Chapter 8
Industrial Waste Management Using Functionalized Magnetic Nanomaterials (FMNs)

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Abstract Industrialization has led to a scarcity of pure and clean water, with contaminants such as metal particles, microbes, dyes, and non-biodegradable organics posing significant health hazards. To address this, sustainable methods to recycle waste and synthesize nanomaterials are being developed. Industrial pollutants, especially liquid pollutants like heavy metals and metalloids, disrupt local ecosystems and need to be removed from wastewater. Functionalized magnetic nanomaterial (FMNs) technology is an effective solution for water remediation, particularly for removing heavy metals. Recent trends focus on fabricating functionalized nanostructures to clean up contaminants. Methods for creating FMNs include using inorganic moieties, organic ligands, surface polymerization, and enzyme immobilization. These materials show promise in adsorbing pollutants and transforming them into safer forms. This chapter highlights the effectiveness of FMNs in eliminating pollutants, including heavy metals, toxic chemicals, and organic dyes. It also discusses wastewater treatment and management technologies in industries using FMNs. Overall, FMNs offer significant potential for environmental remediation, contributing to cleaner and safer water resources.

Keywords Functionalized magnetic nanomaterials (FMNs) · Industrial waste management · Hazardous chemicals · Heavy metals organic pollutants

8.1 Introduction

The provision of clean water has become a major concern due to industrial expansion and population growth. The build-up of harmful contaminants in surface waters is primarily attributed to the discharge of untreated wastewater from industrial, agricultural, factory, and domestic activities. These pollutants endanger aquatic ecosystems and human health, underscoring the necessity for effective treatment systems [1].

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Traditional methods for contaminant remediation (physical, biological, and chemical) have several drawbacks, including the release of harmful compounds, high initial and maintenance expenses, and low remediation effectiveness [2]. Recent research suggests that nanotechnology offers a promising solution with superior features compared to traditional methods [3].

In the past decade, pharmaceuticals have been consistently found in water sources worldwide, including surface water, groundwater, and industrial wastewater. In Africa, for instance, various pharmaceuticals such as antibiotics, painkillers, anticonvulsants, anti-inflammatories, and antiviral drugs have been detected in water resources in Uganda. Similar occurrences have been reported in other regions, including Canada and India, providing strong evidence that pharmaceutical pollution is a global issue affecting water resources [4].

The color of water is commonly seen as an indicator of its purity, and even tiny amounts of certain pollutant dyes (even <1 ppm) can be noticeable and objectionable. Dyes are widely utilized in industries such as textiles, paints, printing, cosmetics, and more. Synthetic dyes form a major category of organic pollutants, often released as wastewater from these industries. Due to their intricate aromatic composition, they are challenging to break down and can endanger aquatic life by obstructing the necessary sunlight in colored water. Moreover, dye pollution can adversely affect humans, causing inflammation, eye irritation, abnormal heart rates, and cytotoxic effects [5, 6].

The growing global population has heightened the demand for food production, leading to increased pesticide usage to safeguard crops from invasive species and aggressive insects. However, prolonged use and exposure to pesticides cause natural resistance, requiring larger amounts of these chemicals over time. Moreover, pesticide molecules tend to accumulate in different environments such as soil, surface, and groundwater, endangering human health [7].

Magnetic nanoparticles are promising for environmental applications because of their large-scale production potential, lower toxicity, and eco-friendliness. Metals like iron, cobalt, nickel, and their oxides are common types. Organic/inorganic nanocomposites and doped TiO_2, ZnO nanostructures exhibit excellent chemical, catalytic, and sustainable properties. Magnetic iron oxide nanomaterials and other nanomaterials improve wastewater remediation by enhancing efficiency and pollutant removal. These smart nanomaterials possess catalytic, photonic, electrical, optical, mechanical, and magnetic characteristics, enabling easy segregation and revival with an external magnetic field. They are widely used in environmental contaminant removal, magnetic photothermal therapy, biochemical product separation, and tissue engineering [8].

Functionalized magnetic nanoparticles (MNPs) are engineered nanoscale particles that can be manipulated using an external magnetic field. They consist of magnetic core elements such as Fe, Co, Ni, and their oxides, including hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), and cobalt ferrite ($CoFe_2O_4$). Magnetite (Fe_3O_4) is particularly favored due to its Fe^{2+} and Fe^{3+} states, which act as electron donors [9]. Functionalized MNPs have garnered attention for their remarkable properties, including easy synthesis, convenient surface functionalization, large surface area, and simple separation. They can be efficiently extracted from complex environments using a magnet, avoiding laborious steps like filtration or centrifugation. However, MNPs have limitations, such as agglomeration and stability concerns. Bare metallic nanoparticles can be chemically reactive and prone to oxidation, leading to reduced or lost magnetism. Effective protection methods include coating the surface of bare MNPs with materials such as carbon, silica, surfactants, or polymers.

