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Fe_3O_4-based magnetic nanoparticles for the removal of water contaminants

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Anthropogenic activities generate industrial wastewater, posing the greatest threat to the environment and requiring cleanup to mitigate environmental impacts and human health risks. Because of their remarkable characteristics, Fe_3O_4-based magnetic nanoparticles (MNPs) have recently gained popularity as powerful tools for wastewater treatment. To alleviate the qualitative strain on water supplies, MNPs have found newer applications owing to their inherent characteristics. Herein, the physical, chemical, and biological/green approaches for the synthesis and assembly of MNPs are deliberated, with biologically derived options found to be environmentally benign and sustainable in the long term. The efficacy of MNPs in the elimination or recovery of various wastewater contaminants, such as heavy metals, inorganic pollutants, dyes, biological pollutants, and microalgae, is presented. Moreover, the advantages and disadvantages of MNPs in their usage for wastewater treatment, the removal mechanism *via* coagulation, and the manufacture of MNPs are appraised in detail. Finally, the potential of Fe_3O_4-based MNPs for deployment in environmental cleanup and their future applications are addressed.

1. Introduction

Water is the primary resource for human life, and consequently, its contamination has become one of the most pressing environmental challenges of our day. The rising demand for water has significantly compromised its quality. Rapid industrialization, agricultural production, and urbanization have resulted in the deterioration of the environment, wherein pollutants adversely affect the quality of vital water resources (rivers and oceans) and eventually compromise human health and sustainable social development.[1–3] Ecosystems and human health are seriously threatened by water pollution from various sources, namely heavy metals, pesticides, viruses, and synthetic chemicals. A large percentage of global industrial and urban wastewater is discharged into the environment without treatment, thus jeopardizing human health and ecosystems. In less developed nations with inadequate wastewater treatment and sanitation infrastructure, this proportion is even greater. These issues are exacerbated by poor disposal of industrial waste, inadequate wastewater treatment, and agricultural runoff, which lead to the deterioration of water quality, loss of biodiversity, and public health risks, including dangerous diseases such as cancer, a cause of many human deaths each year.[4–8] Researchers have increasingly focused on water pollution studies *via* various methods pertaining to the removal of assorted pollutants to improve the quality of drinking water.[9] This interest is signified in the rising trend in publications on water pollutant removal over the past decades (Fig. 1), highlighting the significance of research in this field.

Publication analysis shows that there have been three separate epochs of study on Fe_3O_4-based magnetic nanoparticles (MNPs) and their biomedical and environmental applications. Research before 2010 primarily focused on nanoparticle (NP) production, particles' physicochemical characteristics, and the fundamentals of coagulation and flocculation. As a result of the focus on fundamental and methodological publications largely aimed at determining the mechanisms of action of NPs, their practical applications were confined to laboratory research and straightforward heavy-metal and pollutant separation. There has been a dramatic uptick in the number of articles published between 2010 and 2020, with most of the new studies focusing on environmental applications or the elimination of heavy metals, dyes, pharmaceuticals, or new forms of pollution and emerging contaminations. During this

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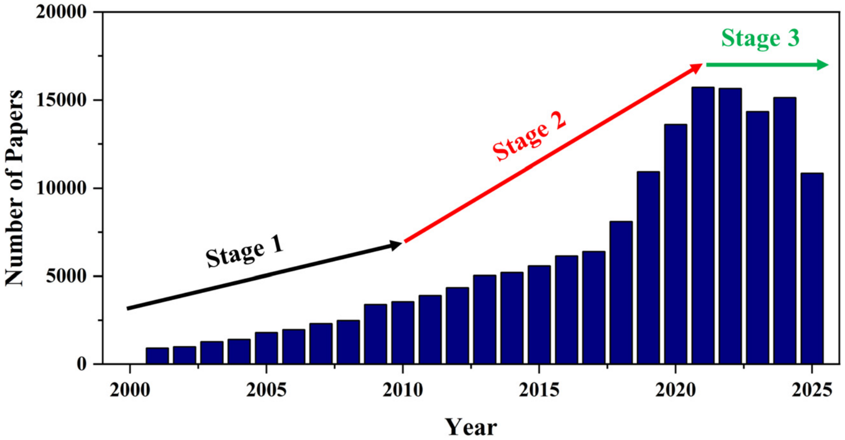

Fig. 1 Rising interest in water pollutant removal, as evidenced by the escalating quantity of publications (from the Web of Science database with the usage of the keyword "Water Pollutant Removal" extracted on 27 November 2025).

time, there was a surge in basic research on practical and integrated environmental and medical applications, as well as consideration of the biomedical, antibacterial, and nanocomposite uses for functionalized NPs to improve their performance in real-world settings. From 2020 onwards, studies have primarily focused on post-placement technologies that are environmentally friendly, have multifunctional applications, and being centered on versatile and greener technologies. Special consideration is given to environmental concerns, sustainability, material recycling, and the creation of eco-friendly NPs. These particles are used for microplastic removal, antiviral systems, photocatalysis, and a wide range of chemical applications.

The general trend indicates that research on Fe_3O_4 and similar NPs has shifted its focus from fundamental and preliminary synthetic investigations to practical, ecological, and biological implications, and the industrialization of these NPs including their pilot usage. This field has matured and moved on from theoretical research to multipurpose and sustainable applications, as is apparent from the explosive growth of papers from 2010 to 2020, with the expansion of practical applications and functionalization, and increased emphasis on sustainability and green technology after 2020. This development is indicative of the growing significance of MNPs in many fields, including medicine, the environment, and fundamental research that makes use of applied technology.

The social, economic, and environmental repercussions of water pollution underscore the importance of deploying efficient water purification technology to safeguard water supplies and advance sustainable development. Undeniably, two major issues facing communities worldwide are water pollution and the supply of clean drinking water. Traditional water treatment techniques for eliminating contaminants from water sources include chlorination and filtration.[10,11] Microplastics and pharmaceutical pollutants are increasingly becoming issues in water treatment that traditional treatment facilities cannot eliminate. Pharmaceuticals and their metabolically-derived chemical entities infiltrate the water sources, causing hormonal imbalances and antibiotic resistance, while microplastics are created by the breakdown of abundant plastics. The use of modern and sustainable technologies is essential to protect the environment and human health, given the ineffectiveness of conventional approaches for eliminating harmful contaminants. Through the technologies deploying ozone, membrane filtration, and ultraviolet (UV) disinfection,[12] there are optimistic future possibilities for the successful management of mounting pollutants and improving the water treatment efficiency.[13]

Water purification is one of the most important processes for maintaining human and environmental health, wherein pollutants and harmful substances in water are removed using various physical, chemical, and biological methods.[14] Common water purification methods such as filtration, reverse osmosis, chlorination, UV radiation, distillation, coagulation, and ion exchange each have advantages and disadvantages. They should be deployed in combination based on the type of contamination, water source, and environmental conditions.[15] Filtration, one of the simplest methods, removes suspended particles and some contaminants by passing water through porous layers, improving taste and odor. However, due to its limited removal of dissolved substances and slow filtration speed, it usually requires being combined with other methods.[16] Reverse osmosis is advanced technology that uses semipermeable membranes to remove ions and dissolved contaminants extensively, but its weaknesses include high energy consumption and high water waste. On the other hand, methods such as distillation purify water through evaporation and redistillation, which are very effective but energy-consuming and costly.[17,18] Chemical methods include processes such as coagulation, chlorination, and disinfection, which aim to remove colloids, microorganisms, and pathogens. Coagulation is typically achieved by adding chemicals to water, which converts suspended particles into flocs that can be easily separated. Chlorination and UV radiation are also primary disinfection methods; however, chlorination can produce hazardous byproducts, and UV radiation is ineffective at removing suspended particles without prior treatment.[19,20] Biological processes are mainly used in wastewater treatment to purify water by breaking down organic matter with microorganisms.[21] Table 1 lists standard water purification methods, their advantages, disadvantages, and usages.

Although conventional water treatment methods can remove many contaminants, each method has its own challenges, including high energy consumption, sludge production, chemical residues, and inefficiency at removing certain compounds. The use of coagulation, especially with the aid of MNPs, can improve water quality more effectively by rapidly adsorbing and separating suspended particles and ionic contaminants. Due to their high specific surface areas and magnetic properties, MNPs can rapidly adsorb metal ions and organic materials and subsequently be easily separated by applying a magnetic field. Also, compared to conventional coagulants, MNPs can be separated after adsorption without the need for additional chemicals, thereby significantly redu-

Table 1 Practical comparison of different water purification technologies

Purification method	Advantages	Disadvantages	Applications	Ref.
Filtration	Low installation and maintenance costs, improved taste and odor, and removal of volatile organic compounds	Relatively low filtration speed. Need for periodic filter changes in case of high contamination load	When high-quality outlet water is required (drinking water, sensitive industrial applications)	16
Reverse osmosis (RO)	Removal of a wide range of ions and dissolved salts, and improves taste	High water and energy consumption. Removal of beneficial mineral salts, and maintenance costs	Drinking water production, seawater desalination, industrial wastewater treatment, water recycling, ultrapure water production for the pharmaceutical and electronics industries, and removal of chemical and microbial contaminants	17
Distillation	Produces water of the highest purity. No need for filters or chemicals	Slow and costly process. High thermal energy consumption	Removal of dissolved salts and minerals, destruction of microorganisms and bacteria, removal of volatile organic compounds, and production of pure, contaminant-free water for laboratory, medical, and drinking purposes	18
Adsorption	Ability to absorb organic pollutants and heavy metals. Selective design capability, and possibility of recovery	Requires large amounts of adsorbent. Saturation and need for regeneration or replacement, and cost of adsorbent	When the concentration of pollutants is relatively low, or as a supplementary step	15
Ion exchange	High efficiency at removing specific ions (nitrate, arsenic). It can be combined with other methods	Medium to high initial cost. Limited resin capacity, and need for frequent reduction	Removing water hardness by removing calcium and magnesium ions, reducing the concentration of heavy metals such as lead and cadmium, removing nitrates and sulfates, recycling resins in industrial systems, and producing ultrapure water for pharmaceutical, power plant, and electronic uses	22
Disinfection by chlorine	Cheap and available. Effective at inactivating bacteria and viruses	Production of dangerous by-products (DBPs), ineffective against some parasites	For ultimate microbial assurance in drinking water systems	20
UV radiation	A physical process without chemicals. Effective against most viruses and bacteria	No residual protective effect. Requires pretreatment to remove high amounts of suspended particles	Inactivation of microorganisms, bacteria, viruses, and fungi without the need for chemicals, prevention of algae and pathogenic agents, disinfection of drinking water and treated wastewater, and use as the final disinfection stage in advanced treatment systems	23
Coagulation/chemical flocculation	Rapid adsorption and separation of suspended particles and ions. Reduction of sludge volume and chemical residues. Possibility of recycling NPs	Need to adjust pH and optimal dosage for better performance	Often used as a primary step in municipal wastewater or surface water treatment	24
Advanced oxidation processes (AOPs)	Decomposition of persistent organic compounds, without adding excessive chemicals. Capable of reducing micropollutant compounds	High energy cost. Low selectivity in some cases. Production of intermediate products	For the removal of resistant organics, pharmaceuticals, and complex compounds	25
Combined methods (*e.g.* coagulation + adsorption)	Combining the advantages of methods, improves efficiency, and reduces problems such as clogging or sludge	Higher design and implementation costs. Process control complexity	In systems where the inlet water is difficult or requires a higher outlet quality	26

cing wastewater generation. Surface coating of these MNPs increases the colloidal stability of NPs and prevents their aggregation. Moreover, MNPs can be removed from the system using a magnetic field and returned to the treatment cycle after washing and regeneration. The rapid magnetic separation and high recycling capacity of these MNPs make this technology a desirable and sustainable option for treating contaminated water. This process can be deployed as a low-cost, effective technology in industrial and municipal water treatment.[27–29]

Coagulation is an essential process in water treatment, removing suspended particles, colloids, and organic substances from raw water to enhance its quality. This approach entails the usage of a coagulant, often a metal salt like aluminum sulfate or ferric chloride, to destabilize and agglomerate particles *via* floc formation. By neutralizing particle charges, coagulants enable collisions to form larger aggregates that can settle preferentially, allowing them to be easily removed from the water.[30] Frequently, the coagulation process is followed by flocculation, in which mild mixing promotes the growth of the floc, enhancing its settling characteristics and facilitating its removal in subsequent sedimentation or filtration operations. Several factors affect the efficacy of coagulation, including the type and amount of coagulant deployed, pH, temperature, and the properties of the water being treated.[31] Conventional water treatment facilities depend on coagulation, which also helps to remove turbidity, color, bacteria, and other contaminants from raw water supplies. In addition to its main purpose of eliminating particles, coagulation also eliminates pathogens, dissolved organic compounds, and certain heavy metals by complexing with coagulant species or adsorbing onto floc surfaces.[32] Advanced coagulation techniques, including pre-oxidation with ozone or chlorine, can enhance the elimination of organic pollutants and the overall efficacy of water treatment. Coagulation-based water treatment systems are versatile and adaptable to many water sources and processing objectives, thus rendering them essential in sustainable water management strategies designed to deliver safe and clean drinking water to global populations.[33]

Ceramic NPs based on iron oxide find widespread usage in several technological areas,[34,35] including catalysis,[36,37] energy storage,[38–40] biomedical,[41–43] and water treatment;[44,45] popular varieties are maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), and magnetite (Fe_3O_4). More recently, the assembly and application of iron oxide-based nanocomposites with innovative attributes and capabilities have been extensively investigated.[46] This attention is in view of their nanoscale size, high surface area-to-volume ratio, and superparamagnetic properties.[47] Superparamagnetism is a form of magnetism that occurs in small magnetic NPs, where magnetization can indiscriminately flip direction due to temperature fluctuation, leading to non-magnetic behavior in the absence of an external magnetic field.

