Advanced nanomaterials and dendrimers in water treatment and the recycling of nanomaterials: A review

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\textbf{ABSTRACT}

Herein an extensive review of the use of nanomaterials and dendrimers for water treatment is presented. The review included the use of nanomaterials in tackling various challenges, including achieving dye removal, antibacterial effects, photocatalysis, heavy metal removal, nanomaterial recycling, and nanowaste removal. The review highlights existing literature bottlenecks and suggests potential remedies, with a focus on the availability of low-cost, recyclable, and bimetallic nanomaterials. Moreover, the review highlights the significance of taking into account practical sample collection and analysis, such as the use of industrial effluents as samples for analysis. The review provides valuable insights into advances in the development of nanomaterial-based water treatment technologies by critically examining existing research.

1. Introduction

Clean water is one of the five essential elements that humans require. The human body is primarily composed of water, and more than 70\% of the Earth’s surface is covered in water. Consequently, water research is an ongoing endeavor, continuously seeking improvements in water management practices. Advancements in water treatment technologies and analysis tools have allowed for the discovery of previously overlooked elements such as microbes. With the rise in industrial activities and their impact on water quality, there is a growing need for research to adapt and address the evolving challenges in water management. For instance, the increased use of dyes in industries such as textile and pharmaceutical has prompted research in dye degradation to prevent their presence in untreated wastewater, which can contaminate drinking water and pose health risks. The presence of dyes and heavy metals in water bodies can lead to diseases in aquatic life, disruption of metabolism, and the development of cancers. Additionally, the study of microbes in water has become a significant subject of research.

Nanomaterials have emerged as a cutting-edge innovation in water treatment, offering diverse applications such as dye adsorption, dye degradation, heavy metal adsorption, polymer removal, antibacterial effects, and more, contributing to the purification and remediation of water resources \cite{1}. Other review papers have touched on the subject of the application of nanomaterials in water treatment including Santhosh et al. \cite{1}, whose discussion focused on the adsorption, photocatalytic, and antimicrobial properties of nanomaterials. Other reviews have focused on specific materials that are commonly used in water treatment, for example, Carpenter et al. \cite{2}, examined cellulose materials, and Mmelesi et al. \cite{3}, reviewed the application of Co-Fe bimetallic nanoparticles (BNPs) in water treatment. Other review papers have presented an overview of papers focused on dye removal only \cite{4}, while others have reviewed heavy metal removal only \cite{5}.

Herein, a comprehensive and critical review is presented, examining both the types of nanomaterials, including nanoparticles and dendrimers, and water treatment mechanisms, such as dye removal, antibacterial effects, photocatalysis, heavy metal removal, and nanowaste removal. The review aims to identify current gaps in the literature and propose potential solutions, providing an in-depth analysis of the field. Specifically, this review addresses two key gaps. Firstly, it explores the application of BNPs as enhanced nanomaterials in water treatment,
highlighting their potential advantages and challenges. Secondly, the review emphasizes the need for recyclable nanomaterials that can be reused for multiple cycles without leaching into the water, which generates nanowaste, another water contaminant. Various recycling methods, such as nanoparticle immobilization and cloud point extraction (CPE), are discussed as potential approaches to achieve this goal. Moreover, this review includes case studies where real-life industrial effluents are used as samples, showcasing the practical relevance and applicability of water treatment analyses. A graphical summary of the content of focus for this review paper is shown in Fig. 1.

2. Types of materials

Nanoparticles (NPs) have become increasingly important in the field of wastewater treatment over the past few decades. NPs are extremely small particles that are often less than 100 nanometres in size. These particles can interact with pollutants in water, making them an attractive option for wastewater treatment. NPs have several advantages over conventional methods of wastewater treatment. First, they can interact with pollutants at a molecular level, allowing for more efficient and effective removal of pollutants from water. This can be beneficial for both industrial and municipal wastewater treatment. Additionally, NPs can target specific pollutants, allowing for more targeted removal of contaminants from wastewater.

With the advancement in technology, the potential of NPs in numerous domains has been actively researched due to their favourable characteristics with small particle size and a large surface area. Additionally, the chemical reactivity of these NPs is also improved by the higher surface to area ratio [11–13]. Furthermore, NPs are appropriate for wastewater treatment due to their effective adsorption and high mobility in aqueous solutions [14]. These materials have controlled, well-defined morphologies with the appropriate size and porosity, making them potential good adsorbents [15]. This section discusses various nanomaterials (see Fig. 2) that are utilized in water and wastewater treatment.