To address the limitations of MNPs, many scientists have developed functionalized MNPs with new structures and surface characteristics. These enhancements aim to provide more active sites, improve water stability, and meet the growing demand for effective pollutant removal treatments. These MNPs have demonstrated notable improvements in pore volume, pore size distribution, specific surface area, high stability, processability, magnetic separation, surface active sites, and catalytic degradation capabilities, all contributing to the elimination of pollutants. MNPs have been extensively researched as effective adsorbents for separating and concentrating pollutants in water, including pesticides, antibiotics, and toxic metals [10].

FMNs are regarded as the smart materials of the future, requiring significant scientific foresight and patience. These materials play a vital role in environmental engineering, especially in addressing challenges like heavy metal and arsenic groundwater remediation. Nanotechnology and nanoengineering are crucial for this purpose. Darwish et al. examined the high reactivity and extensive surface area of nanomaterials at the nanoscale. They highlighted materials derived from semiconductors, silica, metal oxides, precious metals, polymers, and carbon-based substances for environmental protection. These materials are being investigated for the remediation of polluted wastewater, groundwater, surface water, and soil, utilizing techniques such as pollutant sensing, adsorption, nanofiltration, and photocatalytic degradation. The challenges involve potential health and ecosystem risks and the limited reusability of nanomaterials [11].

Traditional wastewater treatment methods, such as coagulation and flocculation, have drawbacks, including the production of large amounts of sludge and toxic byproducts. While ion-exchange treatments and adsorption processes have their advantages, they require pretreatment. Electrochemical methods are efficient but come with disadvantages. This chapter explores the applications of FMNs for tackling hazardous chemicals, heavy metals, organic pollutants, dyes, pharmaceuticals, and antibiotics. It underscores the extensive use of FMNs in waste management technologies, focusing particularly on their application in industrial wastewater treatment [12].

8.2 FMNs in Heavy Metal Removal from Industrial Waste

In wastewater, the accumulation of heavy metals has increased due to industrial and human activities, such as the petrochemical industry, plating, battery production, electroplating, textile manufacturing, mining, and pesticide use. These metals, including lead (Pb), copper (Cu), mercury (Hg), cadmium (Cd), nickel (Ni),

Fig. 8.1 Sources of heavy metal pollution, reprinted from [14]. Copyright [14] Karnwal A and Malik T (2024), Nano-revolution in heavy metal removal: engineered nanomaterials for cleaner water. Front. Environ. Sci. 12:1393694. https://doi.org/10.3389/fenvs.2024.1393694. (Open access)

chromium (Cr), and arsenic (As), are non-degradable and potentially carcinogenic. Their excessive presence in water can cause severe health issues for living organisms [13]. Even trace amounts of these heavy metals are hazardous. Other metals, such as iron (Fe), manganese (Mn), silver (Ag), molybdenum (Mo), antimony (Sb), cobalt (Co), and more, are also commonly detected in wastewater and need to be removed (Fig. 8.1).

Recent wastewater treatment techniques include biodegradation, photodegradation, chemical precipitation, hydrolysis, oxidative degradation, ion exchange, flocculation, neutralization, membrane separation, and ultrafiltration. Each method has its benefits and drawbacks. Magnetic nanoparticles (MNPs) have proven effective in enhancing toxic metal extraction and facilitating magnetic separation, making them favored for environmental cleanup due to their recyclability after separation. In contrast to smaller non-magnetic nanoparticles, which are less efficient due to smaller surface areas and difficult separation, MNPs have large surface areas, are non-toxic, and disperse easily, making them effective and economical for heavy metal removal [15].

Toxic metal ions are introduced into the environment through industrial effluents from sources like paint manufacturing, electroplating, and smelting. These ions are concerning due to their harmful impact on human health and the environment, as well as their tendency to bioaccumulate. Efficient removal techniques have attracted considerable attention.