Through simple preparations, modifications, and coatings, along with the capability of atomic-scale manipulation of matter, unique magnetic features can be realized.[48,49] Additionally, Fe_3O_4 nanocomposites are highly compatible with biotechnology, showing great potential due to their low toxicity, chemical stability, and high biocompatibility.[50,51] Studies have shown that preparative protocols and coatings on the surface of materials play a crucial function in regulating the morphology, size, surface chemistry, and magnetic attributes of the ensuing NPs.[52–54,55] To date, many researchers have developed proficient physical and chemical protocols for synthesizing Fe_3O_4 nanocomposites.[56] Recently, various approaches have been introduced for producing high-quality nanostructures, such as nano-ovals,[57] nanobelts,[58] nanorings,[59] nanoclusters,[60] and other nanoscale structures.[61,62] To better understand the behavior of colloidal iron oxide particles and to improve their performance, scrutinizing their stability is of utmost importance. Iron oxide NPs tend to aggregate in aqueous and natural environments. The surface of Fe_3O_4 NPs is hydrophilic due to the presence of hydroxyl groups, which enhances interparticle attractive forces around neutral pH, leading to aggregation. To prevent this, the electrostatic and steric stability of the NPs must be enhanced. The presence of hydroxyl groups on their surface enables chemical bonding with various functional groups, and through surface modification techniques, the stability of these particles can be improved while introducing new functionalities. Separating contaminants using an exterior magnetic field, along with the straightforward recovery of Fe_3O_4 NPs for reuse, makes this approach a cost-effective and efficient solution for removing toxic heavy metals from water. In general, nanomaterials must be stabilized to prevent aggregation and to ensure low sedimentation rates, thereby maintaining their reactivity and functionality in various environments.[63–65] However, it has been described that nanomaterials tend to aggregate.[66] Most often, electrostatic and van der Waals (vdW) forces determine the colloidal stability of the particles.[67] One promising strategy is altering nanomaterials with varied functionalities. The deployment of surfactants, polymers, and stabilizers has been widely utilized to create stable NPs with specific chemical properties and targeted functionalities.[68–74]

A comparative analysis of the properties, applications, advantages, and limitations of different NPs is presented in Table 2. Table 2 indicates that many NPs possess unique qualities, uses, and limits that influence their efficacy for water purification. Fe_3O_4-based MNPs are recognized for their facile recovery and reusability, while silver NPs are proficient at eliminating biological pollutants owing to their antibacterial properties. Photocatalytic materials like TiO_2 excel at degrading persistent organic compounds, whereas graphene materials provide excellent adsorption of pollutants owing to their large specific surface areas. Bio-inspired NPs, synthesized from biological materials, offer a sustainable alternative to conventional wastewater treatment methods. Their tailored design enhances the efficiency of the removal of pollutants, while their multifunctionality and integration with traditional technologies yield superior treatment outcomes. Although bio-inspired NPs offer many benefits, industrial manufacturing still faces issues in terms of repeatability and scalability. If

Table 2 Review of the properties, applications, advantages, and disadvantages of various NPs employed in wastewater treatment

NP types	Properties	Applications	Advantages	Disadvantages	Ref.
Fe_3O_4-based MNPs	Magnetic characteristics, easy recovery, and good reusability	Heavy metal removal, organic pollutant adsorption, and simple separation	Reusable because of its excellent adsorption capability and magnetic recovery, easily scalable	Lack of stability in acidic environments and susceptibility to aggregation, releasing iron ions	77 and 78
Ag NPs	High contact area and antimicrobial properties	Degradation of organic contaminants, removal of microbiological pollutants	Very efficient at removing a wide variety of bacteria	Expensive, aggregation problems, and possible toxicity to aquatic life and environments	79 and 80
ZnO	High photocatalytic activity in the degradation of organic pollutants and microbial inactivation	Photocatalytic processes related to water purification, although dependence on UV light limits widespread use	Low to moderate material costs	Moderate toxicity risk	81
TiO_2	Photocatalytic efficacy and stability under UV radiation	Degradation of drugs, colors, and organic contaminants	Sustainability, reusability when exposed to ultraviolet light	Expensive, limited action in visible light; activation needs UV light	82 and 83
CuO	Good efficiency for microbial removal and effective adsorption capability	Widespread use and common production; scalable for a variety of purification applications	Low cost; cost-effective materials and synthesis routes	Risk of copper ion leakage and environmental and health hazards	84 and 85
Graphene-based materials	Excellent adsorption capacity due to high surface area	Adsorption of organic contaminants and heavy metal elimination	Excellent adsorption capacity, amenable for functionalization for targeted removal	High manufacturing costs and possible long-term environmental effects	86 and 87
Mn_3O_4	Strong oxidation potential, photocatalytic activity in visible and near-visible light	Adsorption of heavy metals, dyes, and drugs, catalytic degradation of organic pollutants, and antibiotics	Environmentally friendly with minimal toxic byproducts, capable of removing a wide range of contaminants	Lower adsorption rates for some contaminants, the possibility of leaching and surface degradation, and limited selectivity	88
Bio-inspired NPs	Biocompatibility, a wide range of functions	Multi-functional elimination of organic and inorganic contaminants	Minimal toxicity, eco-friendly synthesis techniques	Large-scale manufacturing difficulties and inconsistent synthesis results	89

these limitations can be circumvented, these NPs could improve filtration and oxidation; however, in mass production, they lack advantages over Fe_3O_4-based MNPs and are mostly considered complementary options for water purification.[75,76]

Nanoscale materials comprising the Fe_3O_4 phase possess distinctive magnetic characteristics. This magnetic feature of Fe_3O_4 NPs makes it easier to manage and separate particles; this has led to great interest in their possible deployment in coagulation-based water purification processes.[90,91] The large surface area-to-volume ratio of Fe_3O_4 NPs, which typically range from a few nanometers to several hundred nanometers in size, enables them to interact with water pollutants, thereby improving the effectiveness of the coagulation process. These NPs serve as a substitute coagulating agent, helping eliminate contaminants such as heavy metals, organic compounds, and microbes from water sources during purification protocols.[92] They also help efficiently deposit and separate pollutants from water by encouraging the formation of larger particle agglomerates, enabling simple filtrations or sedimentation processes for their removal.[93] Fe_3O_4 NPs are a better option for use in sustainable and effective water filtration systems because of their capacity to selectively adsorb specific pollutants and their simplicity of post-processing removal *via* magnetic separation. Although additional scientific studies on Fe_3O_4 NPs for water purification coagulation have been conducted, a thorough examination of this topic is still warranted and requires scrutiny. Herein, important new perspectives on the synthesis, mechanisms, and applications of MNPs in coagulation-based water purification systems are presented. Furthermore, the benefits, drawbacks, and opportunities of iron oxide-based MNPs are documented; these may help identify areas of study gaps for further investigations.[94]

Fig. 2 presents a roadmap of the challenges, improvement strategies, and future development paths for Fe_3O_4-based MNPs in water purification. The roadmap is designed with an analytical and forward-looking approach and depicts the relationship between fundamental problems and technological solutions in a chain. In the challenges section, three main obstacles are identified: particle aggregation, which reduces the active surface area and decreases the adsorption efficiency; ion leaching, which threatens chemical and environmental stability; and limited scalability, which hinders the commercialization and industrial application of these nanostructures. In response to these challenges, key strategies are proposed, including coating and surface modification to prevent aggregation and enhance colloidal stability, chemical functionalization to improve selectivity and reduce the risk of ion release, and the design of modular, tunable systems at the pilot scale to enhance industrial-scale applicability. Future directions focus on developing Fe_3O_4 hybrid composites with higher adsorption efficiency and stability, by conducting a comprehensive eco-safety assessment to ensure the sustainable use of

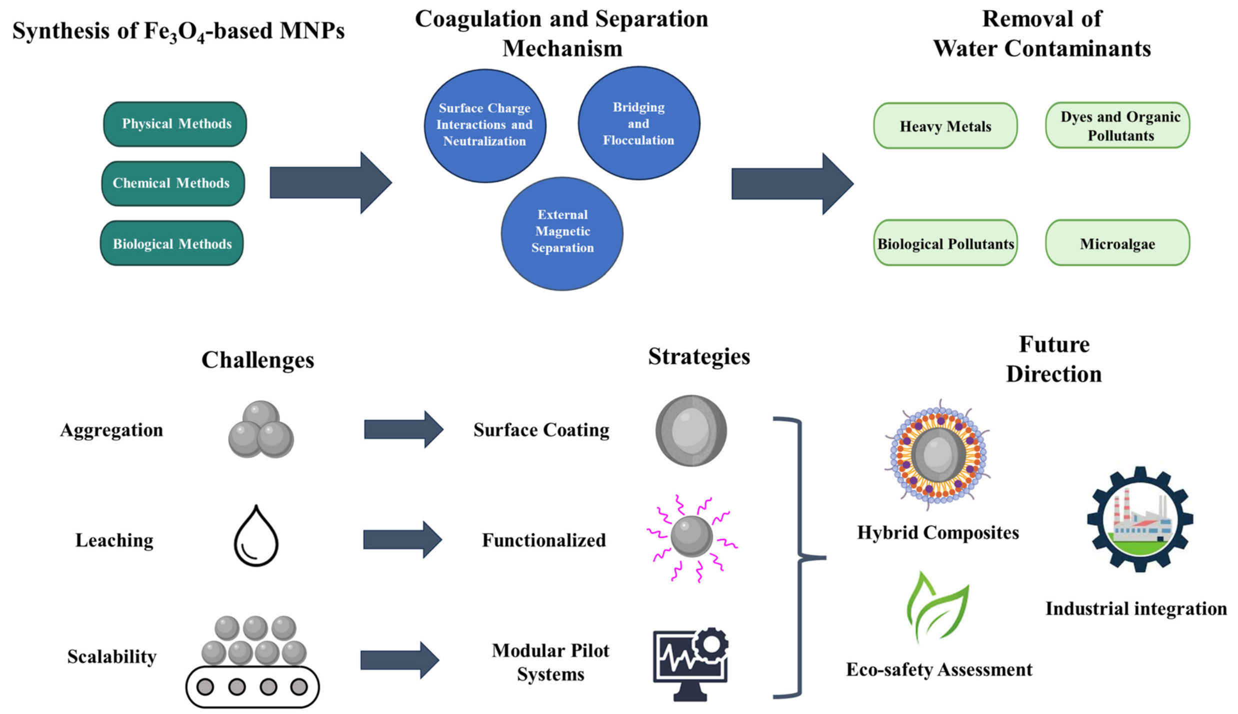

Fig. 2 Roadmap for the usage of Fe_3O_4-based MNPs for water contaminant removal.

these NPs, and integrating the technology into large-scale industrial processes. By providing an integrated viewpoint from the perspectives of materials science, environmental engineering, and nanotechnology, this graphic map presents a coherent framework to better understand the current challenges and guide future research in the field of Fe_3O_4-based MNPs. Furthermore, this can be used as a strategic reference for the development of novel and sustainable water treatment processes.

2. Fe_3O_4-based MNP synthesis methods

Several routes have been deployed for synthesizing Fe_3O_4 NPs (Fig. 3), including chemical, physical, and biological techniques,[95] each with its benefits and drawbacks depending on the application. The term "physical approach" refers to a broad category of methods deployed in the synthesis of Fe_3O_4 NPs, including the use of electrical, radiation, and thermal energy.[96] Some examples of physical approaches include ball milling, laser ablation, wire explosion, sputtering, and flame spray pyrolysis. The ball milling procedure involves crushing iron particles with a grinding agent to generate small particles. This technique is also a popular method for mechanical alloying and the fabrication of composite materials.[97,98] The laser ablation technique involves directing high-energy laser pulses onto a solid iron or iron oxide target submerged in a liquid. This causes the material to evaporate and cool rapidly, ultimately leading to the formation of Fe_3O_4 NPs.[99] During the electrical explosion of a wire, an elevated-density current pulse (exceeding the binding energy) is passed through the wire in a liquid or gas atmosphere. Consequently, the material heats up in a gust, a vivid light blazes, a mix of superheated aerosol and simmering droplets of the shattering wire material, while a shockwave disperses to the ambient atmosphere. The explosion of a base metal wire, such as Fe, generates a mixture of oxides and the metal.[100] In the sputtering technique, a target is bombarded with intense ions, usually from a plasma, which ejects atoms or clusters. These atoms or clusters subsequently deposit onto a substrate in the form of a thin film or Fe_3O_4 NPs.[101] In a vapor-phase synthesis method, often referred to as flame spray pyrolysis, precursors are burned off in the gas phase, thereby generating high-purity nanocrystals, including iron oxides.[102]

Chemical synthesis methods are commonly used for synthesizing Fe_3O_4 NPs.[103] The co-precipitation approach is a commonly utilized process wherein the formation of Fe_3O_4 precipitates is accomplished. This operation involves the hydrolysis of iron compounds, primarily $FeCl_2$ and $FeCl_3$, in a basic aqueous solution, often achieved by adding ammonia or sodium hydroxide.[104] Another method is the hydrothermal method, which exploits superheated water in high-pressure autoclaves to synthesize Fe_3O_4 NPs. Under high temperature and pressure conditions, reactants become more soluble and reactive, enabling the formation of highly crystalline particles.[105] Other techniques include reduction methods, using solvents such as polyalcohols (also known as polyol) to partially reduce Fe^{3+} precursor to produce Fe_3O_4 NPs.[106] In the thermolysis process, typically a metal–organic precursor is

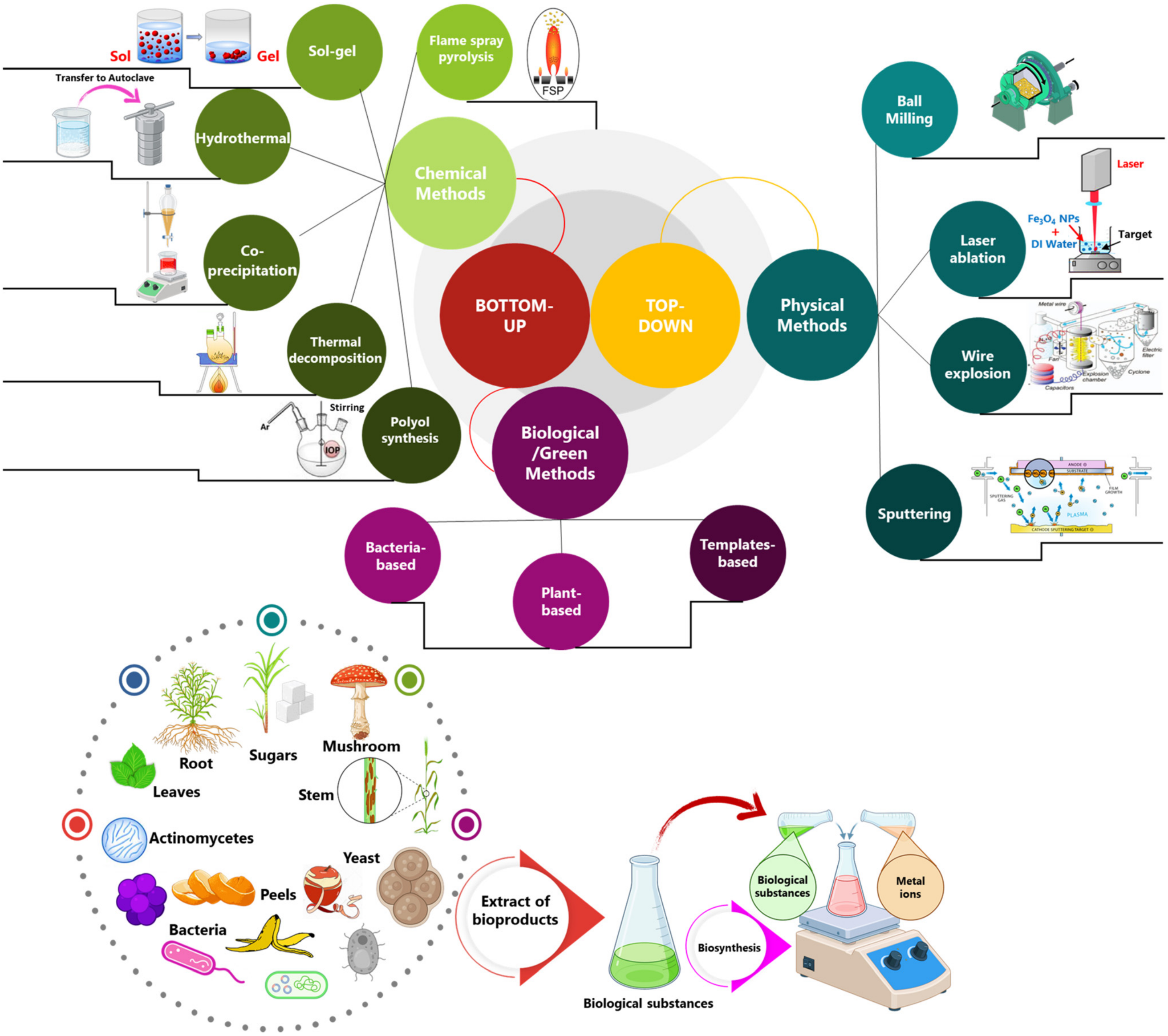

Fig. 3 Schematic illustrations of various Fe_3O_4 NP synthesis methods.