2.1. Carbon based materials

Carbon-based nanomaterials are gaining popularity as nano adsorbents for waste-water treatment among researchers due to their availability, size- and shape-dependent properties, environment-friendliness, and simplicity of usage. The higher surface-to-area ratio, better chemical stability, low cost, and minimal chemical, environmental impact of carbon-based nanomaterials make them advantageous for wastewater treatment [16]. Carbon nanotubes (CNTs), graphene, and graphene oxides or reduced graphene oxides are examples of carbon-based nanomaterials that are very effective and widely utilized in various fields, including drug delivery, biomedicine, and water treatment [17].

2.1.1. Carbon nanotubes

Carbon nanotubes (CNTs), first discovered in 1991, have advantageous mechanical, chemical, thermal, and electrical characteristics that make them ideal for wastewater treatment [18]. CNTs can be divided into three categories: single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs), and CNT composites (including functionalized CNTs) [19]. CNTs have great physical properties due to their one-dimensional structure, including strong physicochemical interactions, well-defined cylindrical hollow structures, high aspect ratios, large surfaces and high sorbent capacities [20]. Multi-walled nanotubes (MWCNTs) and single-walled nanotubes (SWCNTs) may adsorb dye from aqueous solutions. However, SWCNTs have a higher adsorption capacity than MWCNTs [21]. Nonetheless, CNTs are advantageous over activated carbon, but their large-scale applications for effective wastewater treatment are limited because of the high manufacturing costs. Additionally, CNTs should be stabilized in aqueous solutions using surfactants due to their hydrophobic surface to prevent aggregation, which could decrease their active surface area [22]. The mechanisms used by CNTs to adsorb pollutants, including hydrophobic, van der Waals forces, H-bonding, -interaction, electrostatic interaction, and covalent bonding, were relatively comparable to those used by graphene [21].

In the domain of adsorption, pH functions as a pivotal regulatory factor, as detailed in subsequent sections, including the removal of dyes from water. Ghadeli et al. [23] studied into the adsorption capacity of activated carbon and MWCNT for Eriochrome Cyanine R at varying pH,
Electrolyte, temperature, starting dye concentration, and adsorbent amounts. Activated carbon’s adsorption capacity was lower than MWCNTs’ (95 mg/g) but higher than that of MWCNTs (41 mg/g). The use of CNTs to remove dyes from the wastewater produced by the textile industry has been the subject of various investigations [24]. The efficient decomposition of cationic dye contaminants in water, namely Neutral Red (NR), Methylene Blue (MB), and Brilliant Cresyl Blue (BCB), was explored through the utilization of a magnetic MWCNT nanocomposite [25]. Numerous CNT-based nanosorbents, encompassing CNTs-cellulose, CNTs-graphene, CNTs-Fe$_3$O$_4$, CNTs-Al$_2$O$_3$, CNTs-chitosan, and CNT-activated carbon fiber have been identified for the adsorption of dyes [21,26]. A new granular CNTs/Al$_2$O$_3$ composite with good mechanical strength, hydrophilicity, heat resistance, and good sorption efficiency for two pharmaceuticals (diclofenac sodium and carbamazepine) was created by Wei et al. [27]. Pharmaceuticals that have been absorbed may be decomposed in the regeneration process. Granular CNTs-based composites were developed as a result of this hybridization technique. Combining CNT’s adsorption abilities with the magnetic capabilities of FeO makes it possible to remove chromium [28]. The adsorption, electrical, mechanical, and optical properties of CNT can be changed by combining it with different metals. For instance, various CNT functionalization can increase the number of N, O, or other molecule clusters on the CNT surface, increasing the surface area and increasing the dispersibility.

An alternative method for treating wastewater involves employing membrane technology, where CNTs play a significant role. Extensively researched for their application in filtration and water purification, CNTs are widely utilized as adsorbents within membrane technology [29]. CNTs may remove various pollutants from an aqueous media using the sieve concept. CNT is a desirable material for membrane filtration of highly reactive monovalent anions at lower pH because of its large surface area, high aspect ratio, ease of functionalization, and rapid water flow even quicker than the theoretically estimated 4–5 ordered magnitude [30].