Xue and colleagues synthesized Fe_3O_4 nanoparticles combined with oxidized humic acid (Fe_3O_4/HA-O) for metal adsorption studies. These Fe_3O_4/HA-O nanoparticles were utilized to remove Cd(II), Ni(II), Pb(II), and Cu(II) ions from aqueous solutions, achieving optimal adsorption capacities of 111.10, 33.33, 71.43, and 76.92 mg/g, respectively [16].

Kumar and Joshi synthesized polythiophene and Fe_3O_4 (PTh-Fe_3O_4) nanocomposite for the adsorption of Pb(II), Cd(II), and Cr(VI) ions. At pH 2, the maximum adsorption of Cr(VI) was 79.9%, decreasing to 8.9% at pH 6. Pb(II) and Cd(II) adsorption increased from 3.3% and 13.1% at pH 2 to 89.9% and 99.3% at pH 6, respectively [17]. The magnetic Fe_3O_4@BC/APTES composite was synthesized by coprecipitation for the adsorption of Pb(II) and Cr(VI) [18]. The surface area of the aminopropyl triethoxysilane (APTES)-modified adsorbent decreased from 135.90 to 35.66 m^2/g compared to the biochar-capped nanocomposite. Nevertheless, the adsorbent effectively removed 52.8% of Cr(VI) and 93.95% of Pb(II) after one hour at 20 °C. Pb(II) was better absorbed at basic pH, whereas Cr(VI) showed better absorption at low pH.

Sahu et al. [19] reported the synthesis of magnetic nanoparticles made of Fe_3O_4 and its conjugate with the renewable biopolymer chitosan, using Prosopis farcta biomass extract. These nanoparticles were used to adsorb Pb(II) from aqueous solutions. The maximum adsorption efficiencies were found to be 69.02% for Fe_3O_4 and 89.54% for Fe_3O_4-CS adsorbents. Both Fe_3O_4 and Fe_3O_4-CS can be easily recovered using an external magnet, making them viable and cost-effective options for lead removal.

Font and colleagues developed a novel adsorbent nanocomposite (Fe_3O_4@CS@CMC-$SiNH_2$) by functionalizing carboxymethyl cellulose (CMC) cross-linked to magnetic chitosan nanoparticles (Fe_3O_4@CS NPs) with an APTES layer. This nanocomposite exhibited outstanding adsorption performance with a maximum capacity of 555.56 mg Pb(II)/g NC and rapid adsorption equilibrium (30 min). It achieved 98.10% and 97.21% removal of lead (II) ions in the absence and presence of other heavy metal contaminants, respectively [20].

Bao and colleagues presented a novel method for preparing magnetic graphene oxide (GO) to remove heavy metal ions such as Cd(II) and Pb(II). They utilized n-propyltrimethoxysilane (NPTS) as a cross-coupling agent to connect Fe_3O_4/SiO_2 and GO. The resulting magnetic GO can be rapidly separated from water using a permanent magnet and exhibits excellent adsorption capabilities, with maximum capacities of 128.2 mg/g for Cd(II) and 385.1 mg/g for Pb(II) under neutral conditions [21].

Giwa et al. reported the preparation of polyethersulfone-functionalized graphene oxide (PES-fGO) mixed matrix membranes through methods such as crosslinking GO with maleic acid (M1), co-polymerizing GO with hyperbranched polyethyleneimine (HPEI) (M2), and modifying GO with chitosan (M3). The M2 membrane, characterized by its dense structure and abundant nucleophilic amino groups, demonstrated the highest tensile strength and pollutant removal efficiency, achieving up to 99.9% removal of Cr^{6+} and bacteria, and 98% removal of chemical oxygen demand (COD), despite having the lowest water fluxes [22].

Bangari et al. reported the use of Fe_3O_4 functionalized boron nitride nanosheets (BNNS-Fe_3O_4 nanocomposite) for removing As(III) ions from contaminated water. The nanocomposite has a specific surface area of 179.5 m^2/g and exhibits superparamagnetism at room temperature, allowing easy isolation using an external magnetic field. It demonstrates a maximum adsorption capacity of 30.3 mg/g for As(III) ions, which is approximately four times higher than that of bare BNNSs [23]. Researchers have synthesized various nanocomposites and magnetic nanoparticles, such as Fe_3O_4 with different functionalizations, to adsorb and remove heavy metal ions like Cd(II), Pb(II), Ni(II), Cu(II), Cr(VI), and As(III) from wastewater, achieving high adsorption capacities and reusability, making them promising candidates for environmental cleanup.

