba-Abbad et al. [30] found that the photocatalytic activity is increased. Sol-gel synthesis was employed to create the Fe-ZnO nanomaterial, which was then used as a photocatalyst in the degradation of the model organic pollutant 2-chlorophenol in aqueous solution. According to the authors, $\text{Fe}_{0.8}$ -ZnO has higher photocatalytic activity due to a greater surface area, longer light absorption, and a lower rate of charge recombination. Shirdel and Behnajady [201] successfully achieved 98.40% removal efficiency using Ba/ZnO within 68 min of irradiation under mild alkaline conditions after synthesizing ZnO and Ba-doped ZnO (Ba/ZnO) using a sol-gel method and investigating the photodegradation of rhodamine B using the prepared photocatalysts under visible light illumination. Ba-doped ZnO thin film (ZBO) photocatalyst has recently been shown to have great efficiency and exceptional reusability by Jayakrishnan et al. [105].

One of the promising, effective, and reasonably priced metal oxides employed as a photocatalyst for long-term environmental remediation is Ag_2O -NPs [79]. Silver oxide nanoparticles are an appropriate photocatalyst for the degradation of organic dyes when exposed to the visible light radiation due to their low band gap of 1.46 eV [99, 223]. One of the intriguing characteristics of Ag_2O -NPs is their excellent stability, which leads to significant photocatalytic activity. According to Wang et al. [237], there is a partial production of metallic Ag on the surface of the Ag_2O during photocatalysis of organic molecules, which helps to maintain the stability of the nanophotocatalyst. The photocatalysis process is made more effective by the metallic Ag's involvement in the photodegradation of organic contaminants [237]. Hence, Ag_2O -NPs are a potential candidate as photocatalyst for removal of various contaminants from environment [6, 36, 126, 162, 196, 208].

Infectious diseases including cholera, gastroenteritis, malaria, yellow fever, TB, and anthrax are caused by the

microorganisms like pathogenic bacteria, fungi, viruses, and protozoa that can be found in drinking water and the air. Traditional low-cost disinfectants used in a variety of pH ranges include chlorine, chlorine dioxide (ClO_2), hypochlorite (OCl^-), and ozone. However, when the aforementioned disinfectants are used, halomethanes and halo acetic acids are produced, which are hazardous even at low doses. Since sunshine is regarded as an endless and sustainable resource, research into using solar energy for water sterilization has grown over the past few decades [228, 230]. TiO_2 was the starting point for the development of photocatalysts for water purification in 1985 [151]. Therefore, during the past years, an extensive study has been done on photocatalytic disinfection employing nanoparticles as the photocatalyst. When compared to the breakdown and mineralization of organic matter, the mechanism of photocatalytic disinfection of microbes is highly complex due to bacteria and other live microorganisms' larger size and more complex structure compared to chemical molecules. It initiates a number of mechanisms for cell bursting and regeneration. Cho et al. [60] have demonstrated that the hydroxyl radical concentration in the system is directly related to the inactivation time (for 2-log reduction) of *E. coli* under various reaction conditions. In actuality, hydroxyl radicals play a more significant role than reactive oxygen species, and they are more potent oxidants than chlorine, chlorine dioxide, or ozone. According to Matsunaga et al.'s [151] hypothesis, a decrease in concentration of coenzyme A (CoA), a mediator of electron transfer between the cell and TiO_2 , is responsible for the microorganism's cell wall destruction during photocatalytic breakdown. When *Streptococcus sobrinus* was being digested, Saito et al. [187] saw a "rapid" leakage of potassium ions and a "slow" release of protein and RNA when there was UV/ TiO_2 . They came to the conclusion that inactivation is caused by the bacteria's cell wall losing its permeability. Some composites of TiO_2 have also been found to be effective in pathogen removal. For instance, [115, 116] prepared an active composite photocatalyst rhodium-antimony co-doped TiO_2 nanorods and titanate nanotube (RS-TONR/TNT) from rhodium-antimony co-doped TiO_2 nanorod (RS-TONR) which was capable of disintegration of pathogenic microorganisms like *E. coli*, *S. typhimurium*, and *L. monocytogenes*. Table 4 lists some researches that have been done on the deactivation of various pathogens and contaminants using various nanophotocatalysts.

2.4 Sensing and detection

Nanomaterial-based sensors have the potential for detection of contaminants like organic pollutants, heavy metals, toxins from air, water, and soil [20]. Nanosensors are the devices of nanoscale that are able to detect the presence of any chemical species or physical parameters [104].