Carbon-based nanocomposites (especially CNTs) can be a potential building block for hybrid nanocatalysts. Their remarkable electrical, optical, and mechanical capabilities can improve their efficacy in wastewater treatment. The use of semiconductors or metallic NPs to photo reduce various organic and inorganic pollutants is reported in the literature [31]. In order to enable light-mediated biomineralization of methyl blue (MB) by TiO$_2$ nanoshells (5 nm) at the surface of graphitic carbon, Lee et al. [32] produced N-doped CNTs/TiO$_2$ nanowires in core-shell configuration. With no adhesive interlayer present, the TiO$_2$ nanoshell and NCNTs surface came into direct contact, resulting in a unique carbon energy level for the band gap of TiO$_2$, which initiated an effective photo-catalytic destruction of MB using visible light. It is evident that there are still numerous challenges in the way of CNTs’ use in environmental applications, and more research should be done on new CNT adsorbents like CNT composites.

2.1.2. Graphene

According to the International Union of Pure and Applied Chemistry
Graphene has many oxygen-containing functional groups with good π-bonds and exhibits higher surface area. There are typically five possible interactions for the adsorption of graphene-based nanomaterials: the hydrophobic effect, π-bonds, hydrogen bonds, covalent, and electrostatic interactions. Therefore, graphene-based materials are effective adsorbents for different types of contaminants in water [36]. Heavy metals like zinc, copper, cobalt, lead, and cadmium are reduced or eliminated by graphene. Despite having a reduced adsorption selectivity, it has strong adsorption abilities for several heavy metals [37].

By changing the experimental settings, graphene-based NPs are used as efficient adsorbents for cleaning pharmaceutical wastewater. They can also be employed to filter out radionuclides and heavy metals from wastewater. Numerous crucial factors, such as the initial dosage and properties of graphene materials and metal ions, as well as temperature, contact time, acidic organic ligands, and coexisting ions, can affect the adsorption capacity of toxic dyes and heavy metals in water, according to recent research [38]. Graphene can be employed as an effective separation membrane by adding nanoscale pores to its layer. It has unique qualities like flexibility, mechanical stability, and virtually one atom’s worth of thickness. A graphene monolayer has been etched with oxygen plasma to produce nano-sized pores, enabling fine-tuning of the pore size [39].

The manipulation of pore diameters has revealed that single-layered, self-supporting graphene with nanometer-sized holes can effectively separate NaCl salt from water. Furthermore, the hydrophilic nature of naturally occurring hydroxyl groups was demonstrated to significantly enhance the fluidity of water [40]. Although more research is required in this area, toxins can be removed using more ecologically friendly nanotechnology, potentially improving industrial water treatment operations. Carbon nanotubes, carbon and graphene quantum dots, and graphene-based nanomaterials may someday be effective, reasonably priced, and environmentally friendly substitutes for the current treatment supplies from environmental remediation and resource conservation perspectives.

Enhancing the adsorption rate and capacity of CNTs for contaminant removal can be achieved through processes like oxidation and electrochemical assistance, presenting an innovative strategy in environmental remediation. However, thorough assessment of toxicity issues is imperative. While the efficacy of nanomaterials such as CNTs and graphene in wastewater treatment has been demonstrated, efforts should be directed towards pioneering synthetic techniques to reduce the cost of nanomaterial synthesis and improve their catalytic performance. Additionally, it is crucial to conduct comprehensive analyses of the risks and potential effects of nanomaterials on human health and ecosystems, with a particular focus on potential cellular toxicities.

2.2. Zero-valent metal NPs

Water remediation can be accomplished with the help of zero-valent iron (ZVI). The creation of zero-valent iron at the nanoscale level (nZVI) has significantly increased its reactivity. Due to their extensive specific regions, nZVI has numerous unique favorable characteristics, such as a strong reactivity towards various pollutants [41]. According to [42], nZVI has a 343 mg/g average capacity to remove Cu(II). After adsorption, Cu(II) was transformed into metallic copper or cuprite (Cu$_2$O). It was discovered that reduction to elemental arsenic by nZVI was an effective mechanism for arsenic immobilization since As(V) or As(III) was shown to be reduced mainly to As(0) after reacting with nZVI. Additionally, As(III) ended up on the surface of nZVI in the forms of As (0), As(III), and As(V), showing that both reduction and oxidation of As (III) occurred during the reaction with nZVI. The core-shell structure of nZVI, where the inner core had metallic iron with a vital reducing characteristic, and the outer layer contained thin amorphous iron (oxy) hydroxides, promoted oxidation, allowing the compound to perform dual redox functions [43]. According to [44], the most significant capacity for phosphate adsorption onto nZVI was 245.65 mg/g. This was primarily accomplished through adsorption and co-precipitation. Numerous other pollutants, including cadmium and chromium, formed inner-sphere complexes with the iron oxide layer surrounding the nZVI core.