8.3 FMNs in the Removal of Pharmaceutical Industrial Wastes

Pharmaceutical and personal care products have become widely used due to technological and scientific advancements. Researchers are concerned about the waste from these products, particularly pharmaceutically active chemicals, because of their impact on the environment and human health.

Arabkhani et al. synthesized a magnetic nanocomposite (GO/ZIF-8/γ-AlOOH) using solvothermal and solid-state dispersion techniques. This nanocomposite, comprised of graphene oxide (GO) nanosheets coated with zeolitic imidazolate framework-8 (ZIF-8), pseudo-boehmite (γ-AlOOH), and iron oxide (Fe_3O_4) nanoparticles, featured a surface area of 777 m^2/g and a saturation magnetization of 9.75 emu/g. It was employed for the adsorption of diclofenac sodium, demonstrating a strong alignment with the Langmuir model and an impressive adsorption capacity of 2594 mg/g at 30 °C and pH 7.5 [24].

Asgari et al. prepared magnetic Fe_3O_4-chitosan nanocomposite nanoparticles for metronidazole adsorption. The highest adsorption capacity was 98 mg/g at pH 3, with experimental data well described by the Freundlich adsorption isotherm and pseudo-second-order kinetic model [25].

In another study, Fe_3O_4 nanoparticles with an average of 12 nm were functionalized with graphene oxide and carbon nitride to create GO/g-C_3N_4–Fe_3O_4 nanocomposite for tetracycline antibiotic adsorption. The adsorption was pH-dependent, with a maximum capacity of 107 mg/g at pH 3. The nanocomposite was also recovered and reused for five cycles [26].

Researchers have also developed various magnetic nanocomposites for pharmaceutical adsorption, achieving high capacities and reusability. These include GO/ZIF-8/γ-AlOOH for diclofenac sodium, Fe_3O_4-chitosan for metronidazole, GO/g-C_3N_4–Fe_3O_4 for tetracycline, and Fe_3O_4@SiO_2NH_2 for methylparaben.

8.4 FMNs in Dye Extraction from Industrial Effluents

Synthetic dyes are a major challenge due to their persistence and harmful effects on humans and other living beings. These dyes are widely used in industries such as food, cosmetics, leather, pharmaceuticals, paper, plastics, and textiles, with around 0.7 million tons of about 100,000 different types used annually. Azo dyes, typically anionic, are particularly harmful due to their high thermal, optical, and physicochemical stability, attributed to their stable chemical structure involving aromatic rings and azoic linkages. The uncontrolled release of these dyes into water bodies leads to severe environmental issues, including intrinsic carcinogenic effects, toxicity, mutagenic effects, skin sensitization, and reduction of sunlight in aquatic environments, posing a serious threat to aquatic organisms and humans. Therefore, removing these dyes before discharging industrial effluents into natural streams is crucial in current material and environmental research. Adsorption is a surface-based process where ions or molecules adhere to a solid surface of the adsorbent, as shown in Fig. 8.2. Dye molecules can adhere through interactions such as ion exchange, hydrogen bonding, and electrostatic and π-π interactions. This method is beneficial because adsorbents can be reused, it is highly effective, and dye removal from wastewater is quick [27].

Yang et al. polymerized poly(ionic liquid) onto silicon-coated Fe_3O_4 nanoparticles to create an inexpensive and selective composite [29]. The ability of Fe_3O_4@SiO_2@PIL to remove various dyes, such as acid orange II, alizarin red, malachite green, and thionin acetate, was tested. The adsorbent showed rapid adsorption kinetics, absorbing up to 510.2 mg/g of alizarin red.

Keziban Atacan et al. focus on immobilizing peroxidase onto 3-aminopropyltriethoxysilane (APTES)-functionalized $MgFe_2O_4$ magnetic nanoparticles to enhance efficiency, enzyme stability, and recyclability. The immobilized peroxidase retained almost 50% of its activity after 10 uses because of easy magnetic separation. It also showed improved antioxidant activity and a significant enhancement in Congo red dye removal efficiency, achieving 98.6% in 240 min [30].

Juxiang Luo et al. synthesized Magnetic crosslinked copolymer microspheres (MCPMs) using oleic acid-modified Fe_3O_4 as the magnetic source, with α-methyl styrene and maleic anhydride as monomers and divinylbenzene as the crosslinking agent. These MCPMs were then hydrolyzed to obtain MCPMs with carboxyl groups. The MCPMs' adsorption behavior, kinetics, and isotherms for methylene blue (MB) removal from water were analyzed. MCPMs demonstrated an excellent MB removal capacity of 315 mg/g [31].