Table 4 Nanomaterials for photocatalytic pollutant degradation

Sr. no	Nano-photo-catalyst	Contaminant degraded	References
1	TiO ₂	Methylene blue	[12, 117]
2	TiO ₂	Zoxamide	[177]
3	TiO ₂	Phenol	[169]
4	TiO ₂	VOC	[127]
5	TiO ₂	Methylene blue and methyl orange	[155]
6	TiO ₂ /NS	Naphthalene (C ₁₀ H ₈)	[103]
7	Rhodium-antimony Co doped TiO ₂ rods and Titanium nanotubes	Orange (II) dye, Bisphenol A, <i>E. coli</i> , <i>S. typhimurium</i> , and <i>L. monocytogenes</i>	[115, 116]
8	TiO ₂ nanofiber mats	Naphthalene	[157]
9	ZnO	Congo red, methyl orange, and DB38 azo dyes	[57]
10	ZnO	<i>Escherichia coli</i> , <i>Rhodococcus rhodochrous</i> , <i>Bacillus subtilis</i> , and <i>Vibrio cholera</i>	[163]
11	Fe-ZnO	2-chlorophenol	[241]
12	Ba/ZnO	Rhodamine B	[201]
13	Ag ₂ O-NPs	Malachite green	[6]
14	Ag ₂ O-NPs	Azo dye	[126]
15	Ag ₂ O-NPs	Methylene blue	[196]
16	Ag ₂ O-NPs	Tetracycline	[36]
17	Ag ₂ O-NPs	Caffeine	[162]
18	Ag ₂ O-NPs	<i>E. coli</i> , <i>P. aeruginosa</i> , and <i>B. subtilis</i>	[167]
19	NiO-NPs	Azo dyes	[7]
20	CdS-NPs	<i>E. coli</i> , <i>P. aeruginosa</i> , <i>S. aureus</i> , and <i>E. faecalis</i> , sulfisoxazole, malachite green dye	[160]
21	CdS	Nitrate	[260]

Nanomaterial-based sensors are basically consisting of three components, the first one is a nanomaterial, the second one is a recognition element, and the third is transducer that is used for transduction of signals [166]. When there is the presence of any pollutant (analyte) in the environment, the recognition element (enzymes, antibodies, DNA, proteins) detects the pollutant and produces a signal, and a transducer transduces that into a readable signal [97] (Fig. 4). These nanodevices can be designed to detect only one analyte or more than one analyte called multiplex detection [225].

The use of nanosensors is advantageous as they can detect the unforeseen contaminants of environment that cannot be sensed by the conventional methods (Table 5). These nanodevices are very small in size so are portable, are highly sensitive, specific to the target species, cost-effective, and can be executed very efficiently [21].

The specificity of nanosensors can be employed by use of recognition element that will bind only the target material specifically, and the sensitivity of the nanosensors is a function of magnetic electrical and optical properties of the nanomaterial used and the signal transduction method that is used to generate the signal [93]. Nanomaterials can be classified into various classes based on the nanomaterial used, analyte they detect, and the transduction method. Based on

the signal transduction method, sensors can be optical, electrical, and magnetic [159].

Carbon-based nanomaterials contribute much toward the nanosensor-based detection of pollutants. Carbon nanotube field effect transistor sensors work on the principle that the presence of target molecule causes the change in the electrical conductivity of the CNTs [202]. According to reports, single-walled carbon nanotube (SWCNT)-based nanosensors can detect the presence of Hg²⁺ in water. The detection is based on the response of SWCNTs on exposure to the Hg²⁺ ions that result in change in conductivity of SWCNTs. A strong redox reaction between Hg²⁺ and SWCNTs makes the sensor specific toward Hg²⁺ over other heavy metal ions [41]. Carbon nanotube-based gas sensors are also being designed to detect the harmful and poisonous gases from environment. SWCNT-based nanosensors designed on substrate polytetrafluoroethylene are used for the detection of NO₂ gas. These sensors are about 1.5 to 2.7 times more sensitive than those which are fabricated on the silicon substrate [4]. These sensors are also applicable in the detection of harmful agrochemicals such as pesticides. For example, electrochemical sensors designed using multi-walled carbon nanotubes functionalized with carboxyl group detect organophosphates [164]. Graphene is another carbon-based