decomposed in an organic solvent at elevated temperatures to form the desired NPs.[107] The sol–gel method for Fe_3O_4-based MNPs involves reacting chemical solution precursors to form NPs through hydrolysis and condensation of the precursors, which can be performed in both aqueous and non-aqueous solvents.[108] The ambient-air fabrication of MNPs entails their synthesis under ordinary atmospheric conditions, eliminating the need for controlled conditions such as under vacuum or inert gases. Benefits of this approach include decreased costs and more production scalability.[109] This approach is more straightforward and cost-effective than techniques that require a controlled environment, and sol–gel synthesis in air can be one of these methods.[110]

Another group of Fe_3O_4 NP synthesis techniques is classified as biological or greener methods. Live organisms or byproducts of biological processes are essential in the biological processes deployed to generate Fe_3O_4 NPs. This approach is considered more eco-friendly because it can produce NPs with the desired sizes and properties without deploying hazardous chemicals.[111] Using energy-efficient, environmentally friendly processes and abundant materials is central to the green synthesis method for producing Fe_3O_4 NPs, which aims to reduce negative impacts on the environment and human health.[112]

Table 3 presents a comparative analysis of different synthesis methods for the fabrication of MNPs, and for each method, a brief description of the synthesis mechanism, along with key parameters affecting the process, is provided. Biological and environmental conditions, particle size and degree of crystallinity, shape controllability, and scalability are among the indicators that have been considered for a more comprehensive analysis of these methods. Also, the advantages and disadvantages of each method have been identified

Table 3 Comparison of different synthesis methods for MNPs in terms of process, structural, and application characteristics

Synthesis methods	Brief explanation	Important parameters/biological–environmental conditions	Particle size/crystallinity	Shape control/scalability	Advantages	Disadvantages	Potential applications	Ref.
Co-precipitation	Reaction of iron salts in an alkaline environment and at controlled temperature	pH, temperature, Fe^{2+}–Fe^{3+} ion ratio, and stirring speed/eco-friendly	5–20 nm/medium	Low/high	Simple, cheap, mass-produced	Less precise control of NPs size	Medicine, catalysis, magnetic storage	113 and 114
Hydrothermal	Reaction in an autoclave under high pressure and temperature	Temperature, pressure, time, concentration of precursors/eco-friendly	10–50 nm/high	Good/medium	NPs with high crystallinity, shape control	Requires autoclave, time-consuming	Medicine, catalysis, sensors	115 and 116
Thermal decomposition	Decomposition of organoiron precursors at high temperatures in the presence of surfactants	Temperature, time, type, and concentration of precursors, type of surfactant/need for organic solvents	5–15 nm/high	Good/medium	Precise size and shape control, uniform NPs	Higher cost, special equipment required	Medicine, magnetic data acquisition, sensors	117 and 118
Sol–gel	Gel formation from chemical precursors and then heating	pH, temperature, gelation time, type of precursor/chemically dependent	5–30 nm/medium to high	Good/low	Uniform production, ability to control the composition	Time-consuming, may require calcination	Catalysis, coatings, medicine	119 and 120
Microemulsion synthesis	Formation of small emulsion (water/oil) droplets that act as nano-reactors	Type of emulsion, ratio of different phases, reaction time/eco-friendly	3–10 nm/medium	Very good/low	Very good control of size and distribution	Less scalability, higher cost	Medicine, nanomedicine, catalysis	121 and 122
Electrochemical synthesis	Iron oxide deposition on the electrode by applying an electric current	Electrical current, time, electrolyte concentration/depends on the electrolyte	5–20 nm/medium	Medium/medium	Good thickness control, simple	Need for electrochemical equipment	Magnetic films, catalysis	123 and 124
Microwave-assisted synthesis	Using microwave heating to accelerate reactions	Microwave power, time, temperature/depending on the type of material	5–20 nm/medium to high	Good/medium	High reaction speed, uniformity	Special equipment	Medicine, catalysts, sensors	125 and 126
Flame spray pyrolysis	Spraying the precursor solution into a very high-temperature flame	Temperature, flame speed, precursor type, spray speed/dependent on flame fuel	5–50 nm/medium to high	Low/very high	Fast production, suitable for industrial scale	Challenging size control	Industrial production, medicine, energy storage	127 and 128
Ball milling (mechanical milling)	Mechanical grinding of powders to produce NPs	Grinding time, grinding speed, ball size, ball to powder ratio/depends on the grinding conditions	20–200 nm/medium	Low/high	Simple, cheap, mass-produced	Pollution, irregular size, high energy	Industrial production, magnetic materials, catalysis	129 and 130
Sputtering	Vapor deposition of atoms from a metal target onto a substrate by ion bombardment	Gas pressure, power, target–substrate distance/requires a vacuum and special equipment	1–10 nm (thin film)/high	Good (film)/low	High-quality thin films	High cost, special equipment	Manufacturing of magnetic films, sensors	131 and 132
Spray pyrolysis	Precursor solution spraying and rapid heating	Temperature, spray speed/dependent on precursors	20–200 nm/medium	Low/high	Scalable, rapid production	Less size control	Industrial production, catalysis, sensors	133 and 134
Ultrasonic-assisted synthesis	Using ultrasound to enhance the reaction	Ultrasound intensity, time/a relatively consistent environment	5–30 nm/medium	Good/low	Better size distribution	Low scalability	Catalyst, nano-drug, nanostructures	135 and 136
Laser ablation	High-energy laser irradiation of a metal target in liquid to produce NPs	Laser power, pulse time, liquid type/chemical-free	5–30 nm/high	Good/low	Chemical-free, good control	Expensive equipment, small scale	Medicine, catalysis, electronics	99 and 137
Thermal plasma synthesis	Using plasma for evaporation and the formation of NPs	Temperature, pressure, and carrier gas/dependent on plasma conditions	10–100 nm/high	Medium/high	Rapid production of NPs	High cost	Industrial production, energy storage, catalysis	138 and 139

Table 3 *(Contd.)*

Synthesis methods	Brief explanation	Important parameters/biological–environmental conditions	Particle size/crystallinity	Shape control/scalability	Advantages	Disadvantages	Potential applications	Ref.
Wire explosion	Electric explosion of metal wire in a gaseous or liquid environment to produce NPs	Explosion current, environment, wire/dependent on the explosion environment	5–50 nm/medium to high	Medium/medium	Rapid production of uniform NPs	Need for specialized equipment	Industrial production, energy storage	140 and 141
Polyol synthesis	Synthesis in a polyol solvent (such as ethylene glycol) as the reducing agent and reaction medium	Temperature, time, type of polyol, precursor concentration/eco-friendly	5–20 nm/high	Good/low	Size control, good dispersion, and simple	Long reaction time	Nanomedicine, catalysis	142 and 143
Biosynthesis	Using bacteria or plant extracts to reduce ions	Type of microorganism, culture conditions/very eco-friendly	10–50 nm/medium	Low/low	Eco-friendly, environmentally friendly	Less control over size and shape	Medicine, pharmacy	144 and 145

separately to enable their critical evaluation. Finally, the potential applications of each method are listed according to the characteristics of the final product. Table 3 provides a comprehensive overview of the strengths and weaknesses of each technique and can be used as a good reference for selecting a synthesis method tailored to specific needs in different fields, especially environmental applications.

Bio-reduction allows some microbes, such as fungi and bacteria, to reduce Fe compounds into iron oxide NPs. Alternatively, some plant extracts or enzymes might be employed as reducing agents during the MNP synthesis process.[146–148] Also, the use of plant extracts or natural components as stabilizing and reducing agents is a common component of this approach during the synthesis of MNPs.[149,150]

As presented in Table 4, biosynthesized Fe_3O_4 NPs can be divided into two main groups, namely microbial synthesis and phytosynthesis. The general steps for the synthesis of Fe_3O_4 NPs using the microbial method entail the selection of the appropriate microorganism, cultivation of the microorganism in a medium enriched with metal ions, bio-reduction of ions, extraction and purification of NPs, followed by analysis and identification of NPs.[151,152] The advantages of the microbial method include biocompatibility and non-toxicity, a lower energy requirement than physical and chemical methods, the production of NPs with uniform size and shape, and the ability to control the surface coating of the NPs (utilizing biological materials produced by cells).[153] Additionally, among the broader applications of MNPs synthesized by microbial methods, targeted drug delivery, MRI imaging, magnetic hyperthermia (in cancer treatment), and the removal of environmental pollutants (such as heavy metals) can be mentioned.[154–157]

In the synthesis of MNPs *via* microbial means, there are two main sites for the formation of NPs: intracellular and extracellular synthesis. In intracellular synthesis, NPs are formed inside the microorganism cell; metal ions enter the cell and are reduced by enzymes or metabolic pathways to generate NPs.[158] Wu *et al.*[159] investigated the intracellular synthesis of Fe_3O_4 NPs using the bacterium *Acidithiobacillus ferrooxidans* (Fig. 4A). Results revealed that the addition of sulfur to a medium containing divalent iron delayed microbial growth and iron oxidation. TEM micrographs showed that iron was an essential energy source for NP synthesis in cells and that varying the iron-to-sulfur ratios did not significantly affect the bacterial appearance or NP size, whereas in the absence of iron, MNPs were not formed. Furthermore, the observed morphology was club-shaped under ferrous iron and rod-shaped under elemental sulfur. Lang and Schuler[160] examined the process of magnetosome biomineralization in magnetotactic bacteria (*Magnetospirullum gryphiswaldense*). Magnetosomes are nano-sized organelles that are membrane-enclosed, form magnetic iron crystals, and are arranged in a regular chain structure within the cell. This process is genetically controlled and involves the accumulation of iron, crystal deposition in a specific compartment, and organization and alignment of the particle chains. Contrary to what is expected from most in-

Table 4 A survey of biosynthesized MNPs through microbial and phytosynthesis routes

Microbial synthesis				Phytosynthesis			
Intracellular		Extracellular		Plant extract (beans, roots, fruits, leaves, seaweed, seeds)		Plant wastes	
Magnetospirillum sp. AMB-1	162	*Geobacter metallireducens* GS-15	163	*Annona muricata* hot water extract	164	*Musa acuminata* peel ash hot water extract	165
Aquaspirillum magnetotacticum	166	Thermophilic bacteria TOR-39	167	*Mimosa pudica* hot water extract	168	Banana peel ash and *Colocasia esculenta* leaf water extract	169
Pseudomonas aeruginosa Kb1	170	*Lactobacillus casei* cytoplasmic extract	171	*Platanus orientalis* L. hot water extract	172	Watermelon rind water extract	173
Magnetospirillum magnetotacticum	174	*Clostridium* sp.	175	Carob hot water extract	176	Plantain peel extract	177
Magnetospirillum magneticum AMB-1	161	*Verticillum* sp.	178	Carob extract	179	Aqueous extract of spent tea waste	180
Acidithiobacillus ferrooxidans	159	*Actinobacter* spp.	181	*Kappaphycus alvarezii* aqueous extract	182	*Syzygium cumini* seed extract hot water extract	183
Magnetospirillum gryphiswaldense	160	*Spirogyra* sp.	184	Aloe vera water extract	185	Chinese cabbage (*Brassica rapa* subsp. *pekinensis*) outer leaves extract	186
		Bacillus cereus strain HMH1	187	*Cicer arietinum* L. water extract	188	*Citrus unshiu* tangerine peel water extract	189
		Geobacter sulphurreducens	190	*Padina pavonica* hot water extract	191	Pomegranate, lemon, orange, and apple peels in hot water extract	192
		Spirulina sp.	184	Shanghai white tea (*Camellia sinensis*)	193	Corn silky hair (*Zea mays* L.) water extract	186
		Fusarium oxysporum	178	Brown *Sargassum muticum* water extract	95		
		Thermoanaerobacter ethanolicus TOR-39	194	Stevia fresh water extract	195		
		Clostridium sp.	196	Urea and gram-bean (GBE, *Cicer arietinum* L.) extract	180		
		Shewanella sp.	197	*Desmodium gangeticum* hot water extract	198		
		Protoparmeliopsis muralis	199	Carica papaya hot water extract	185		
				Passiflora tripartita methanol/water extract	200		
				Neem leaf hot water extract	201		
				Rhus coriaria hot water extract	202		
				Amaranthus spinosus water extract	203		
				Psidium guajava and *Moringa oleifera* hot water extract	204		
				Chromolaena odorata extract	205		
				Hordeum vulgare water extract	206		
				Sargassum acinarium hot water extract	191		
				Azadirachta indica hot water extract	207		
				Soya bean sprouts	208		
				Albizia adianthifolia hot water extract	209		
				Flax extract	179		
				Andean blackberry hot water extract	210		
				Fig (*Ficus carica*) ethanolic extract	211		
				Eichhornia crassipes hot water extract	212		