Naveen Kumar et al. explored the use of molybdic acid (MA)-functionalized iron oxide magnetic nanoparticles (MNPs) for removing RB dye from wastewater via adsorption. At optimal conditions, they showed a maximum adsorption capacity of 60 mg/g, and it is proven that the MA-functionalized iron oxide nanoparticles are potential for efficient textile dye removal from wastewater [32].

Qazi et al. examined amine-functionalized MWCNTs (f-MWCNTs) as a potential material for removing Mordant Black Dye 11 (MBD 11). The study found a

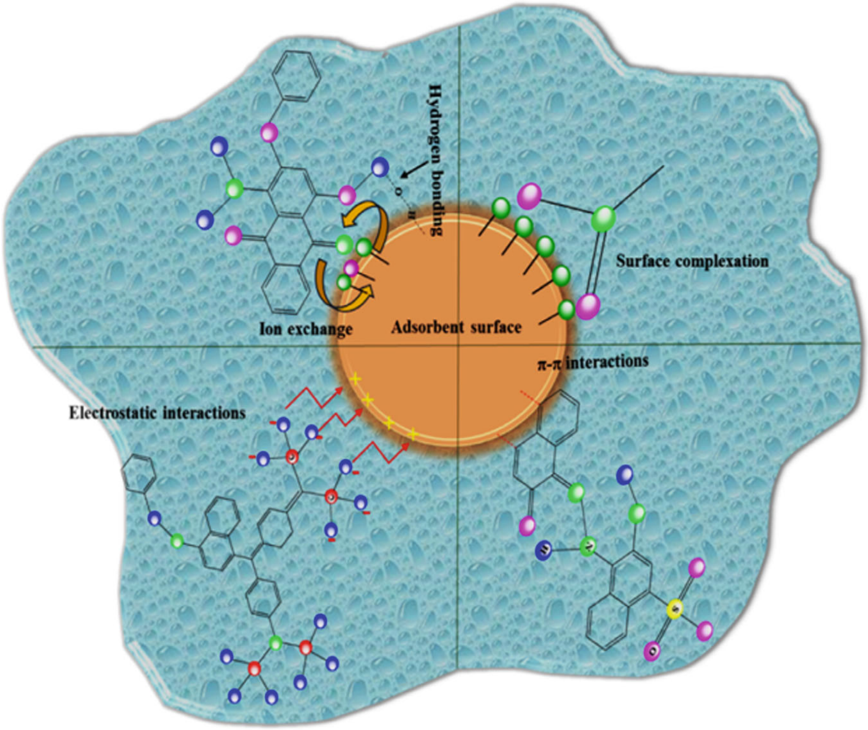

Fig. 8.2 Removal of dye from aqueous solutions by the adsorption method, Reprinted from [28]. Copyright @ From [28] Mbuyazi, T. B., & Ajibade, P. A. (2024). Magnetic iron oxides nanocomposites: Synthetic techniques and environmental applications for wastewater treatment. Discover Nano, 19, 1548. https://doi.org/10.1186/s11671-024-04102-9. (Open access)

strong interaction between the dye and f-MWCNTs. The highest removal efficiency occurred in an acidic medium (pH 2) with an initial dye concentration of 50 mg/L, achieving 99% dye adsorption within 40 min using 0.05 g of f-MWCNTs [33].

Said and colleagues synthesized SnO_2–Fe_3O_4 nanocomposites to explore their potential for photodegrading Congo red. The SnO_2–Fe_3O_4 nanocomposite exhibited a magnetic saturation value of 64.96 emu/g and demonstrated a photodegradation efficiency of 50.76% under optimal conditions (90 min, dye concentration 18 mg/L). The magnetic saturation value remained unchanged after the photocatalytic reaction [34].

Roostaee et al. prepared Fe_3O_4@Au core–shell nanoparticles and Fe_3O_4@Au/rGO nanocomposites for the photocatalytic degradation of crystal violet dye. Fe_3O_4@Au-rGO outperformed Fe_3O_4@Au and rGO in photocatalytic activities. Increasing the amount of Fe_3O_4@Au/rGO nanocomposite sped up the degradation, achieving complete degradation of crystal violet dye in 1 min with 20 mg of nanophotocatalyst [35].