Hamdy et al. [45] investigated using zero-valent Fe NPs to remove MB. This particular study found that MB had a 72.1% removal effectiveness. It was further demonstrated that the best MB removal effectiveness was achieved with an adsorbent dosage of 10 g/L and an elevated pH of 6. Reduction, sorption, degradation, and precipitation are a few of the mechanisms that can remove heavy metals from an environment. The ions are directly absorbed onto the NPs surface, or metallic hydroxide is formed. Each technique helps remove different metals from aqueous solutions. Zero-valent zinc (ZVZ) has been shown to have better reducibility than zero-valent iron (ZVI), although there is little information on its use in wastewater treatment alone. Lin et al. [46] used ZVZ to reduce bromate to avoid adverse effects on water systems. The ZVZ NPs were made by reducing bromate to bromide with a higher dosage that displayed greater efficiency. Similar to this, nitrate was successfully converted to nitrite when ZVZ was made using acid washing, namely hydrochloric acid. The ability of nitrite to be further reduced to ammonium ions was another reason the acidic circumstances were considered advantageous. The previous work also showed that the prepared ZVZ NPs could be recycled repeatedly.

2.3. Noble metal nanoparticles

Some transition metals, such as Au, Ag, Pt, and Pd, are referred to as noble metals. Due to their small atom size, they often have high ionization energy and low oxidation potential. However, their ionization energy and oxidation potential significantly changed at the nanoscale, making numerous novel reactions with noble metals possible [47]. Noble metal NPs were typically fabricated by reducing the suitable metal salts and controlling the nucleation and development of nanocrystals while using a stabilizing agent. Surfactants and polymers were frequently used to increase the stability of noble metal NPs.

In order to remove heavy metals, Ag NPs have been used since they may be compatible with green efforts. Priority is given to reducing or eliminating the usage of risky materials while efficiently removing harmful metals from wastewater. Ag NPs made from cocoa pod extracts have also been investigated for the immobilization of heavy metals in soil. Heavy metal mobility was reduced, while the elimination of heavy metals was increased. Ag NPs are a strong candidate for wastewater treatment due to their high adsorption capacity, antibacterial characteristics, and environmentally friendly synthetic methods [48]. Green synthesis was used to create zero-valent Ag NPs with potent antibacterial activities and quick dye degradation. The potential of NPs is increased by the shift to a sustainable strategy while using Ag NPs. As a result, the NPs work better and are more cost-effective. However, there have been concerns that the high levels of Ag in water systems could...
have a negative impact on the environment and ecosystems [49]. Over the past twenty years, there has been much interest in ceramic materials and membranes coated with Ag NPs for the treatment of household water (at the point of use). E. coli removal efficiency from ceramic filters made of clay and sawdust has been observed to be improved by Ag NPs [50]. Additionally, it was discovered that the porosity of filters affected how well bacteria were removed, with higher porosities resulting in higher rates of bacteria removal. Due to their distinctive optical properties, Au and Ag NPs have been widely used to detect trace levels of organic pollutants. The presence of Ag nanostructures resulted in a noticeable Raman signal amplification [51]. Additionally, a direct relationship was discovered between the concentration of pesticides and the shift in plasmon resonance wavelength. In addition to detecting impurities, noble metal NPs can absorb contaminants and destroy bacteria. With a 4.065 g/g Au capacity, Au NPs could successfully adsorb Hg by producing AuHg, Au,Hg, and AuHg3 [52]. Waterborne microorganisms like E. coli could be rendered inactive upon contact with Ag NPs thanks to the biocidal activity of Ag NPs. It was claimed that the particle size and crystal structure influenced Ag NPs’ antibacterial action and that they may harm cellular membranes when they come into close contact [53]. Additionally, photo-catalytic degradation of various water contaminants like pesticides, dyes, and halogenated organics was being done using noble metal NPs.

2.4. Nanocomposites

A nanocomposite material is created when two or more materials form a single substance. At least one of the constituent materials must be on the nanoscale. The nanomembrane, made of organic and inorganic NPs and resembles a membrane, is one of the newest additions to the collection of nanocomposite materials [12]. Over the past decade, it has been used more frequently to remove wastewater pollutants like heavy metals and organic pollutants. Better hydrophilicity, chemical and thermal stability, porosity, and permeability are key features of more recent nanocomposite materials, all crucial toxin remediation techniques [54]. E. Coli, a common contaminant present in domestic wastewater, can be easily treated by Ag nanocomposite, making it an effective antibacterial agent [55].