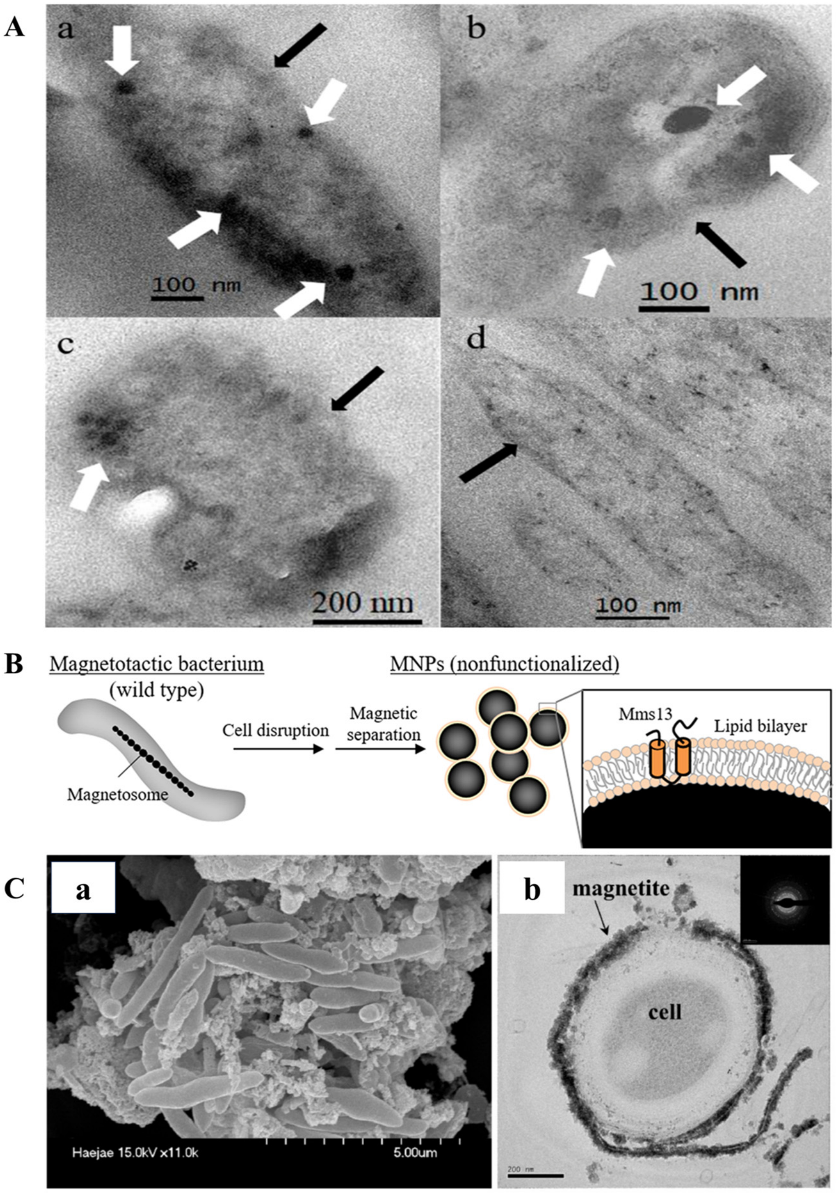

Fig. 4 (A) TEM images of individual cells collected from media with various ferrous/sulfur element concentrations (g per 100 mL) in the growth medium: (a) 4.47/—, (b) 4.47/0.8, (c) 4.47/1.6, and (d) —/1,[159] reproduced from ref. 159 with permission from MDPI, copyright 2025; (B) procedure for the production of ELP-MNPs by the magnetosome display system,[161] reproduced from ref. 161 with permission from American Chemical Society, copyright 2025; (C) (a) SEM image of Haejae-2 and (b) TEM image of the cell's cross section showing precipitated Fe_3O_4 NPs adjoining the cell exterior,[175] reproduced from ref. 175 with permission from MDPI, copyright 2025.

organic systems, the Fe_3O_4 crystals produced by these bacteria have uniform morphology and size. Yoshino *et al.*[161] synthesized thermo-responsive MNPs using a magnetosome display system (Fig. 4B). The results revealed that bio-nanoparticles were synthesized from magnetotactic bacteria (*Magnetospirillum magneticum* AMB-1) and a decamer peptide called ELP10, which became hydrophobic above its transition temperature, thereby immobilizing on the NPs. Similarly, at 60 °C, the hydrophobicity of the NP surface increased compared to that at 20 °C, leading to particle aggregation *via* hydrophobic and magnetic interactions. Size distribution analysis confirmed that with increasing temperature up to 60 °C, the immobilization effect of ELP10 caused more particle aggregation, resulting in faster collection of MNPs under an external magnetic field at 60 °C.

On the other hand, in extracellular synthesis, NPs are synthesized in the environment outside the cell (*e.g.*, culture medium or supernatant solution). Microorganisms secrete enzymes, proteins, or metabolites into the environment that reduce the metal ions to form NPs.[213–215] Fatemi *et al.*[187] succeeded in the biosynthesis (extracellular) of magnetic iron oxide NPs using the *Bacillus cereus strain* HMH1. The results showed that the NPs produced had nearly monodisperse spherical morphology with an average diameter of around 29 nm. In another study by Kim and Roh,[175] the microbial growth conditions were investigated to control the size of Fe_3O_4 NPs synthesized by Fe(III)-reducing bacteria, isolated from sediments of intertidal areas of South Korea (Haejae-2 mixed culture bearing *Clostridium* sp.) (Fig. 4C). The results showed that these bacteria were capable of producing Fe_3O_4 NPs with diameters ranging from 2 nm to 10 nm. Furthermore, MNPs produced through microbial processes exhibited superparamagnetic behavior, rendering them highly valuable for various biotechnological and medical applications.

Another biosynthesis process for Fe_3O_4 NPs is the phytosynthesis method, which is a greener biological means to generate NPs wherein plant extracts (from beans, roots, fruits, leaves, seaweed, and seeds) or residual plant wastes are deployed to reduce metal ions and convert them into metal or metal oxide NPs.[216] Table 4 highlights some of the research conducted *via* this phytosynthesis strategy. Plant extracts such as aloe vera,[185] green tea leaf,[203,217] and soybeans[208] have been successfully employed to synthesize MNPs. Some examples of beneficial secondary metabolites found in plant extracts include polyphenols, which are present in both green tea and grape seed extracts. Stabilization and agglomeration of MNPs are two crucial roles that these metabolites perform. By conducting the synthesis at moderate temperatures and pressures, this approach can eliminate the use of organic solvents and hazardous compounds, which are detrimental to the environment. This approach not only produces high-quality MNPs but also promotes sustainability by enabling their use in various areas, such as water purification, waste treatment, heavy metal removal, and biomedical applications. Prodigious adoption of this methodology has the potential to accelerate the development of nanotechnology and its potential applications to improve people's lives worldwide by advancing technologies that are less harmful to the environment and more sustainable.[218–220]

3. Coagulation mechanism for Fe_3O_4-based MNPs

The coagulation mechanism generally removes organic substances through three primary mechanisms: negatively charged organic colloids aggregate with positively charged metal ions; organic molecules form precipitates with metal ions; or adsorption onto the surface of alum, leading to coagulation. In recent years, the use of MNPs has gained significant attention in view of their exclusive magnetic attributes, large specific exterior area to volume ratios, and relatively easy recovery through the application of magnetic fields. The coagulation mechanism involving MNPs can operate through various physical or chemical processes, enabling the removal of heavy metals, suspended pollutants, and other water impurities. The coagulation methods for each mechanism *via* the deployment of Fe_3O_4 NPs are described in the following sections.[221]

3.1. Surface charge interactions and neutralization

The mechanism of electrostatic interactions and charge neutralization involves several steps. Techniques include zeta potential assessment, which is used to evaluate the surface charge of particles, thereby providing insights into their stability and inclination to assemble. This helps to manage electrostatic interactions between the NPs. Theoretical models, such as DLVO theory, provide a systematic framework for understanding how vdW and electrostatic forces interact to determine the stability or instability of colloidal systems during coagulation.[222,223] Industries may maximize operations, such as flocculation in wastewater treatment or the generation of stable dispersions in pharmaceutical formulations, by altering these interactions *via* pH adjustment or the addition of electrolytes. A schematic for the neutralization of MNPs is depicted in Fig. 5a. Initially, Fe_3O_4 molecules dissociate in water and release Fe^{2+} and Fe^{3+} ions, which have the opposite charge to that of the colloidal particles. These ions are adsorbed onto the surface of the negatively charged colloids, reducing their surface electrostatic charge and, consequently, inducing electrostatic repulsion between them. This phenomenon initiates the flocculation process. In addition to reducing electrostatic charges, Fe_3O_4 coagulants also function as a bridging agent through vdW forces, facilitating further binding between colloidal particles and promoting the formation of larger aggregates. As the repulsive forces diminish and the bridging effect of the coagulant increases, the colloidal particles readily adhere to one another, forming larger flocs that can either settle under the effect of gravity or be removed *via* simple filtration.[224–226]

Among the factors influencing the efficiency of coagulation *via* this mechanism, pH is a key parameter, along with the coagulant dose, which must be precisely controlled to achieve optimal pollutant removal. pH affects not only the ionization of coagulants but also the behavior, or speciation, of contaminants dissolved in water. An optimal procedure for pollutant removal *via* Fe_3O_4-based MNP coagulation requires careful pH control. Assorted pollutants require different pH ranges for effective coagulation.[227,228] For example, neutral pH is generally suitable for inorganic particles, whereas an acidic pH is preferred for the removal of humic organic substances *via* charge neutralization mechanisms.[229] Moreover, lower pH increases the positive charge on coagulant species, thus enhancing the neutralization of negatively charged colloids.[229,230] However, extremely low or high pH levels may reduce the efficiency of the coagulation process, either by decreasing the reactivity of the coagulant or by altering the physicochemical characteristics of the particles in solution.[229]

Studies have demonstrated the significant impact of pH on removal efficiency for pollutants. For example, as reported by El-Nemr *et al.*,[231] the removal percentage and equilibrium adsorption capacity of substances like Pea-B and Pea-BO-NH_2 tend to increase with rising pH values. By increasing the pH

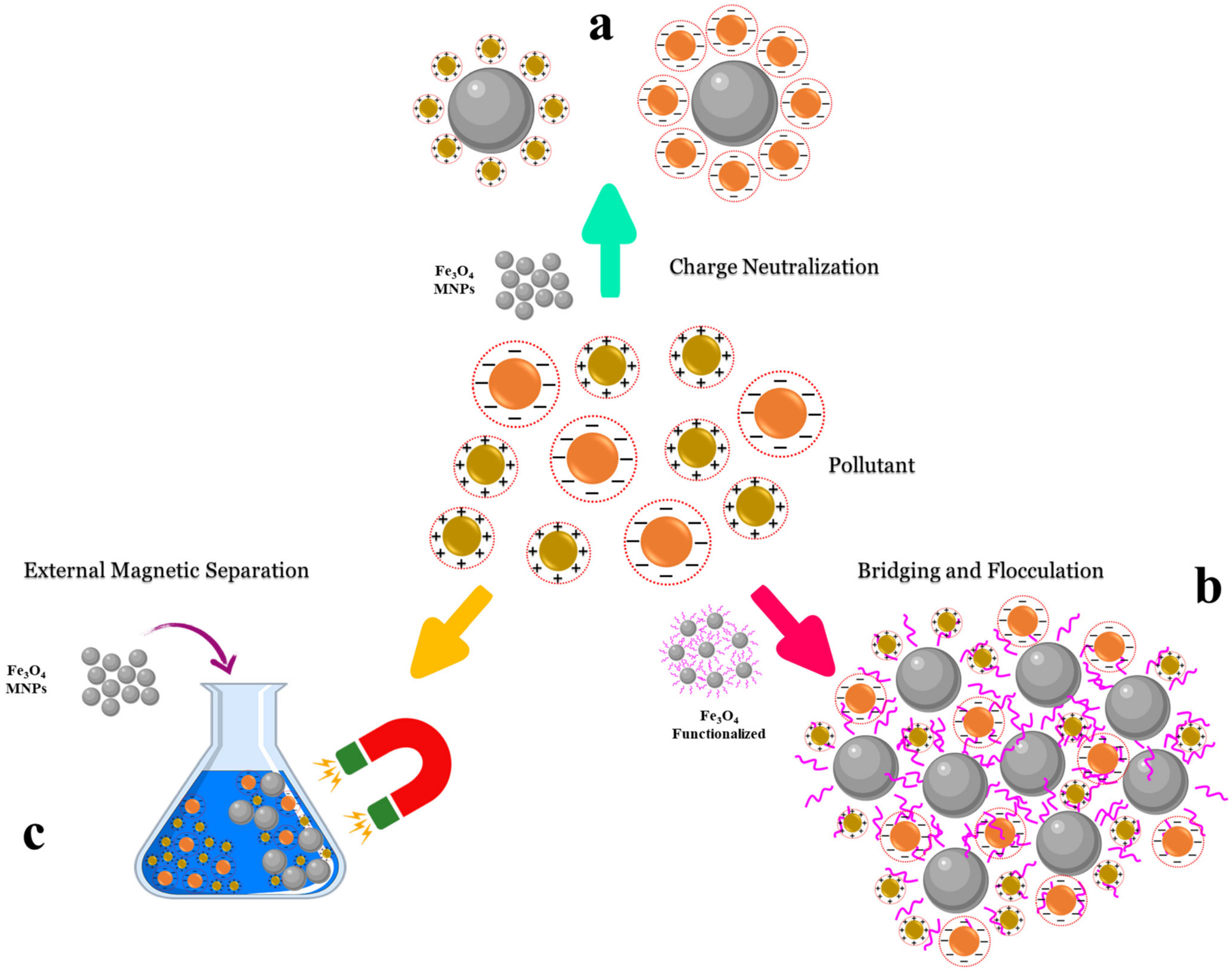

Fig. 5 Schematic of the coagulation mechanism using Fe_3O_4 NPs: (a) charge neutralization, (b) bridging and flocculation, and (c) external magnetic separation.

(from 2 to 7), the removal efficiency and the amount of adsorbed Cu^{2+} ions increased significantly for both biochars, because at low pH, H^+ ions competed with Cu^{2+} ions for adsorption sites. Still, at higher pH, the biochar surface functional groups are deprotonated and acquire a more negative charge, thereby enhancing the electrostatic adsorption of Cu^{2+}. In the context of Fe^{3+} ion removal with activated carbon generated from horse chestnut shells, the removal percentage begins at around 75% at pH = 2, ascends to about 95% at pH = 4, and thereafter declines to around 85% at pH = 12. The equilibrium adsorption capacity for Fe^{3+} ions fluctuates with pH, reaching a minimum at pH 6 and increasing at both lower and higher pH values.[232] In conclusion, pH and coagulant dosage are critical factors for optimizing the coagulation performance of Fe_3O_4-based MNPs. These parameters influence the surface charge of both the coagulant and contaminants, thereby affecting the primary coagulation mechanisms, including charge neutralization and adsorption.[233,234]

3.2. Bridging and flocculation

The bridging and flocculation mechanism plays a key role in the coagulation process. It involves the interaction between colloidal particles and coagulant molecules, resulting in the formation of larger flocs that can be easily settled or filtered. Initially, in the bridging mechanism, polymeric coagulant molecules form bridges between colloidal particles. Polymers such as polyacrylamides or polysaccharides physically adsorb multiple colloidal particles, forming connections that lead to particle aggregation. Unlike the charge neutralization mechanism, which relies on electrostatic forces to neutralize surface charges, the bridging and flocculation mechanism relies on the physical adsorption of polymer chains onto colloidal particles. This brings the particles closer together, thereby promoting the formation of larger aggregates. These interactions may occur through chemical bonds or electrostatic forces, leading to the formation of initial clusters known as microflocs (Fig. 5b).