Rehman et al. synthesized γ-Fe_2O_3, Fe_3O_4 nanoparticles, and γ-Fe_2O_3@GO nanocomposites for methylene blue photodegradation. BET analysis showed surface areas of 50 m^2/g for γ-Fe_2O_3 and 73 m^2/g for γ-Fe_2O_3@GO composite. The degradation efficiencies were 37.5%, 77.7%, and 90.6% for γ-Fe_2O_3, Fe_3O_4, and γ-Fe_2O_3@GO, respectively. The highest photodegradation rate was 0.0325 min^{-1} for the γ-Fe_2O_3@GO nanocomposite. The studies indicate that decreasing the band gap energy can enhance the degradation efficiency of organic dyes. However, photocatalyst performance is significantly influenced by slight morphological differences [36].

Researchers have explored various magnetic nanocomposites and functionalized magnetic nanomaterials for dye removal. These include Fe_3O_4@SiO_2@PIL for removing dyes like alizarin red, Fe_3O_4-chitosan for metronidazole, GO/g-C_3N_4–Fe_3O_4 for tetracycline, and Fe_3O_4@SiO_2NH_2 for methylparaben. Other advancements include MCPMs for methylene blue, MA-functionalized iron oxide for RB dye, and f-MWCNTs for Mordant Black Dye. These materials show high adsorption capacities, rapid kinetics, and good reusability, making them effective for water purification and environmental applications.

8.5 FMNs in the Removal of Pesticides from Wastewater

Pesticides, due to their extensive use and rising toxicity, are major organic toxins. Defined by the Environmental Protection Agency as chemicals employed to avoid, eradicate, deflect, or manage pests, pesticides pose a significant risk to aquatic life even at trace concentrations. They are associated with various illnesses, including endocrine disruption, cancer, respiratory disorders, Parkinson's disease, and reproductive issues. Thus, removing these contaminants from water is crucial [37]. Researchers have also explored using magnetic nanocomposites for pesticide removal through adsorption.

Zhou et al. examined the efficiency of Fe_3O_4@SiO_2-MWCNT for pentachlorophenol adsorption, finding that the capacity was pH-dependent, with a peak at pH 2.5 (96.4 mg/g) [38]. Wanjeri et al. synthesized Fe_3O_4 nanoparticles (mean diameter 12.3 ± 3 nm) via co-precipitation, treated them with silica, and modified them with graphene oxide and 2-phenylethylamine (PEA), creating Fe_3O_4@SiO_2@GO-PEA. This nanocomposite was used to adsorb malathion, chlorpyrifos, and parathion, achieving maximum removals of 76%, 88%, and 85% after 15 min, respectively. Adsorption capacities were 10.6 mg/g for malathion, 11.1 mg/g for chlorpyrifos, and 10.9 mg/g for parathion, unaffected by pH changes from 3 to 11 [39].

Fe_3O_4/reduced graphene oxide nanocomposite was also tested for adsorbing atrazine, ametryn, simazine, prometryn, and simeton, achieving 75.24%, 93.61%, 88.55%, 91.34%, and 81.22% efficiencies after 70 min, respectively [40]. Additionally, Researchers have investigated magnetic nanocomposites for pesticide removal via adsorption, achieving notable results. Fe_3O_4@SiO_2-MWCNT was effective for pentachlorophenol, Fe_3O_4@SiO_2@GO-PEA for malathion, chlorpyrifos, and parathion, and Fe_3O_4/reduced graphene oxide for atrazine, ametryn, simazine, prometryn, and simeton, demonstrating high adsorption efficiencies and capacities.

8.6 Waste Management Technologies Using FMNs

Functional Magnetic Nanomaterials (FMNs) have emerged as effective sorbents, providing novelty, high efficiency, and simplicity, which attract researchers' interest. Various reports highlight the use of FMNs in contaminant removal, such as carboxyl- and amine-functionalized nanoparticles, thiol-functionalized magnetite nanoparticles, poly rhodamine-functionalized aluminum oxide, polymer-functionalized magnetic nanoparticles, silica-functionalized magnetic nanoparticles, and others. The operation of functionalized magnetic nanomaterials (FMNs) involves specific pathways based on their applications. For environmental remediation, NMs adhere to particular routes to eliminate contaminants. Several procedures utilizing FMNs have been reported so far, with two methods being particularly notable due to their simplicity and efficiency in sorption and photocatalytic pathways [41].