The combination of polystyrene and nano FeO demonstrated a potent sorption feature. Improved adsorption efficiency and rate were also seen in a magnetic composite based on chitosan [56]. Due to the specific ionic radius of heavy metals like cadmium and lead, polymer materials incorporated into precisely tuned pore-sized nanocomposite membranes are highly effective at removing them. Nanocomposites made of polymers have gained popularity due to their usefulness. They are helpful in wastewater treatment due to their film-forming capabilities, dimensional plasticity, and active activities. However, precise design is necessary to ensure that PNCs produce their maximum output. The PNC produced through in situ polymerization and composite synthesis with inorganic components (metal and metal oxide nanocomposites) have been shown to operate as an efficient sorbent and are also capable of catalysis, sensing, acting as reducing agents, and acting as bactericides [57]. The hybrid nanocomposite material may have improved electrical conductivity due to the synergistic effect, and employing nanocomposites in waste-water treatment could have long-term consequences.

3. Mechanisms of water treatment

3.1. Dye removal

3.1.1. Risks of dyes in water

Numerous industries employ over 10,000 different dyes, amounting to approximately 1 million tons, primarily for coloring purposes. Among these, the textile industry stands out as the largest consumer [58]. Another report added that, globally, roughly 700 million kg of dyes are produced each year and 10–20% of the output from industrial activities, mainly in the textile industry, ends up in the aquatic environment as runoff [59]. These dyes can be categorized based on the sources from which they come, as shown in Fig. 3a. The textile, dyeing, paper, tannery, cosmetic, food, and pharmaceutical industries, among others, have a significant impact on the introduction of dyes into the environment as shown in Fig. 3a. Up to 49% of dye discharges into water bodies come from the textile industry alone. Another report mentioned similar large quantities of dyes produced globally quoting 70 million tons of synthetic dyes being manufactured globally each year, with over 10,000 tons of such dyes used by the textile industry [60]. Although the exact numbers in tons of dyes released per year differ per article, most of the reports agree that the textile industry is the biggest user and releaser of dyes.

These dyes have a strong chemical structure that prevents microbial degradation and sunlight penetration which calls for a need for innovative removal techniques. Dyes pose a risk when released into water bodies because of their high persistence, toxicity, and propensity to bioaccumulate in living organisms [59–63]. Dyes have the potential to harm, interfere with, and devalue the ecosystem’s fundamental processes and functions. When absorbed through the intestinal system, epidermis, or respiratory system, they typically disrupt blood production, form hemoglobin adducts, and cause serious medical complications. Additionally, dyes reduce the capacity of aquatic organisms to absorb sunlight and lower the oxygen content of soluble water. Additionally, they have the power to quickly deteriorate the quality of water bodies by changing factors like color, odor, and mineral content. Dyes have been shown to be mutagenic, neurotoxic, teratogenic, and carcinogenic. The dangers of dyes are brought home by their extreme toxicity and potent ability to cause eutrophication [60].

Increased levels of waste streams containing persistent organic pollutants like phenols, pesticides, and dyes are released into the environment as industrialization picks up speed. It should be noted that the byproducts produced can also be more dangerous than the original compounds, necessitating the creation of creative and effective removal techniques. Dyes exhibit exceptional persistence in aquatic environments due to their exceptional resistance to hydrological and photo-chemical processes. It is possible for dyes to temporarily change the molecular structure of colored materials when they are applied to surfaces [64]. This results in the appearance of a new coloration. They exhibit a strong resistance to degradation once exposed to water because complex hydrogen bonds form between them. Due to the dyes’ prolonged persistence in aquatic environments, turbidity has increased and the need for biological oxygen has increased. In some cases, these dyes can mimic natural seafood, contaminating aquatic organisms’ bio-ecosystems and possibly spawning carcinogens and other endocrine disruptors. Due to their low capacity for biodegradation and toxic characteristics, synthetic colorants used in the tanning and cosmetics industries present serious difficulties. Notably, colorants made from 4-amino biphenyl and phenylene diamine have serious problems with toxicity and biodegradability. Concerns have also been raised over the years about the use of benzidine-based dyes in the pharmaceutical industry [65,66]. In the subsequent subsections, we will explore different categories of dyes that are presently present in water, along with the methods to eliminate them, focusing specifically on the application of nanomaterials.