During the flocculation stage, due to water flow and agitation, microflocs interact and connect, forming larger and denser flocs. This process is governed by vdW, electrostatic, and hydrophobic forces between adjacent particles. The growth of flocs during flocculation largely depends on Brownian motion, collision kinetics, and the adhesiveness between microflocs.[235–237] However, the nature and strength of the interparticle forces determine whether these collisions result in effective attachment and growth of the floc. As flocs grow, their density increases, facilitating their sedimentation or flotation and allowing their removal from the water. The sedimentation or flotation behavior of the flocs depends on the specific gravity of the surrounding liquid, which serves as a regulatory factor. Finally, sedimentation under gravity and subsequent filtration are employed for separation. This process is critical for achieving clean water suitable for drinking, industrial, and agricultural applications. Temperature has a significant impact on reaction rates and molecular mobility in solution.[221,238,239] Generally, higher temperatures can enhance coagulation and flocculation rates by increasing the kinetic energy of particles in solution.[240] However, it should be noted that the effect of temperature is not uniform and depends on the type of coagulant deployed and the specific reaction conditions. Therefore, adjusting the temperature based on these operational parameters is crucial for achieving optimal performance in the coagulation process.[241] Studies have shown that higher temperatures lead to higher adsorption by the coagulant, and the mechanism of colloidal particle adsorption may shift from physical to chemical.[94]

3.3. External magnetic separation

Contaminants such as heavy metals and organic compounds often carry electric charges but lack magnetic properties, so they cannot be directly attracted by magnets. Therefore, one effective approach to remove colloidal particles and pollutants is to use magnetic intermediaries that enable magnetic field-based separation. In the external magnetic separation mechanism, MNPs are used for pollutant removal and can be dispersed in water; their mechanism is illustrated schematically in Fig. 5c. First, these MNPs are surface-functionalized and bestowed with an electric charge. These charged NPs then adsorb oppositely charged pollutants *via* surface adsorption, thereby attaching to them. Once the MNPs bind to specific contaminants in water, such as heavy metals, organic pollutants, or microorganisms, an external magnetic field is applied to the water sample. The magnetic field attracts MNPs, and since the pollutants are attached to them, the entire NP–pollutant complex is influenced by the magnetic field. Ultimately, this process facilitates the aggregation of pollutants into larger clusters in a specific area of the water sample. After magnetic separation, the pollutants can be easily removed from the water using magnets or magnetic separation techniques.[27,242,243] This rapid process eliminates contaminants without requiring complex filtration systems or chemicals, making it an affordable and environmentally friendly method for water purification. Achieving the ideal efficiency in the separation process depends critically on the MNP dose (*i.e.* the quantity of MNPs added to the solution). Generally speaking, increasing the MNP dosage improves the process efficiency, as more material becomes available to adsorb dissolved particles and form larger flocs.[244]

Overdosing with MNPs can result in chemical waste. Moreover, the ensuing numerous encounters between MNPs can promote aggregation and clumping, thereby lowering their efficiency. Furthermore, excess MNP application might increase the electrostatic repulsion in the solution, thereby separating colloidal particles and inhibiting their aggregation. These factors could together cause the MNP's total adsorption capacity to drop. Consequently, a key phase in the design and running of water or wastewater treatment systems is the adjustment of the MNP dosage.[94,245]

4. Removal of water contaminants by MNPs

Contaminants found in wastewater are among the most problematic, as they do not biodegrade in most cases. Examples of these pollutants include heavy metals, organic pollutants, microalgae, bacteria, and viruses, which are responsible for causing significant health issues in living organisms.[246] This section discusses the elimination of water pollutants utilizing iron oxide-based MNPs.

4.1. Heavy metal removal

The crust, soil, and water on our planet contain a variety of heavy metals. Anthropogenic demands, such as the use of pesticides and herbicides, as well as industrial waste and the combustion of fossil fuels, cause these substances to be present at greater quantities than they normally occur. Industrial runoff containing heavy metal ions has been more prevalent over the last many decades.[247] Heavy metal ions are dangerous to humans, animals, and the environment, even at low concentrations, and therefore are a major problem for freshwater supplies.[248] Mental disorders, musculoskeletal discomfort, gastrointestinal issues, visual difficulties, chronic weariness, and a heightened vulnerability to fungal infections are some of the chronic degenerative illnesses that may be caused by heavy metal poisoning.[249–251]

The heavy elements mentioned are usually introduced into the environment through human activities such as mining, fossil fuel combustion, industrial waste disposal, and wastewater treatment. Although these elements are used in many areas, such as the production of electronic equipment, paints, batteries, and advanced alloys, their uncontrolled release into the ecosystem can cause severe biological effects. These effects include cytotoxicity, neurological disorders, damage to the kidneys and immune system, and even the occurrence of chronic diseases such as cancer. Therefore, understanding the sources, uses, and effects of these elements is essential for pollution control and environmental risk assessment.[35,36] In this regard, the advancement of nanotechnology, especially in the field of NP development, has provided new solutions for removing heavy metals from water. MNPs play a key role in the purification of water contaminated with heavy metals due to their high specific surface areas, easy recovery, and high adsorption efficiency. Table 5 examines the heavy elements from various perspectives and categorizes them by source of release into the environment, industrial applications, and biological effects.

As shown in Fig. 6a, the number of publications on heavy metal removal from water has risen significantly from 2000 to 2022. This trend has continued steadily since then, indicating that this problem is becoming more prevalent. Over the last several years, there has been a growing emphasis on the use of inexpensive alternative nanomaterials as prospective sorbents for the elimination of heavy metals. To enhance the exterior adsorption capacity and to form stable complexes with aqueous-based metal ion species, it is desirable to have high porosity and a large surface area among small particles.[285] The use of Fe_3O_4 NPs for the adsorption and deposition of metal ions, as well as for magnetic separation, is an essential method for managing waste and recovering valuable components from metal-containing waste.[286] The interactions between metal ions and functional groups present on the surface of Fe_3O_4 NPs enable the sorption of metal ions from a medium onto the surface of the MNPs, an adsorption process.[287,288] The surfaces of Fe_3O_4 NPs carry specific charges, such as carboxylate (COO^-) or hydroxyl (OH^-) groups, and may serve as sites for metal ion adsorption.[289,290] Metal ions may undergo adsorption and then precipitate out as bigger solids; these can then be separated by magnetic separation methods. Metals may be more efficiently and effectively removed from solutions or debris with this method.[291,292] Fig. 6b presents some of the recent research on the usage of Fe_3O_4 NPs to remove heavy metals.[28,293–300]

Fe_3O_4-based MNPs are promising adsorbents and demonstrate exceptional reusability for the elimination of aqueous metal ions in wastewater treatment processes. Rajput *et al.*[293] produced Fe_3O_4 MNPs *via* the chemical co-precipitation method for the removal of aqueous Cr^{6+} and Pb^{2+} (Fig. 7a). The study examined the impact of pH, revealing that maximum removal of Cr^{6+} and Pb^{2+} occurred at pH 2.0 and 5.0, respectively (Fig. 7b). Xue *et al.*[28] synthesized Fe_3O_4 MNPs modified with oxidized humic acid (HA-O/Fe_3O_4) by chemical amendment to enhance the adsorption capacity and investigated its adsorption of Ni^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} ions (Fig. 7c). HA-O/Fe_3O_4 demonstrated accelerated kinetic performance for the removal of these ions, adhering to the pseudo-second-order kinetics equation, while the adsorption isotherm aligns with the Langmuir model, exhibiting the highest adsorption capacities of 111.10, 76.92, 71.43, and 33.33 mg g^{-1}, respectively. The interaction among metal ions and the functionalities on the adsorbent was further examined, revealing that adsorption occurred *via* complexation at high pH and cation exchange at low pH (Fig. 7d).

One important part of waste management is magnetic separation, which is both efficient and environmentally safe, with the key component being the materials' response to magnetic fields.[301] The process of metal removal involves exposing materials containing metal to a magnetic field, thus enabling their separation from non-magnetic material.[302] Sophisticated automated magnetic separation equipment is often used to accomplish this partition, thereby improving processing efficiency and allowing capacity enhancement.[303] Adsorption and deposition of metal ions onto MNPs, combined with magnetic separation methods, enhance the elimination of metal and metal ions from waste and solutions. Magnetic precipitation and separation allow for more complete separation of metals from solution or waste materials while also separating them from other materials.[304] This technique improves metal removal efficiency, minimizes environmental impact, and reduces the need for additional raw materials.[305]

4.2. Removal of dyes and organic pollutants

In the context of our day-to-day operations, dyes and other organic pollutants are encountered to a significant extent due to their widespread usage in textiles, food, medicines, medical diagnostics, cosmetics, and other industries.[306–308] The occurrence of these substances in aquatic effluent, even at very low dilutions, is exceedingly hazardous and undesirable.[309] The projected yearly average total amount of dyes deployed worldwide by enterprises is deemed considerable.[310] Consequently, studies conducted by academic researchers on the elimination of organic pollutants and dyes have shown considerable growth (Fig. 8a). Various metal oxide-based NPs are utilized for the removal of dyes from wastewater.[311–314] Among different metal oxides, the elimination of dyes from such marine liquids is a common application of Fe_3O_4 NPs, whether they are pure, doped, or in composite form.[315,316]

Organic substances may be adsorbed onto Fe_3O_4 NP surfaces from solutions, wherein hydrogen or vdW bonds can form between organic molecules and functional groups.[317] Surfaces of MNPs with varying charges may reduce the concentration of liquid organic pollutants by acting as adsorption sites for these compounds. In addition to adsorption, Fe_3O_4 NPs can oxidize or undergo photocatalytic processes, both of which degrade organic contaminants.[318] Numerous recent studies have used Fe_3O_4 NPs for the adsorption and degradation of dyes and organic chemicals, as depicted in Fig. 8b.[319–327]

The synthesis of the Fe_3O_4@MnO_2 core–shell nanocomposite for the removal of methylene blue and As^{5+}, two major pollutants, from water (Fig. 9a) has been described.[320] As shown in Fig. 9b, Fe_3O_4 cores are coated with a MnO_2 shell. The Fe_3O_4@MnO_2 core–shell nanocomposite exhibited ferromagnetic behavior and a maximum adsorption capacity of 146.1 mg g^{-1} for methylene blue and 16.6 mg g^{-1} for As^{5+}; it has the potential to be an effective adsorbent for the elimination of methylene blue and As^{5+} from aquatic media.[328]

Using a green and safe wet-chemical process, Singh *et al.*[327] produced superparamagnetic Fe_3O_4 NPs coated with polyphenols from green tea (Fe_3O_4@GTP MNPs). Due to the hydrophilic coating of GTPs, the MNPs produced were highly stable

Table 5 A review of the sources, uses, and ecology of heavy metals in the environment

Heavy metals	Sources of release to the environment	Applications	Biological effects	Ref.
Aluminum	Natural and industrial resources, exchange with magnesium and calcium	Food, pharmaceutical, and construction industries	Effects on biological systems, binding to citrate, transport in blood, storage in bone, accumulation in the brain, involvement in Alzheimer's disease, bone weakness, and oxidative stress	252 and 253
Antimony	Batteries, flame retardants, ceramics, alloys	Coal combustion, plastics industry, flame arresters	Skin and eye irritation, respiratory toxicity, cardiac disorders, and potential carcinogenicity	254 and 255
Arsenic	Gold mining, natural erosion, geological processes, biological activity, volcanic eruptions, and fossil fuels	Car batteries, paints and pigments, pesticides, textiles, medical waste, semiconductors, electronics industry, food additives, cement, and the glass sector	Skin damage, hyperkeratosis, skin cancer, lung, liver, kidneys, bladder, digestive problems, high blood pressure, reproductive problems	222 and 256
Cadmium	Weathering of rocks, forest fires, volcanic eruptions, waste incineration, metal plating, fertilizers, PVC products, cadmium alloys, batteries	Industrial products, batteries, alloys, and plastics	Accumulation in the body causes damage to the nervous system, liver, lungs, kidneys, heart, carcinogenicity, mutagenicity, pulmonary fibrosis, severe digestive problems, and death	257 and 258
Chromium	Industrial activities, leather, paints, stainless steel	Chromic acid production, dyes and pigments, wood preservation, tanning, paint and printing, oil refining, stainless steel, textiles, pulp	Cancer, kidney and liver damage, lung tumors, severe diarrhea, skin allergies, breathing problems, internal bleeding	259 and 260
Cobalt	Paint industry, rechargeable batteries, special alloys, and mining	Automotive, metalworking, paint, and electronics industries	Low blood pressure, vomiting, nausea, heart disease, vision problems, loss of appetite, thyroid damage, hair loss, bleeding, diarrhea, genetic changes	261 and 262
Copper	Submarine sediments, wiring, plumbing, alloys, and dietary supplements, using contaminated water for irrigation, garbage disposal	Electrical wiring, plumbing, electronics, white goods, brass and bronze alloys, dietary supplements, oil refining, mining, tanning	Diarrhea, vomiting, stomach pain, dermatitis, asthma, bronchitis, anemia, kidney and liver damage	263 and 264
Iron	Natural, insoluble at normal pH, water sediments, iron pipes, municipal and industrial wastewater, erosion of rocks and soil	Body needs, enzymes, hemoglobin, metallurgy, energy storage	Excess iron leads to oxidative stress, liver damage, fibrosis, cirrhosis, and damage to cell membranes	265 and 266
Lead	Batteries, paints, paper, galena ore (PbS), mining, papermaking, tanning, metal smelting, pesticides	Batteries, paint, soundproofing materials, metal industry, agriculture	Decreased IQ in children, mental disorders, high blood pressure, anemia, migraines, muscle pain, memory disorders, Alzheimer's, and bone formation disorders	267 and 268
Mercury	Mining, thermometer and barometer production, electroplating, catalysts, fluorescent lamps, batteries, electric switches, pharmaceuticals	Thermometers, medicines, and solar cell industry	Tremors, insomnia, memory loss, neurological disorders	269 and 270
Nickel	Waste incineration, mining, fuel, coal, ash, boilers, cement, pesticides, and electroplating	Ceramic industry, plating, glazing, and power plants	Lung and bone cancer, chest pain, shortness of breath, dermatitis, skin allergies, cyanosis, headache	271 and 272
Selenium	Chemical fertilizers, oil refining, and power plants	Dietary supplements (in low doses), semiconductors	High doses cause hair loss, brittle nails, nervousness, and nerve damage	273 and 274
Platinum	Platinum group elements in the Earth's crust, automotive catalysts, jewelry, anticancer drugs, road dust	Jewelry, anti-cancer drug, car catalyst, automotive and pharmaceutical industries	Allergies, asthma, nausea, hair loss, miscarriage, eczema	275 and 276
Tellurium	Industrial waste, heavy metal purification	Alloys, electronics industry, and solar energy	Garlic breath odor, fatigue, digestive disorders, liver toxicity	277 and 278
Tin	Metal containers, alloys, and preservatives	Cans, kitchenware, polyvinyl	Chronic toxicity, kidney damage, abdominal pain, nervous irritation	279 and 280
Vanadium	Earth's crust, shock-resistant alloys, therapeutic supplements, ceramic pigment	Ceramic industry, complementary therapy, spring steel, and additives	Throat, nose, and eye irritation, nosebleeds, dizziness, headache, nausea, skin rash, nervous disorders, liver and kidney bleeding, tremors, paralysis, behavioral changes, heart disease	281 and 282
Zinc	Paint, sulfate fertilizers, battery, and plating industries	Paint, pigments, rubber, and chemical industries, batteries, manufacturing, electroplating, needed by the body, enzymes, nervous system	Gastroenteritis, peritonitis, growth retardation, stomach pain, skin irritation, diarrhea, vomiting, anemia, shock, death	283 and 284