Sorption stands out among contaminant removal methods due to its straightforward operation, cost-effectiveness, and energy efficiency. The composition of the sorbent material is crucial for the capacity of the sorption process. This method is popular for its simplicity, making it a practical and feasible strategy, especially in underdeveloped and developing countries. Sorption is versatile, being widely researched and successfully used in industrial waste treatment. The novelty of sorption relies on the variety of materials used as sorbents, including both natural and synthetic substances. Examples of low-cost recycled materials include fly ash, scrap tires, coconut shells, fruit extracts, and more. Synthetic materials include activated carbon, metal oxides/hydroxides, and zeolites, among others [42].

Photocatalysis is a method that uses functionalized magnetic nanomaterials (FMNs) to remove contaminants by absorbing energy and producing photons to accelerate chemical reactions without degrading the catalyst itself. Researchers frequently use this method for its efficiency and advanced follow-up capabilities. Sunlight is usually used as the energy source for the photocatalytic process due to its natural abundance, reducing energy-related costs. UV light can also be used, depending on the contaminants. Photocatalysis involves using semiconductor materials with dual functions, acting as both cathode and anode, suitable for various applications such as photodegradation, photocatalytic CO_2 reduction, photocatalytic synthesis, and more. The growing interest in photocatalysis for environmental restoration is due to its broad applicability [43].

The significant factors in choosing photocatalytic materials include excellent energy position, appropriate bandgap, low electron-hole recombination, and non-toxicity. Common materials include metal oxides, metal sulfides, and others. The use of FMNs in fabricating photocatalysts enhances their properties and efficiency. Examples of potent photocatalysts include azole-functionalized TiO_2, Ag-modified metal oxide, and more. Carbon-based nanomaterials (NMs) are recognized as next-generation materials with extensive applications across various fields, including biosensors, drug delivery, biomedical applications, superconductors, and electrically conductive materials. Due to their advantageous properties, such as high electrical conductivity and well-defined thermal and mechanical characteristics, carbon NMs are widely used in wastewater treatment. They serve as excellent sorbents and photocatalysts due to their high surface-to-volume ratio, uniform pore distribution, and highly porous structure. However, the application of carbon NMs can be limited by their tendency to agglomerate in solvents due to weak van der Waals forces and lower solubility. Additionally, impurities formed during synthesis can hinder their activity. To overcome these limitations, the functionalization of carbon NMs is performed to enhance their properties and activity. Functionalized carbon NMs come in various forms, including carbon nanotubes (CNTs), graphene and its derivatives, and fullerenes [44].

Carbon nanotubes (CNTs) are a common form of carbon nanomaterials, visualized as graphene sheets rolled into tubular cylinders with nanoscale diameters. They are categorized into single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). SWCNTs consist of a single rolled graphene sheet, while MWCNTs have multiple concentric graphene sheets [45].

Graphene is the simplest form of carbon and the thinnest known material, consisting of a two-dimensional single-layer sheet of carbon atoms arranged in a sp^2-bonded honeycomb-like lattice structure. Graphene-based nanomaterials exhibit excellent sorption capacity due to their high surface area, delocalized π-electron system, and numerous active sites. Functionalization with groups like thiol moieties or carboxylic groups further enhances the properties of graphene nanomaterials. Zamani and Salem studied the photocatalytic behavior of graphene oxide sheets coupled with carbon nanotubes, achieving 96.5% efficiency in degrading MB dye [46]. Firdaus et al. functionalized graphene nano-platelets (GNPs) with oxygen-containing groups, resulting in higher sorption capacity and better dispersion in aqueous solutions [47].

Fullerenes are spherical molecules composed entirely of carbon atoms, considered allotropes of carbon, with high symmetry and solubility in various organic solvents. They consist of a carbon cage with a fused ring system of hexagons and pentagons. The most common fullerenes are C_{60} and C_{70}. Wu et al. achieved 94.7% efficiency in degrading RB dye using a photocatalyst made of fullerene-cored star-shaped polyporphyrin-incorporated TiO_2. The high efficiency is attributed to the high specific surface area and unique electronic properties of fullerol, a fullerene derivative extensively hydroxylated with polyhydroxy groups [48]. Elessawy et al. prepared functionalized magnetic fullerene nanocomposites (FMFN) for ciprofloxacin removal, showing a high surface area and superparamagnetism, with a sorption capacity of 65 mg/L [49]. Mahdavian demonstrated the removal efficiency of heavy metals (nickel and cadmium) using modified nano-fullerene (C_{60}) with tetrahydrofuran, achieving 91% efficiency for ion removal, with a sorption capacity of 1261 mg/g for cadmium and 3704 mg/g for nickel [50].