The kaleidoscope of industries and day-to-day activities contributes to the presence of various types of dyes in water bodies. These dyes often pose health concerns to all living organisms, including fish, humans consuming fish and water, as well as aquatic and water-dependent plants. Dye pollution, due to their widespread use, causes the ecosystem to suffer and can find their way into the human diet. Activities like washing clothes or using dyes as indicators in experiments further contribute to this kaleidoscope of sources introducing dyes into the water. Dye can be characterized according to their origin for example natural vs synthetic dyes. Natural dyes have a long history of plant-based dyes such as indigo, known for its deep blue hue. Akane produces
shades of red, orange, and pink. Synthetic dyes, on the other hand, offer a wide range of possibilities. Reactive dyes form strong bonds with fibers, resulting in excellent color fastness. Water-soluble acid dyes are often used on protein fibers to achieve intense and diverse colors. On the other hand, in the case of synthetic fibers, disperse dyes, which are insoluble in water but can be dispersed with an appropriate agent, are preferred because they provide long-lasting and vivid colors.

A qualitative study examined consumers’ understanding of apparel coloration and their willingness to choose sustainable alternatives, particularly natural dyes versus synthetic dyes [67]. The findings highlight limited knowledge and various factors hindering the adoption of naturally dyed apparel, such as affordability and availability. Participants stressed the importance of information provision, marketing campaigns, retail displays, and third-party verified labels to promote sustainable options. Fashion designers and manufacturers were identified as key players in driving change. Further research is needed to address consumer knowledge, overcome constraints, and identify preferences regarding natural dyes in the textile industry. Dyes can also be classified into anionic dyes and cationic dyes. They are currently several ways employed to remove dyes from water bodies including physical methods such as photo-absorption, coagulation-flocculation, adsorption and membrane filtration, chemical methods such as the use of catalysts to degrade the dyes, ion-exchange, chemical precipitation and oxidation and biological methods such as using bacteria to degrade the dyes into its by-products [68]. The following subsections discuss some of the most commonly studied cationic and anionic dyes.

3.1.2. Methylene blue

Methylene blue (MB) is a cationic and organic dye commonly used in industries such as dyes, textiles, lab experiments (indicator) and plastics [61,69–71]. Unfortunately, it is a significant pollutant in the aquatic environment and poses potential toxicity risks. MB can cause severe problems to humans such as blood pressure increasing, nausea, shock, vomiting, Heinz body formation, profuse sweating, jaundice, and mental confusion. Its presence in wastewater has prompted the need for effective removal methods. Several techniques, including membrane separation, biological methods, electrochemical treatments, photolysis, and adsorption, have been employed to reduce MB levels in wastewater. However, the chemical methods face challenges in sewage treatment plants due to electricity requirements, particularly in developing countries [70]. Nanomaterials have shown promise in decomposing MB, with various nanocomposites demonstrating effective dye removal. Adsorption using nanomaterials has emerged as a widely reported method for dye removal. The use of nanomaterials as adsorbing agents to remove dyes has been extensively reported. The adsorption mechanism can be classified as physiosorption and chemisorption [69]. Physiosorption, a reversible process, involves weak forces such as van der Waals forces, electrostatic interactions, and hydrogen bonding. These forces allow the nanomaterial to attract and retain dye molecules on its surface without significant electronic exchange. After physiosorption the dye can be easily detached under suitable conditions, allowing regeneration and reuse of the adsorbent. In chemisorption, on the other hand, a strong covalent bond is formed between the adsorbent surface and the adsorbed dye molecules. This occurs through coordination interactions in which the adsorbent provides binding sites for the dye. Although chemisorption increases dye retention, it is usually irreversible, making regeneration and reuse of the sorbent more difficult. The choice of adsorption mechanism depends on factors such as dye and adsorption
properties, intended application, and desired dye removal efficiency. Understanding these mechanisms will help researchers design nanomaterials with enhanced adsorption capacity and selectivity for specific dyes.