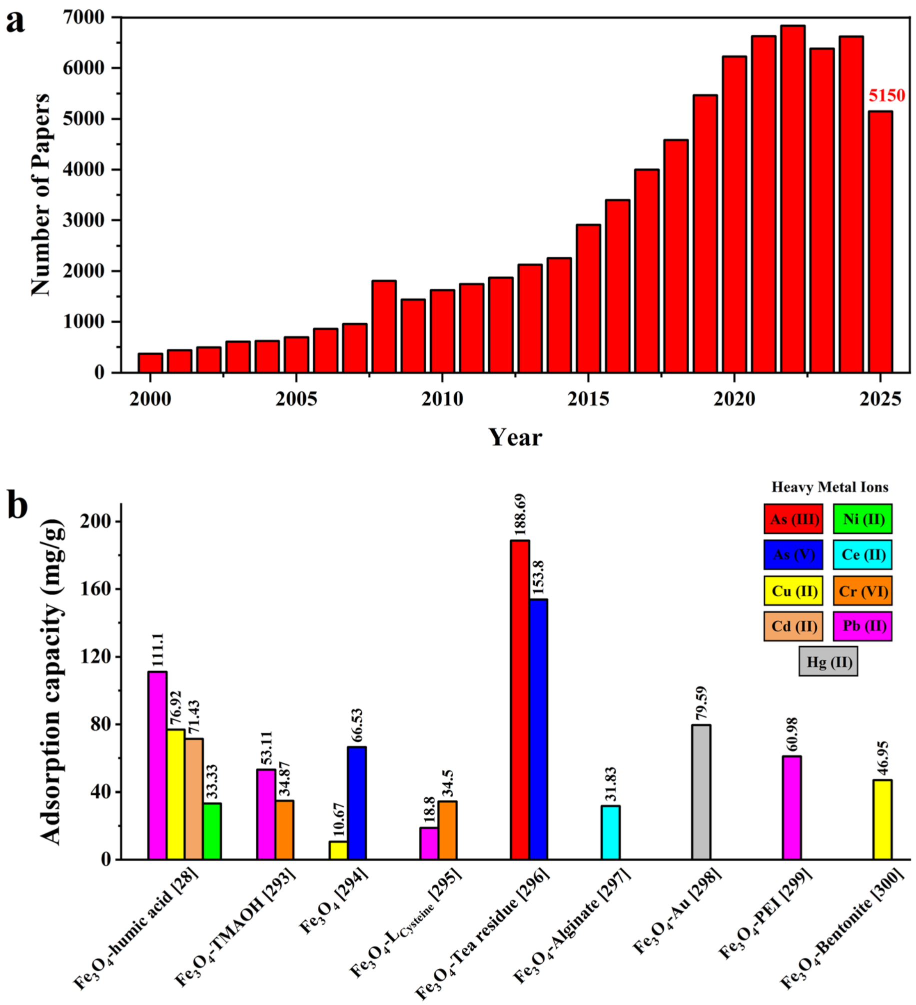

Fig. 6 (a) Rising interest in heavy metal removal, as evidenced by the increasing number of publications (from the Web of Science database using the keyword "Heavy metals removal" extracted on 15 November 2025), and (b) adsorption of heavy metals *via* Fe_3O_4-based MNPs.

and well dispersed in an aqueous medium. The cationic dye methylene blue could be rapidly adsorbed onto Fe_3O_4@GTPs due to the high concentration of negatively charged polyphenolic hydroxyls (single bond OH) on the surface of these MNPs. These groups could form an effective complex with the cationic dye methylene blue *via* electrostatic interactions, thereby significantly improving its adsorption. Fig. 9c depicts a schematic representation of the methylene blue adsorption process on the Fe_3O_4@GTP MNPs, which are ideal for this investigation due to their broad surface area and excellent dispersibility in aqueous medium. The methylene blue percentage removal rate was significantly elevated during the initial adsorption phase, followed by a considerably slower elimination rate, ultimately reaching an equilibrium state after 16 min of interaction. Up to ~60% methylene blue was removed within the initial 2 min of contact, while over 95% removal could be achieved in the subsequent 16 min of interaction (Fig. 9d). In wastewater treatment, these MNPs demonstrated a high methylene blue dye removal capacity (7.25 mg g^{-1}). Magnetic separation also makes it easy to remove the MNPs from the liquid, enabling multiple recycling cycles.

To enhance the removal efficiency of contaminants, particularly organic chemicals, surface functionalization of Fe_3O_4 NPs is crucial.[329] The catalytic activity and affinity of Fe_3O_4 NPs can be enhanced for specific contaminants by altering their surface characteristics through the addition of specific functional groups, such as amino or carboxylic groups. For example, amino groups may promote the adsorption of organic molecules at an acidic pH, while carboxylic groups can do the opposite.[330] Because of this unique attribute, Fe_3O_4 NPs can degrade organic molecules in solutions more efficiently, leading to better overall waste processing.[331]

4.3. Elimination of biological pollutants

The employment of antibacterial compounds has essential relevance in multiple applications, which extend from medical to industrial sectors, owing to the compelling need to combat bacterial infections and maintain product longevity.[332] Fe_3O_4-based MNPs have promising biological and environmental

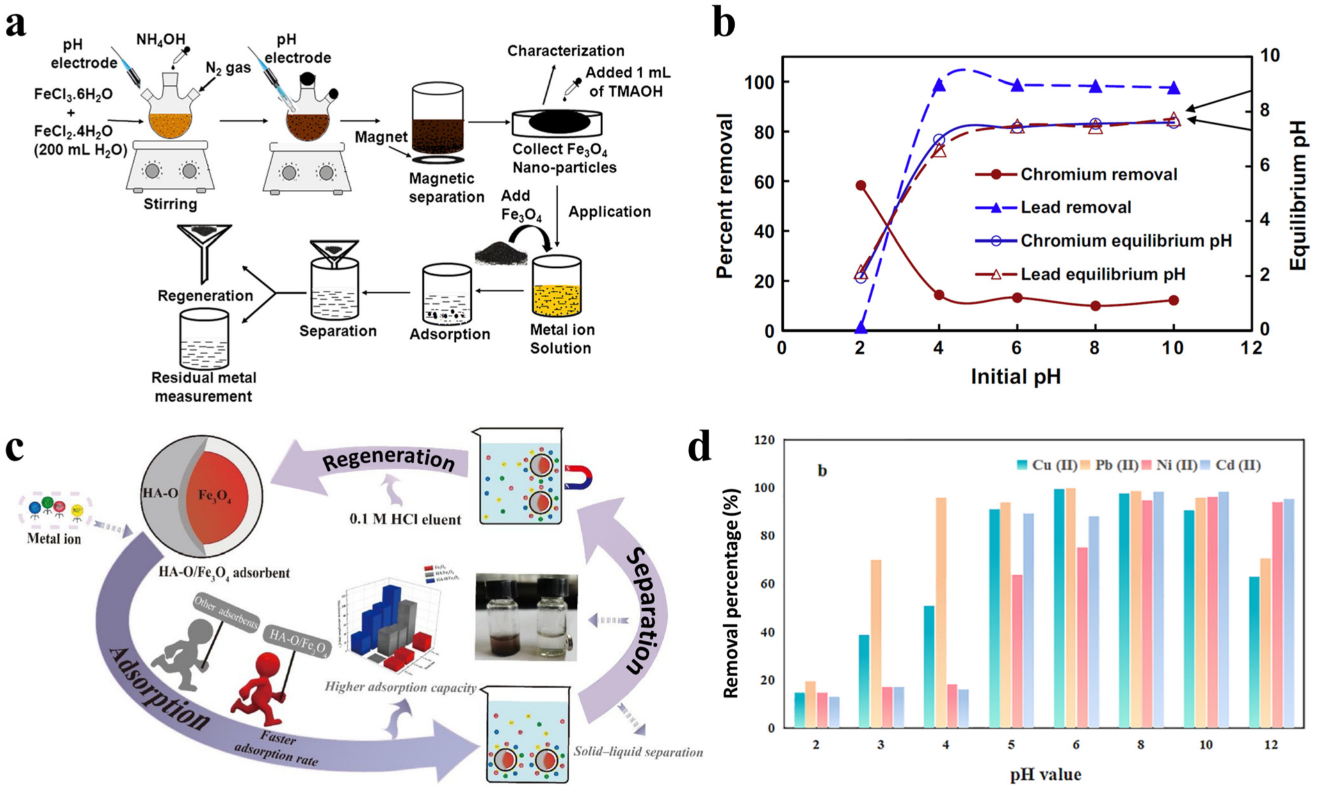

Fig. 7 (a) Schematic of the synthesis process and heavy metal removal steps for Fe_3O_4 MNPs, (b) effect of pH on chromium (Cr^{6+}) and lead (Pb^{2+}) adsorption of Fe_3O_4 MNPs,[293] reproduced from ref. 293 with permission from Elsevier, copyright 2025; (c) schematic of heavy metal removal steps and separation of HA-O/Fe_3O_4 MNPs, (d) effect of pH on heavy metal adsorption of HA-O/Fe_3O_4 MNPs,[28] reproduced from ref. 28 with permission from Elsevier, copyright 2025.

usages due to their antibacterial and antiviral characteristics.[333] Several kinds of bacteria and viruses are susceptible to MNPs' antimicrobial activity, which may limit the proliferation of harmful microbes and decrease the transmission of illnesses caused by microbial contamination.[334] Breaching microbial membranes and rendering pathogens inactive is the principal mechanism by which MNPs exhibit antibacterial and antiviral activities;[335] they display this action primarily by disrupting microbial membranes. Interactions between MNPs and bacterial cell membranes may cause structural damage, thus compromising membrane integrity.[336] The death of bacteria may result from this damage, leading to cell membrane leakage and the loss of intracellular contents.[337] Additionally, MNPs can damage the viral membrane, thereby preventing the virus from infecting host cells and replicating, and thus preventing it from infecting other people.[338]

In addition to their antiviral effects, MNPs can inactivate pathogens. By preventing the virus from spreading, attaching to, or penetrating the host cells, MNPs may interrupt the viral life cycle.[339] Furthermore, MNPs can hinder the progression of infection by interfering with the activity of enzymes that are essential for viral replication. There are good prospects for limiting the spread of infectious diseases and preserving a clean environment by deploying MNPs for pathogen inactivation.[340] Accordingly, Fe_3O_4-based MNPs have been deployed for antibacterial applications against *S. aureus*, *B. subtilis*, *E. coli*, *K. pneumonia*, *C. albicans*, and *S. mutans* bacteria.[29,341–343]

In addition to the antibacterial properties of MNPs, antifungal applications of MNPs are additional options for these NPs. Azadi *et al.*[344] evaluated the cytotoxicity and antifungal activity of a novel nano-antifungal agent targeting drug-resistant *C. species*, the $Fe_3O_4@SiO_2$/Schiff-base combination with Cu^{2+} MNPs. There is an immediate need for novel treatment approaches, as fungal infections are becoming more common and resistant to conventional antifungals. These MNPs were synthesized from Schiff-base ligands, known for their broad-spectrum antibacterial activity. *C. tropicalis*, *C. glabrata*, *C. dubliniensis*, *C. krusei*, *C. parapsilosis*, and *Candida albicans* were the six Candida species assessed by deploying the broth microdilution procedure to determine the antifungal capability. With a minimum inhibitory concentration of 8 μg mL^{-1} against *C. parapsilosis*, the findings showed robust antifungal activity in the 8–64 μg mL^{-1} range. *C. albicans* was identified as the most prevalent cause of infection, with a minimum inhibitory concentration of 32 μg mL^{-1}. Fungal cell wall and membrane breakdown, combined with enhanced reactive oxygen species formation and cell death, is likely the antifungal mechanism (Fig. 10). These NPs show great promise for the management of serious fungal infections, as well as infec-

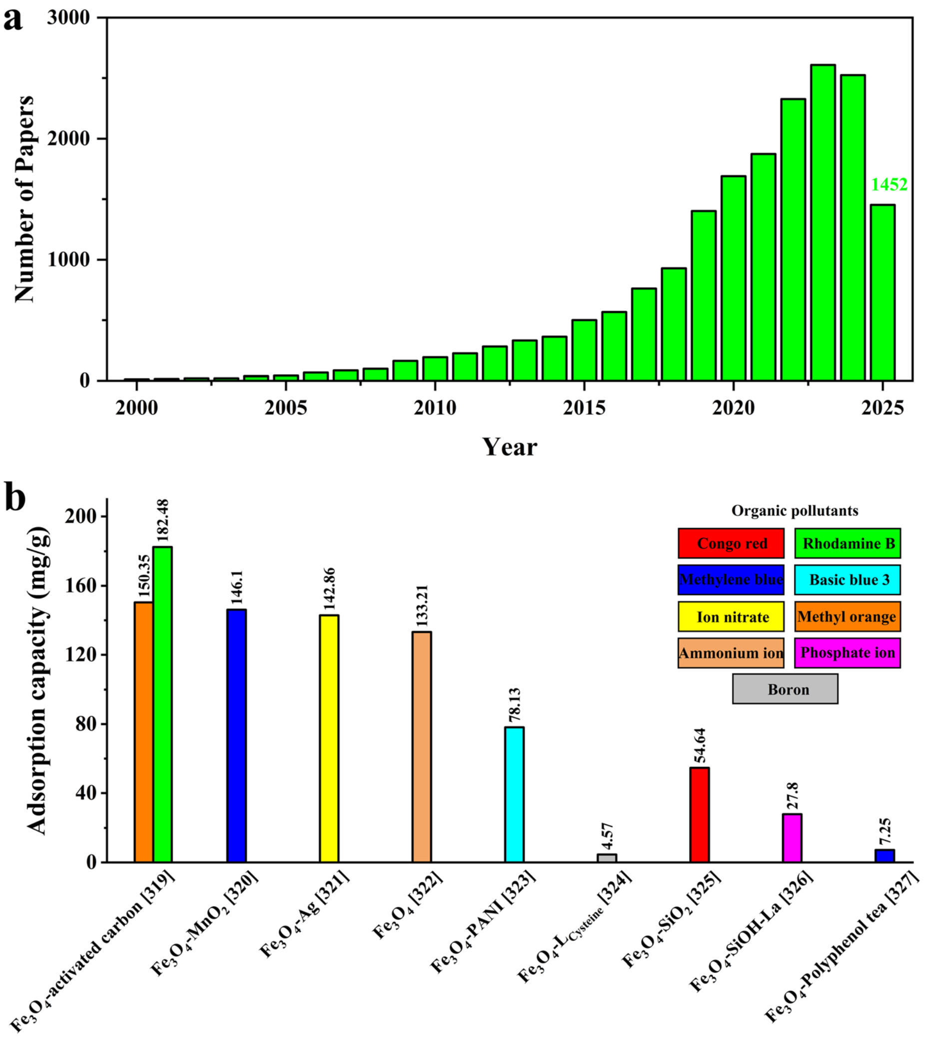

Fig. 8 (a) Rising interest in the removal of dyes and organic pollutants, as evidenced by the escalating quantity of publications (from the Web of Science database using the keywords "Dyes and organic pollutants removal" extracted on 15 November 2025), and (b) adsorption of dyes and organic pollutants *via* Fe_3O_4-based MNPs.