Chitosan (CS) is a natural adsorptive polymer with an affinity for pollutants in wastewater due to its amino ($-NH_2$) and hydroxyl ($-OH$) groups. However, it suffers from low mechanical strength and poor stability, making regeneration inefficient. Structural and chemical modifications have been proposed to overcome these drawbacks. Cross-linking imparts strength by bridging between polymer chains and functional groups, though it reduces uptake. Grafting involves the covalent bonding of functional groups on the CS backbone, significantly increasing adsorption capacity. Combining CS with other adsorbents can enhance its adsorption capacity, mechanical strength, and thermal stability. Ion-imprinting techniques also provide high selectivity for target metal ions. The uptake of CS depends mainly on the protonation or non-protonation of its amino and phosphoric groups, which affect the pH value of the wastewater. Without modifications, CS-based adsorbents show low reusability due to strong metal ion bonds, low stability, incomplete desorption, and limited adsorption sites. Alternative regeneration methods and modifications are needed to improve the reusability of CS adsorbents [51].

8.7 Removal of Contaminants by Using Membrane Technology

Nanotechnology offers solutions for removing pollutants through conventional membrane processes, enhancing adsorption capacity, photocatalysis, and disinfection. Various nanomaterials, such as nanoparticles, nanowires, nanofibers, nanotubes, metal-organic frameworks, and two-dimensional nanosheets, have been used for detecting and removing contaminants from wastewater. Membrane technology is cost-effective, small in equipment size, low in energy consumption, and highly efficient, with processes including reverse osmosis, ultrafiltration, and nanofiltration. Integrating nanomaterials with existing membranes enhances wastewater treatment efficiency. Membranes with nanomaterials can be classified as surface-coated, surface-deposited, surface-grafted, surface-assembled, mixed matrix, and pore-filled membranes, although issues like nanomaterial leaching can occur. Leaching impacts membrane efficiency, but advancements in polymeric membrane technology can mitigate these problems. Choosing the appropriate functionalization method and material depends on the contaminants to be removed. New membranes and nanomaterials have extended membrane life through regeneration processes, increasing usage efficiency. Unmodified membranes can remove various pollutants by adjusting pore size or combining them with coagulation/flocculation [52]. Advances in fabrication technology have enhanced conventional membranes with hydrophobicity, tunable pore size, specific modifications, and faster water efflux. Nanomaterial functionalization has added large surface areas, photocatalytic properties, and fouling resistance, making membranes multifunctional and efficient for removing a wide range of pollutants, including dye molecules, metal ions, microbes, biomass, and toxic sulfur/nitrogen-containing organic molecules.

8.8 Concluding Remarks and Future Perspectives

The rapid growth of industrialization and population has led to significant water pollution, posing risks to ecosystems and human health. Traditional remediation methods are often costly and ineffective. Nanotechnology offers promising solutions, with functional magnetic nanoparticles (MNPs) showing great potential due to their high adsorption capacity, stability, and recyclability. Functionalized magnetic nanomaterials (FMNs) are highly effective in contaminant removal through methods like sorption and photocatalysis, while carbon-based nanomaterials, including carbon nanotubes and graphene, also play a crucial role in environmental remediation. Researchers have developed various functionalized nanocomposites and magnetic nanoparticles, such as Fe_3O_4, to efficiently remove heavy metals, dyes, and pesticides from wastewater. These materials demonstrate high adsorption capacities, rapid kinetics, and excellent reusability, making them effective for environmental management. Integrating nanomaterials with existing membranes further enhances wastewater treatment efficiency. Overall, functionalized nanomaterials hold significant potential for advanced contaminant removal techniques and sustainable environmental management.

Abbreviations

APTES	Aminopropyl Triethoxysilane
BNNS	Boron Nitride NanoSheets
CNTs	Carbon Nanotubes
FMFN	Fullerene Nanocomposites
f-MWCNTs	Functionalized MWCNTs
FMNs	Functional Magnetic Nanomaterials
GO	Graphene Oxide
MCPMs	Magnetic Crosslinked Copolymer Microspheres
MNPs	Magnetic Nanoparticles
MWCNTs	Multi-Walled CNTs
PEA	2-Phenylethylamine
SWCNTs	Single-Walled CNTs
ZIF	Zeolitic Imidazolate Frameworks

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