Altowyan et al. [71] used C-Ni hybrid NPs to remove MB from water. The NPs were synthesized via a green laser technique called Pulsed Laser Ablation in Liquid (PLAL). NiO-MWCNT nanocomposites were synthesized in a single step using the PLAL technique for catalytic decomposition of MB. This nanocomposite exhibited excellent catalytic activity, reducing dye by over 70% in 10 min, making it a promising option for wastewater treatment. To synthesize nanocomposites, Ni targets were cleaned and immersed in water or f-MWCNT solutions and ablated using a Nd:YAG laser resulting in the generation of NiO NPs or NiO-MWCNT respectively. The nanomaterials were added to the dye solution and stirred. UV-Visible analysis confirmed the degradation of the dye. The hybrid nanocomposite exhibited better dye-decomposing activity compared to the pure NiO NP catalyst, highlighting the importance of hybrid nanomaterials and the importance of simple and controllable synthesis methods such as PLAL. The study showed that the degradation efficiency of the hybrid NPs was pH depended, the pH and the efficiency exhibited a quadratic-like relationship as shown in Fig. 3b (i). The degradation efficiency also increased with increasing reaction time for both the monometallic NPs (NiO) and the hybrid NPs as shown in Fig. 3b (ii-iii). The degradation efficiency of the nanocomposite showed excellent stability even after 4 cycles as shown in Fig. 3b (iv).

Similarly, Rahman et al. [72] used silica NPs incorporated into a hydrogel matrix for the removal of MB. The adsorption of MB was attributed to the network structure and active groups. Similarly, Santos-Beltrán et al. [73] used MoO3 NPs for the removal of MB in water. The carboxinic dye was effectively separated from water without the need for light irradiation, reaching 98% separation in 25 min at a concentration of 20 ppm. The removal process was studied using UV-Vis, FTIR and Raman spectroscopy to obtain evidence of dye removal. Another research team removed MB from wastewater using cellulose NPs [74]. A sodium periodate-modified nanocellulose adsorbent (NaIO4-NC) was prepared from readily available lignocellulosic biomass. This demonstrated effective removal of the cationic MB dye from the effluent.

3.1.3. Methyl violet

Similar to many other cationic dyes, Methyl Violet (MV) poses a health hazard to various forms of life, encompassing plants, humans, and fish, when present in water. MV exhibits toxicity towards aquatic organisms, including fish, algae, and invertebrates, and can enter the human body through traces in drinking water or by consuming contaminated fish. MV is deemed carcinogenic, has the potential for genotoxic effects, and may elevate the risk of cancer in individuals exposed to it. Tiwari et al. [75] used magnetite NPs to effectively remove MV from wastewater. Modification of magnetite NP was performed using the anionic surfactant sodium dodecyl sulfate to efficiently remove the cationic dye MV. At low pH, the positively charged surface of magnetite NPs attracts sodium dodecyl sulfate. This interaction increases the surface area and enhances the dye removal efficiency. Magnetite NPs can be easily collected by applying an external magnetic field, which facilitates the addition of sodium dodecyl sulfate. As the concentration of sodium dodecyl sulfate in the solution increases, the adsorption of the MV dye also increases. However, when the sodium dodecyl sulfate concentration exceeds its critical micelle concentration value (2 mg in this case), aggregation occurs, resulting in a decrease in dye adsorption. Another research team used Fe NPs to remove MV from water [76]. Fe is a magnetic material, making it easier to remove and reuse after the water purification process. Jafari et al. [77] removed MV from drinking water using hybrid Ti NPs. They concluded that pure Ti NPs could absorb MV for a while but began to desorb the MV rendering them unstable (physisorption). However, the introduction of Ag-I to form hybrid nanoparticles enhanced stability through chemisorption.

This study and others highlight the necessity for advanced or hybrid nanostructures to ensure effective performance. However, for nanomaterials to establish themselves as the gold standard for large-scale and global water treatment, a controllable and precise method of manufacturing nanomaterials is essential.

Shamsipur and coworkers also removed MV from water using ZnS quantum dots and Fe-dopped ZnS quantum dots under UV light irradiation [78]. The chemical co-precipitation method was employed to fabricate the nanomaterials and the photocatalytic activity was measured via UV-Vis analysis. The 587 nm absorbance value decreased under UV light irradiation and almost cleared off after 1.5 h, representing the degradation of MV in the presence of 80 mg/L of nanomaterials. The rate of decolorization of MV decreases with increasing the initial MV dye concentration. For ZnS quantum dots, the presence of Fe as a dopant causes a blue shift of the fundamental absorption edge with increasing UV photocatalytic activity and hence MV dye removal. Although this material worked well at removing MV, the 1.5 hrs required to remove the dye and the requirement of dopant (Fe) could hinder practical applications of this material globally and researchers should aim at designing low-cost materials that can work with or without intense UV irradiation (which could come from the sun).