tions that may occur in healthcare settings. These MNPs have also been exploited in the treatment of medicinal and antibiotic wastes.[345–348]

4.4. Recovery or elimination of microalgae

An interesting example of integrating water treatment with sustainable agriculture is the Fe_3O_4-based technology deployed in the coagulation process for microalgae cultivation.[349] Herein, MNPs minimize algae overgrowth and enhance microalgae culture efficiency across a variety of appliances, including biofuel generation, wastewater treatment, and nutritional supplement production.[350] To facilitate harvesting microalgal cells, MNPs can be added to the growth media, which causes cells to aggregate and recover, thus simplifying the harvesting process.[351] By using a magnetic field to separate aggregated microalgae masses from the culture medium, these particles' magnetic characteristics make harvesting easier and more resource- and energy-efficient.[352]

While solving the problem of excessive algal growth in water resources, this innovative method also paves the way for the sustainable usage of microalgae in other biotech applications.[353] Microalgae cultivation that incorporates MNP coagulation technology could significantly advance eco-friendly farming practices. Compared to other chemical methods, this one is safer for the environment and may lessen negative effects on the planet.[354] Several obstacles could limit this method's broader adoption, including the high cost of producing MNPs and worries about the environmental implications of their manufacture.[355] In addition, restoring ecological balance and improving water quality may be achieved by removing excess microalgae from water resources susceptible to algal blooms.[356,357] Recently, in the application of removing these microalgae, researchers investigated MNPs, including Fe_3O_4, Zn-doped Fe_3O_4, and Fe_3O_4–PACI for *Microcystis aeruginosa*[358–360] and Fe_3O_4–CPAM for *Chlamydomonas* sp.[361] Research has also been conducted on their recovery, including

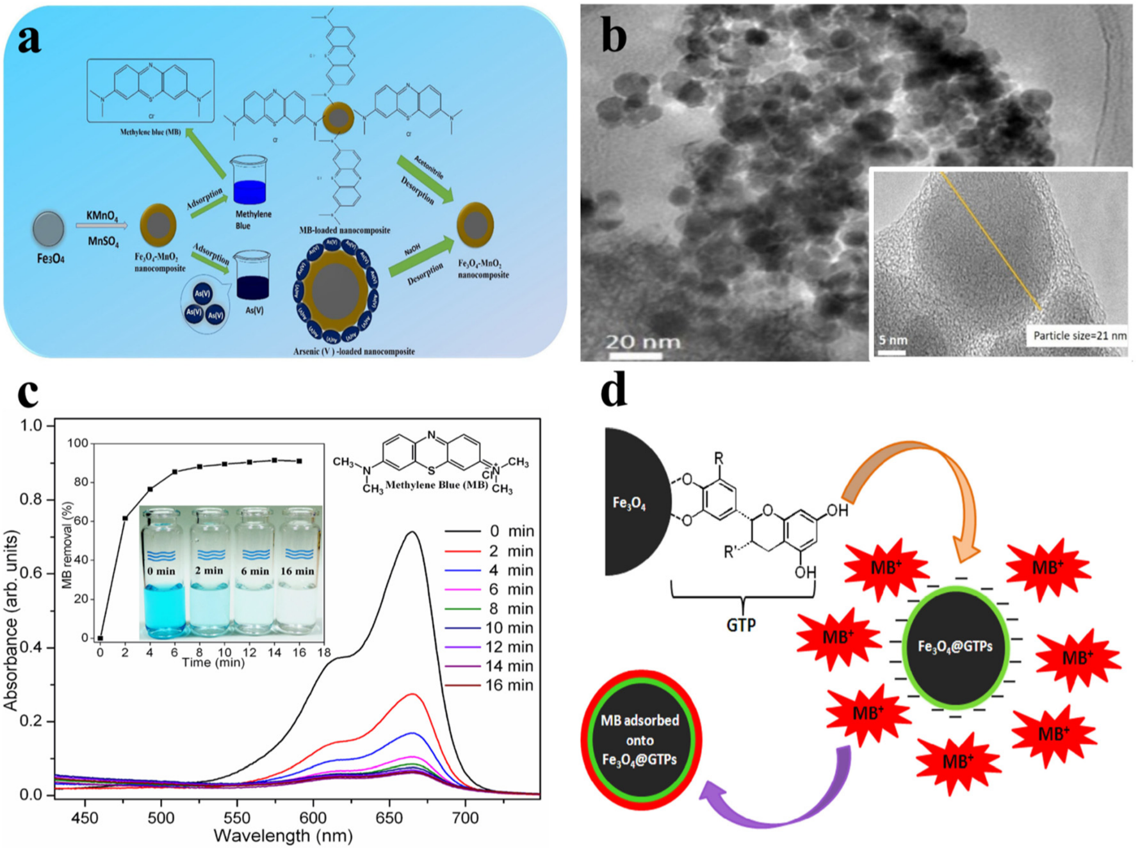

Fig. 9 (a) Schematic of the synthesis process and organic pollution steps of $Fe_3O_4@MnO_2$ MNPs, (b) TEM images of the Fe_3O_4–MnO_2 magnetic nanocomposite,[320] reproduced from ref. 320 with permission from Elsevier, copyright 2025; (c) UV-vis spectra of methylene blue adsorption in the presence of Fe_3O_4@GTPs MNPs at varying time intervals, and (d) schematic of the adsorption mechanism of methylene blue on the Fe_3O_4@GTP MNPs,[327] reproduced from ref. 327 with permission from Elsevier, copyright 2025.

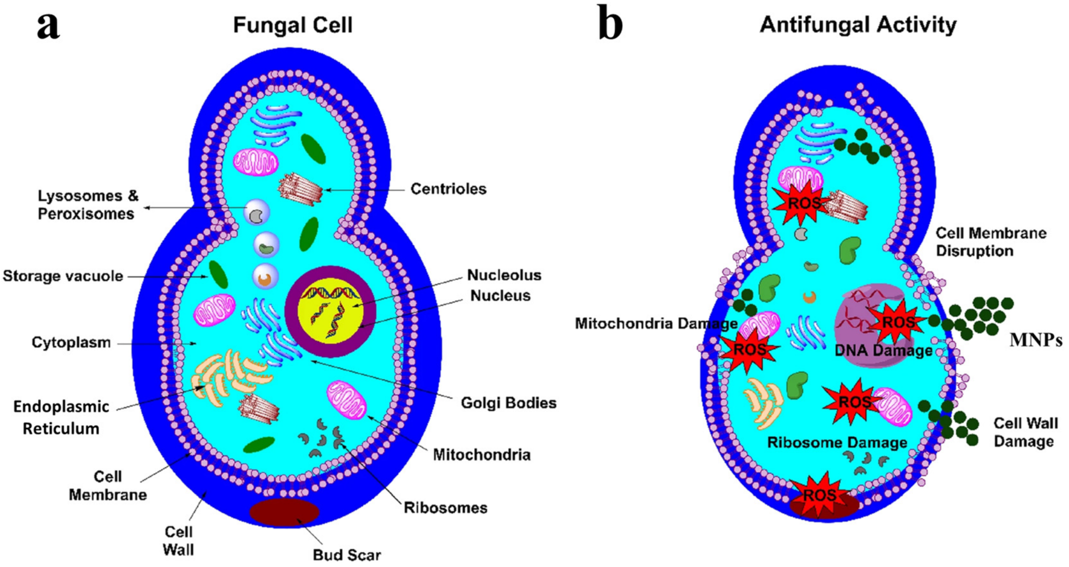

Fig. 10 (a) Cell structure schematic of a fungal cell, (b) antifungal action of $Fe_3O_4@SiO_2$/Schiff-base/Cu(II) MNPs, and plausible cell structure disruption,[344] reproduced from ref. 344 with permission from Nature, copyright 2025.

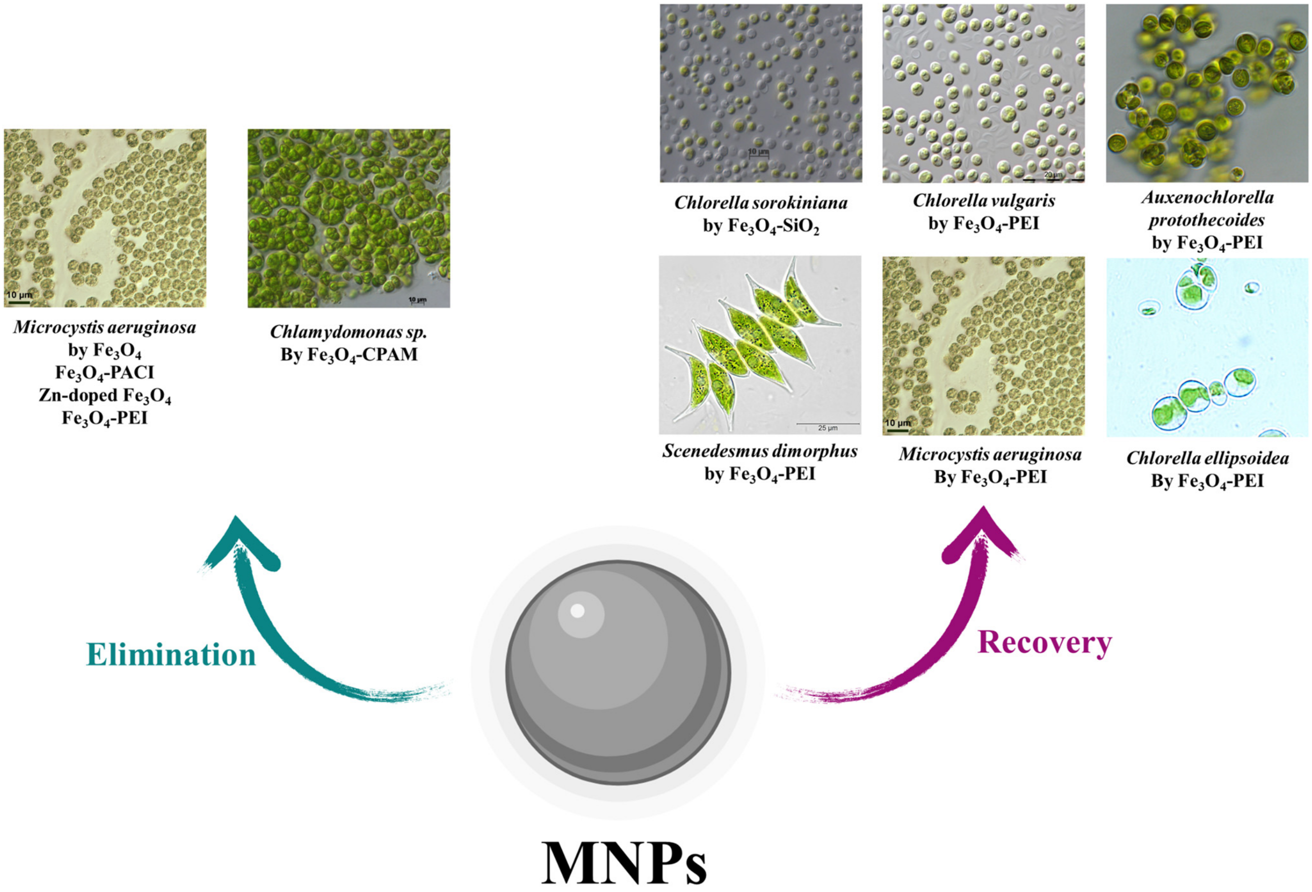

Fig. 11 MNPs in the elimination and recovery of microalgae.

Fe_3O_4–PEI for *Scenedesmus dimorphus*,[362] *Chlorella vulgaris*, *Chlorella ellipsoidea*, *Microcystis aeruginosa*, and *Auxenochlorella protothecoides*,[363] and Fe_3O_4–SiO_2 for *Chlorella sorokiniana*[364] (Fig. 11).

5. Challenges in the application and development of Fe_3O_4-based MNPs

A wide range of treatment methods and procedures, comprising membrane separation, ion exchange, solvent extraction, evaporation, precipitation, and reverse osmosis, have been utilized to remove metal ions from wastewater. On the other hand, many of these techniques have limitations, namely significant operational and capital expenses, particularly in the management and removal of the metal sludge produced.[365–367] Given this, efforts have been focused on developing inexpensive materials capable of eliminating pollutants from aqueous solutions. An interesting and potentially game-changing possibility is the utilization of MNPs for water purification, notably *via* the exploitation of coagulation processes. In light of ongoing nanotechnology development, these NPs offer a novel approach for addressing water pollution worldwide. MNPs can improve the effectiveness of coagulation processes, permitting more precise removal of contaminants and impurities from water. This is because of the unique magnetic qualities that they possess and the high specific surface areas that they encompass. This technology not only promises to enhance water quality but also has the potential to facilitate the development of more cost-effective and sustainable treatment systems. Nevertheless, to make MNPs more widely applicable, it is necessary to address their cost and sustainability. This calls for an integrated strategy that includes developing synthesis techniques that are both energy-efficient and environmentally friendly, improving manufacturing efficiency to lower prices, and promoting innovation through collaboration among governments, companies, and research institutions.[94,368–373]

The utilization of MNPs for the adsorption of heavy metals has been the subject of a significant number of recent studies. For instance, the elimination and retrieval of hexavalent chromium (Cr^{6+}) has been accomplished by employing maghemite NPs. The results from this experiment demonstrated that the adsorption capacity of these NPs for Cr^{6+} was superior to that of conventional adsorbents, such as activated carbon and clay.[374,375] A further investigation conducted by the same group revealed that the adsorption of Cr^{6+} onto γ-Fe_2O_3 that had been coated with γ-FeOOH was primarily controlled by outer-sphere complexation.[376] The researchers also demonstrated that surface-modified jacobsite NPs could effectively remove Cr^{6+} from simulated model wastewater. The adsorption process, which is then followed by magnetic separation, is what makes this technology possible for the elimination of hazardous ions in a quick, efficient, and cost-effective manner.[377] In other studies, it has been demonstrated that MNPs comprising structured Fe_3O_4 are capable of effectively adsorbing metal ions. Within the scope of this discussion, the utilization of both biosorption and magnetic separation offers synergistic benefits comprised of operational adaptability, environmental friendliness, and cost-effectiveness.[378] The removal of Cr^{6+} was also shown to be effective by the use of iron electrodes in electrocoagulation, as reported more recently.[379] Despite these benefits, the application of Fe_3O_4 NPs in the purification of water is now confronted with several obstacles. The tendency of these particles to clump together is a primary concern, as it can reduce their effective surface area and adsorption capacity. In addition, iron ions may leak into the water under some circumstances, potentially generating secondary pollution. There is a possibility that the lifespan of these NPs may decrease with frequent use and recycling, which highlights the necessity of approaches that include effective regeneration or replacement. Additionally, although magnetic separation is typically effective, it may require expensive equipment and may not be effective enough for treating large quantities of water involving magnetic separation. Fig. 12 presents a brief overview of the applications, merits, and demerits of Fe_3O_4-based MNPs for water purification.[94] In the following section, these challenges are examined in detail to assess their various dimensions, including iron ion leakage, the effects of particle agglomeration, limitations of magnetic separation, reduced lifetime due to recycling, and industrialization.