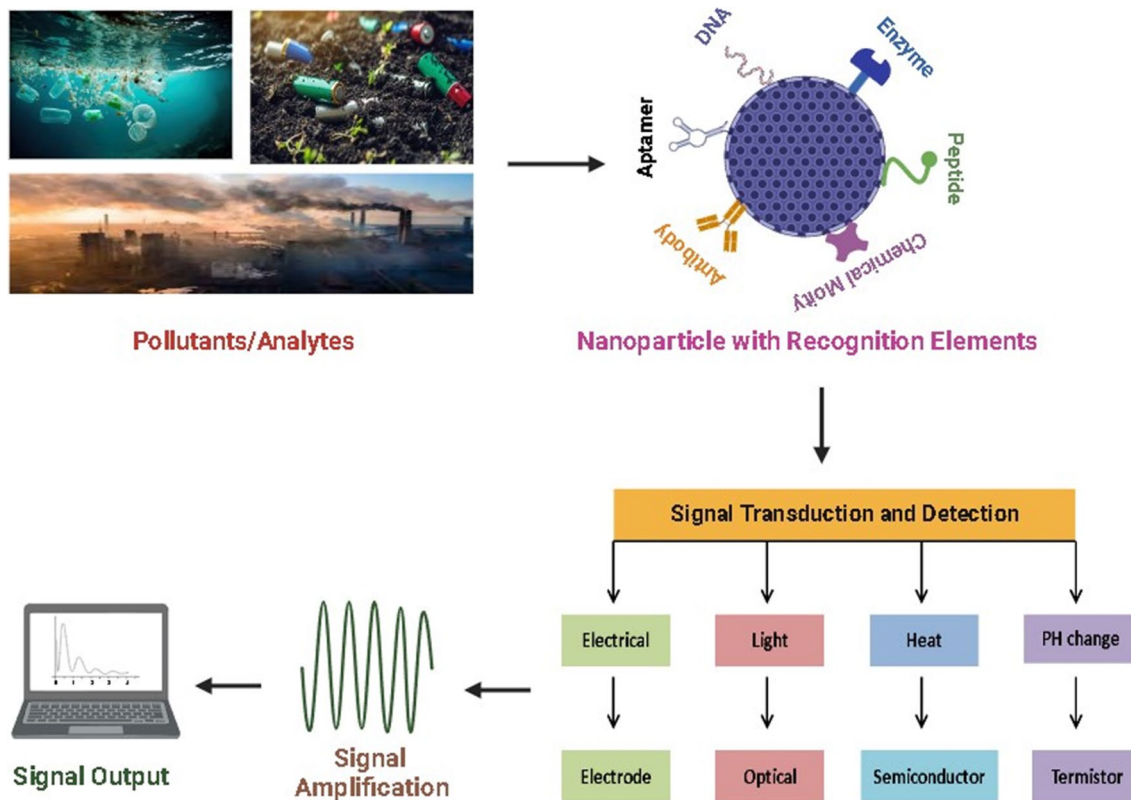


Fig. 4 Nanomaterial-based sensing for environmental monitoring

Table 5 Highly sensitive nanomaterials for pollutant detection

Sr. no	Nanosensor	Contaminant detected	References
1	SWCNTs	Hg ²⁺	[41]
2	SWCNTs	NO ₂	[4]
3	MWCNTs	Organophosphates	[164]
4	Graphene quantum dots	Ag ⁺	[255]
5	ZnO-graphene	NO ₂ , NO, H ₂ S	[224]
6	AgNPs	Hg ²⁺	[54]
7	AgNPs	Pb ²⁺	[231]
8	AgNPs	Thiram, Paraquat	[183]
	AgNPs	Cu ²⁺	[91]
9	AuNPs	Pb ²⁺	[24]
10	AuNPs	Hg ²⁺ , Pb ²⁺	[71]
11	AuNP-based DNA nanosensor	Mycobacterium tuberculosis	[37]
12	DNA nanosensor	SARS-CoV-2 (COVID-19)	[215]
13	DNA nanosensor	Zika virus and SARS-CoV-2	[257]

compound that is used for making nanosensors for the detection of contaminants. One example is radiometric fluorescent nanosensor designed using graphene quantum dots (GQD) as reference fluorophore for the detection of Ag⁺ ions. Another compound O-phenylenediamine (OPD) is used as specific recognition probe. In the presence of Ag⁺ ions, O-phenylenediamine is oxidized to and produces 2, 3-diaminophenazine

(DAP) emitting a strong fluorescence at 577 nm. This DAP quenches the fluorescence of GQD at 445 nm through fluorescence resonance energy transfer (FRET). So, when there is increase in Ag⁺ ion concentration, the fluorescence intensity ratio of DAP to GQD increases [255]. Surface properties of graphene can be modified to increase the efficiency of the sensors. For example, a ZnO-graphene hybrid sensor

efficiently detects the presence of contaminant gases NO_2 , NO , and H_2S by chemisorption of gases with high adsorption energy and large charge transfer that result in alterations in conductance of the sensor [224].