5.1. Iron ion leaching in Fe_3O_4-based MNPs in water treatment

As noted, one challenge that may be encountered during Fe_3O_4-based MNP treatment is the release or potential leaching of Fe (Fe^{2+}/Fe^{3+}) ions. Some factors, such as partial dissolution of the iron oxide structure, surface phase changes, oxidation or erosion, inadequate surface coating or performance, pH conditions, heat, contact time, and corrosive environments, can affect this challenge. Fe_3O_4-based MNPs (composite Fe^{2+}/Fe^{3+}) used in water as an adsorbent, coagulant, or coagulant aid, under certain conditions, release some of the iron contained in their structure due to reaction with water/oxidant/acid/base.[380] For example, in a study by Jiali Yi *et al.*,[381] deploying a heterogeneous photo-Fenton system with Fe_3O_4/ZSM-5/Schwertmannite, the amount of leached Fe was reported to be between 0.18 and 0.23 mg L^{-1} after six cycles (30 mg of catalyst was added to 50 mL of solution, corresponding to a loading of 0.6 g L^{-1}). Additionally, the surface of Fe_3O_4-based MNPs might be affected by environmental factors (highly acidic or alkaline pH, the presence of chloride ions, oxidants, and salts, and electrolyte flow), potentially leading to corrosion, oxidation, or surface dissolution, which could result in the release of iron ions.[380,382] An active surface on the NPs and the transformation of iron from a solid to a soluble state are both possible outcomes in the absence of an adequate protective coating.[383]

Consider the scenario when MNPs are not completely removed from water after the treatment process. In that case, the remaining particles can gradually undergo oxidation, surface corrosion, or partial dissolution, releasing Fe^{2+} and Fe^{3+} ions into the environment. This can not only reduce the quality of treated water, but if these ions or particles enter natural environments, they may have long-term environmental impacts, including causing changes in pH, increasing iron

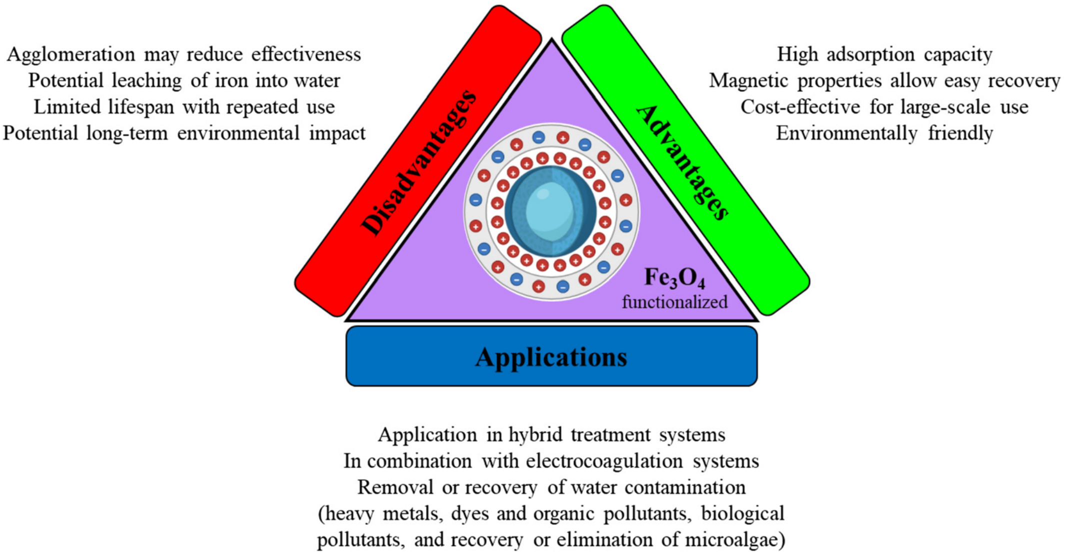

Fig. 12 Description of the applications, merits, and demerits of Fe_3O_4-based MNPs in water purification.

deposition, and having possible impacts on microorganisms and aquatic ecosystems. For this reason, it is essential to adopt a multi-level and comprehensive approach for controlling and monitoring NPs' behavior. These solutions include designing and coating the NP surfaces to prevent oxidation and release of iron (Fe^{2+}/Fe^{3+}), implementing a complete magnetic recycling process to effectively remove particles from water, conducting multi-cycle durability tests to assess the stability of the coatings, maintaining magnetic properties and pollutant adsorption efficiency during repeated use, and carefully monitoring the amount of iron released during operation cycles. In addition, the determination and compliance of the permissible iron release limit should be consistent with legal requirements and local and international standards related to drinking water and wastewater discharge to ensure human and environmental health. Ultimately, the combination of these engineering and management measures, along with the safe and sustainable design of NPs, can significantly increase long-term reusability, reduce environmental risks, and improve the safety of the water treatment process with MNPs.

5.2. Stability, fate, and reusability of Fe_3O_4-based MNPs in water treatment

Furthermore, one of the fundamental challenges in the widespread application of MNPs is the comprehensive assessment of their chemical and physical stability after purification and the determination of their final fate across various recycling stages and natural environments. This issue not only affects the overall efficiency of the purification process but is also of vital importance from the perspective of environmental safety, long-term sustainability of the technology, and prevention of unwanted effects on ecosystems.

A significant benefit of MNPs is their facile separation from aqueous media using a magnetic field. This feature enables the rapid recovery of NPs post-contaminant adsorption, allowing for reuse in successive cycles after washing or surface regeneration.[384] Several studies indicate that Fe_3O_4 NPs with various surface coatings (including silica, polymers, and organic ligands) can be deployed for multiple cycles.[325,385]

In a study by Ya Pang *et al.*,[386] PEI-coated MNPs exhibited stability in both acidic and basic solutions at various concentrations, with no notable dissolution of iron detected within the 0.2–1 M range. The NPs exhibited sufficient magnetic strength for post-treatment separation and retained their structure, unlike uncoated Fe_3O_4 NPs, which completely disintegrated in strong acid. The MNPs exhibited only 9% reduction in Cr^{6+} removal efficiency across six successive adsorption–desorption cycles, demonstrating commendable repeatability and stability of adsorption capacity over repeated applications. The recycling of NPs is economically significant, since the expense of manufacturing new NPs substantially exceeds that of cleaning and renewing used particles. The regeneration technique, particularly the use of washing solutions such as HCl or NaOH, or complexing agents such as EDTA, must be carefully selected to prevent structural deterioration or excessive oxidation of the NP surface.[387]

Notwithstanding the potential for recycling, research indicates that the efficacy of MNPs may progressively diminish throughout repeated cycles. This phenomenon is primarily attributed to three factors, including surface oxidation, deterioration of the surface coating, and aggregation or agglomeration.[388] In the presence of dissolved oxygen or at acidic pH, the magnetite phase (Fe_3O_4) progressively converts into maghemite (γ-Fe_2O_3) and, in further phases, into hematite (α-Fe_2O_3). This process diminishes magnetic characteristics, complicating magnetic recycling.[389] On the other hand, damage to or removal of the protective layer (such as silica or polymer) leaves the active Fe^{2+}/Fe^{3+} surface vulnerable to corrosion or dissolution. Finally, repeated cycles of vdW forces and magnetic interactions among particles lead to aggregation, diminishing the active surface area and altering the particle size distribution. This process results in a decreased adsorption capacity in subsequent iterations.[390]

Upon collecting the MNPs, several techniques are employed to restore efficiency and facilitate reproduction, including chemical washing with acidic or alkaline solutions to eliminate adsorbed contaminants, chemical reduction using reducing agents such as sodium borohydride ($NaBH_4$) or ascorbic acid to convert Fe^{3+} into Fe^{2+}, and re-coating to reinstate the protective layer. Keerthana *et al.*[391] demonstrated that increasing the amount of the reducing agent $NaBH_4$ led to the synthesis of smaller, well-arranged, and more functional Fe_3O_4 NPs, which significantly enhanced the photocatalytic efficiency and increased pollutant removal to 97%. Whenever NPs lose their functionality due to significant oxidation, irreversible adsorption of contaminants, or the loss of magnetic properties, they are disposed of as solid waste. In this instance, stabilization and decontamination techniques, including encapsulation in cement, glass, or ceramic matrices, have been suggested to prevent the re-leakage of iron or related contaminants.[392,393]

5.3. Environmental behavior and lifecycle management of Fe_3O_4-based MNPs in water treatment

If some MNPs remain in the environment for any reason, their behavior and stability are determined by several factors. In natural aquatic environments, pH, ionic strength, natural organic matter (NOM), and oxidation–reduction potential (E_h) all play critical roles.[394,395] Fe_3O_4 NPs oxidize and dissolve in acidic pH and in the presence of chloride or nitrate ions, but aggregate and precipitate in alkaline pH and in the presence of phosphate or silicate ions. From an environmental perspective, iron released from NPs at low concentrations is usually non-toxic. However, the presence of stable or aggregated NPs in aquatic sediments may affect microorganisms and biofilms. In reducing environments such as sludge or anaerobic soils, Fe^{3+} can be reduced to Fe^{2+}, altering the chemical behavior of NPs. Fe_3O_4-based MNPs, owing to their large active surface area and the release of Fe^{2+}/Fe^{3+} ions at low pH, can generate reactive oxygen species (ROS) and induce oxidative stress upon direct contact with aquatic cells, including algae and bacteria.[396]

From a sustainability perspective, the recycling and reuse of MNPs, contingent on regulating iron ion release and preventing surface oxidation, constitute a significant advantage of this technology.[397] The development of stable and corrosion-resistant coatings, including silicate or polymer coatings enhanced with functional ligands, can markedly prolong the lifespan of NPs. Nonetheless, life cycle assessment (LCA) indicates that improper recycling processes or NP leakage into the environment may pose potential risks, including alterations in aquatic sediment quality and bioaccumulation in organisms.

Overall, the stability of MNPs after treatment is determined by their initial particle design (structure and coating), the operating conditions of the system, and the recycling method. While Fe_3O_4-based MNPs are generally biocompatible, their gradual oxidation or dissolution can release iron ions into the environment. Thus, selecting the appropriate coating, monitoring surface changes during each usage cycle, and employing principled recovery and stabilization methods are critical for achieving sustainable and safe water treatment technology.

5.4. Pilot-scale and industrialization of Fe_3O_4-based MNPs in water treatment

A crucial bridge between laboratory-scale research and industrial implementation is the successful deployment of Fe_3O_4-based MNPs at the pilot scale for water purification. The practical usage of Fe_3O_4-based MNPs in water treatment systems relies on data from pilot-scale investigations and assessments using real wastewater matrices, which present significantly greater operational complexity than controlled experimental settings. Due to their distinctive characteristics, such as magnetic responsiveness and quick, selective separation, Fe_3O_4-based MNPs are an attractive choice for massive, economically viable water treatment projects. To improve their adsorption capability for pollutants, including phosphates, heavy metals, and organic compounds, these flexible NPs may be functionalized with a variety of materials like $La(OH)_3$ and g-C_3N_4. Acceptable synthesis techniques, such as co-precipitation and low-temperature precipitation, enable the manufacture of NPs at the low temperatures required for pilot-scale applications. Magnetic separation devices, such as MagNERD, may be deployed in pilot-scale applications to collect these NPs after they have adsorbed pollutants from a suspension. Research in the lab has shown that $Fe_3O_4/La(OH)_3$ composites are highly effective for phosphate removal, and that functionalized composites such as g-$C_3N_4@Fe_3O_4$ can remove microplastics and persistent organic pollutants with efficiencies over 90%. Also, heavy metals such as Pb^{2+} and Cd^{2+} may be chelated with high capacity by water-dispersible Fe_3O_4 NPs.[398–401]

In an example of a real-world application, Kim *et al.*[402] investigated the use of iron oxide NP–chitosan composites for phosphate removal from natural water collected from the Seoho stream in Suwon (Republic of Korea). Under dynamic flow conditions, the composites were able to remove phosphate in fixed-bed column experiments. An adsorption tower and dissolved air flotation/chemical reactor were built next to the Seoho stream as part of a factory-scale pilot test. The findings demonstrated a phosphorus removal rate of approximately 52.3% and a capacity of 0.059 mg phosphorus per gram of composite, which affirmed that MNPs could effectively remove phosphate in both laboratory and field settings.

Nevertheless, pilot-scale applications are accompanied by challenges, including ensuring uniformity of particle size and surface properties on a large scale, optimizing and minimizing synthesis costs, and efficient recovery of NPs after treatment. To overcome these constraints, one may use magnetic recovery devices, renewable bioreaction routes, and greener synthesis methods. Reducing NP discharge into aquatic environments by encapsulating or coating them with biocompatible polymers is another environmental factor. To advance this technology, more research ought to be conducted to determine which pollutants can be effectively removed, how to improve continuous filtration systems at the pilot scale, how to ensure compliance with environmental protocols and regulations, and how to assess the operational and long-term effectiveness of these systems in real-world water treatment applications.[398,400,403–405]

6. Conclusion

The increasing demand for potable water and ever-growing industrial developments have resulted in water pollution from various sources, including heavy metals, pesticides, viruses, and synthetic chemicals. As a result, organizations and industries have expressed their tremendous interest in developing and manufacturing materials for purifying water and eliminating harmful impurities. MNPs are considered one of these materials for the efficient removal of water contaminants. This work has examined a considerable proportion of newly published research on the preparation and beneficial attributes of MNPs. Special focus has been on the synthesis and mechanism of coagulation for Fe_3O_4 NPs, including surface charge interactions and neutralization, bridging and floc formation, external magnetic separation, and the removal of water contaminants such as heavy metals, dyes, and organic pollutants, as well as biological pollutants, and the recovery or elimination of microalgae. Water contamination and the shortage of clean water are global crises, but stakeholders may help find solutions by concentrating on the aforementioned areas. Aiming to develop cutting-edge water purification technology, Fe_3O_4 NPs might be a game-changer, helping to better and sustainably treat polluted water resources worldwide.

Author contributions

Ali Moeini: writing – original draft, writing – review & editing, methodology, data curation, visualization, Iman Khezri: writing – original draft, data curation, visualization, Reza Ahadi Dolatsara: writing – original draft, data curation, Maryam Hajiebrahimi: writing – original draft, data curation, Hamed Beydaghi: writing – original draft, data curation, Aziz Shahraki: writing – original draft, data curation, A. Malek

Khachatourian: writing – review & editing, conceptualization, methodology, supervision, M. S. Toprak: writing – review & editing, conceptualization, supervision, R. S. Varma: writing – review & editing, conceptualization, supervision.

Conflicts of interest

The authors have no competing interests to declare that are relevant to the content of this article.

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

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