Metal nanoparticles such as silver, gold, and zinc are also used for designing the nanodevices that can sense the pollutants [245]. Nobel metals like silver and gold works on the principle of surface plasmon resonance [46]. These nanoparticles when excited by light generate a strong electromagnetic field in their surroundings. Surface electrons of nanoparticles resonate at a specific wavelength and result in an absorption band known as localized surface plasmon resonance (LSPR) that depends on the shape, size, and local environment of the nanoparticles [182]. Surface-enhanced Raman scattering (SERS) technique utilizes the LSPR for signal transduction. SERS is a phenomenon when any molecule undergoes much higher scattering efficiency by adsorption on the metal nanoparticle surface [53]. There is an enhanced electromagnetic field around the nanoparticle surface because of LSPR. When any analyte enters this enhanced electromagnetic field, the Raman signals are enhanced by several folds of magnitudes. Gold surface-enhanced Raman scattering nanosensors are found to detect heavy metal ions like Hg^{2+} and Pb^{2+} [71].

Calorimetric assay is another use of the localized surface plasmon resonance in which the chemical interaction between the analyte and the nanoparticle leads to a change in color. This is because the colloidal solutions of gold and silver nanoparticles have higher extinction coefficients, and they show different colors in the visible spectrum of light when they are well spaced when compared to the aggregated form [254]. When the analyte interacts with the nanoparticles, there are interactions such as electrostatic interaction and hydrogen bonding which causes the change in color (yellow to brown for AgNPs and red to blue for AuNPs). This change in color helps in visual detection of the target analyte. For example, functionalized silver nanoparticles are found to detect calorimetrically the fungicide thiram and herbicide paraquat [183]. Gold calorimetric nanosensors are found to detect lead heavy metal ions [24].

Another example of nanosensors is DNA nanosensors which are highly sensitive and easy to design. In DNA nanosensors, single-stranded DNA, double-stranded DNA, or aptamers are used as probes for the detection [95]. These DNA sequences can detect various pollutants from water and soil such as pathogens, agrochemicals, antibiotics, and heavy metals. Nanomaterials like metals, metal oxides, and carbon-based nanomaterials like quantum dots can be used in the DNA nanosensors [120]. These DNA nanosensors have many practical applications, such as AuNP-based DNA nanosensors, which have been employed for the direct visual detection of *Mycobacterium tuberculosis* in clinical specimens. This approach proves to be cost-effective when

compared to two other molecular methods that have received approval from the US Food and Drug Administration for the direct detection of *M. tuberculosis* [37]. Furthermore, the utilization of peptide nucleic acid and DNA/RNA-functionalized nanoparticles has been applied for the identification of SARS-CoV-2 (COVID-19) through plasmonic colorimetry, localized surface plasmon resonance, and plasmonic photothermal techniques [215]. Additionally, DNA nano switches have been specifically engineered to identify the highly contagious Zika virus and SARS-CoV-2 viruses in saliva samples [257].

3 Conclusion and Future Perspective

Utilization of the nanoparticles for environmental remediation holds a great promise in addressing the diverse environmental challenges. Nevertheless, it also presents a range of obstacles and uncertainties. A significant concern is the potential toxicity of nanoparticles, as their improper handling may inadvertently introduce new pollutants into the environment, thereby impacting the ecosystems and human well-being. Understanding how nanoparticles behave in complex environmental systems is vital, as they may exhibit distinct characteristics compared to bulk materials, affecting their distribution and potential bioaccumulation. Ensuring the enduring stability of nanoparticles is also essential to sustain their efficacy in removing pollutants over extended periods. However, achieving scalability and cost-effectiveness in their production and implementation remains a major challenge for wider application. Looking toward the future, research endeavors should concentrate on developing the nanoparticles with improved selectivity, stability, and reduced toxicity to enhance their environmental impact. Integrating nanoparticles with biological processes could yield enhanced environmental remediation through nanobioremediation approaches, providing better performance and eco-friendly alternatives. The advancement of smart nanomaterials that respond to specific environmental conditions or pollutants will be a critical area of exploration to enhance efficiency and mitigate unintended side effects. Additionally, the progress in analytical techniques can facilitate better monitoring and characterization of nanoparticles in the environmental matrices, assisting in risk assessment and regulatory compliance.

To ensure the safe and responsible use of nanoparticles, comprehensive risk assessment protocols should be established to evaluate potential hazards associated with their deployment. Encouraging the collaboration among researchers, industries, and policymakers can foster knowledge sharing and a holistic approach to nanoparticle-based environmental remediation. By addressing these challenges

and adopting responsible practices, we can fully exploit the potential of nanoparticles in environmental remediation and safeguard the environment for future generations.

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Data Availability No datasets were generated or analyzed during the current study.

Declarations

Conflict of Interest None.

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