3.1.4. Crystal violet

Saad and co-workers demonstrated the removal of crystal violet (CV, a cationic dye) from water using polyaniline NPs that were synthesized via the polymerization method [79]. Similarly, Bhukal and co-workers used Fe NPs synthesized from bacteria to remove CV from water [80]. The Fe NPs was synthesized via a green technique utilizing Spirulina, an edible biomass of cyanobacteria bacteria rich in protein and often used as a supplement that is sold off-the-shelf. The efficiency of the Fe NPs in removing dyes increased steadily with increasing pH values from 2 to 12. At pH 2, the nanosorbent removed 60% of the dye, while at pH 12 and 14, the removal rates rose to 98% and 96%, respectively. Previous research suggests several factors that contribute to lower dye removal efficiency at low pH, such as unfavorable adsorption, a high concentration of H+ ions, and competition between CV dye molecules and H+ ions for adsorption onto the Fe NPs surface. Additionally, the protonation of the Fe NPs surface hinders CV adsorption due to the repulsion between charged particles. Conversely, when the Fe NPs are deprotonated at higher pH levels, their adsorption capacity improves, resulting in enhanced dye removal efficiency.

Ahmad and co-workers also removed CV from water using a different type of nanomaterial composed of Ag NPs and alginate that formed a bionanocomposite [81]. FTIR studies were used to measure the adsorption of CVs on the bionanocomposites as shown in Fig. 3c. In particular, the CV-loaded bionanocomposite showed that the absorption peak at 1380 cm−1 disappeared, while the other peaks (3401 and 1617 cm−1) shifted which demonstrated the involvement of the OH and C=O groups in the adsorption of CV dye. Adsorption studies were conducted at 30 °C and a pH range of 2–10 for 240 min. Neutral pH was found to be optimum for dye adsorption owing to the positively charged bionanocomposites. The positively charged surface sites of the Ag-based bionanocomposites featured electrostatic interactions, which enhanced the adsorption of dyes to the surface. As the pH of the solution increases, more negatively charged sites are formed by absorbed OH ions. At high pH, the negatively charged surface of bionanocomposites exhibits significant electrostatic repulsion towards dye molecules, resulting in decreased dye adsorption. In another publication, Pd NPs were synthesized using a biogenic approach and incorporated into thin-film nanocomposite membranes to enhance properties such as hydrophilicity, antifouling, mechanical strength, flux, stain repellency and desalination. Cellulose membranes containing 2% Pd NPs showed improved hydrophilicity, high dye removal (99%), and good mechanical strength. The effectiveness of nanocomposite membranes in CV separation is demonstrated by experimental results, offering potential for addressing water pollution. Further research is needed, focusing on more cost-effective
materials like cellulose, and exploring combinations with economical nanomaterials such as Fe, Al, Mg, and C instead of the pricier and rarer metals Pd, Pt, Au, and Ag. Additionally, researchers should investigate the simultaneous removal of multiple dyes using a single nanomaterial to replicate real-world scenarios with diverse cationic and anionic dyes in polluted water. Considering the presence of heavy metals and organic compounds in polluted water, the development of a versatile nanomaterial capable of efficiently operating under such conditions is essential. An ideal nanomaterial would simultaneously remove dyes, organic contaminants, and heavy metals while being recyclable and reusable.

3.1.5. Methyl orange

Methyl orange (MO) comes under anionic dyes and causes several health problems when consumed in drinking water. MO is one of the most famous dyes which is used in analytical chemistry, textile industry and biological staining. MO is also commonly used in virtually all high school chemistry courses as an indicator during titrations. The reagents are usually disposed through the drain which enables MO to easily find its way in water bodies, wastewater and if left unchecked, in drinking water. MO can cause cancer, genetic mutation, allergic reactions and irritation and its removal in water systems is important. Pirsaheb and co-workers used Ni-Ti BNPs to remove MO from water accompanied by UV and sunlight irradiations [82]. Dye removal efficiencies by Ni-Ti BNPs were 96% and 94% under UV and solar irradiation, respectively, within 45 min of contact time, whereas the monometallic Ti NPs could only achieve a maximum dye removal of 46%. This study represented the impact of BNPs in water treatment, the efficiency can be doubles by simply combining multiple materials that can produce synergic effects and increased photocatalytic activity owing to increased photo absorbance. Different nanomaterials tend to absorb light of different wavelengths and combining these will enable nanomaterials to absorb a larger percentage of the solar energy which increases the dye removal/degradation efficiency. Additionally, the research team immobilized the BNPs onto a Scoria, a type of volcanic rock for improved efficiency and ease of removal of nanomaterials afterwards. This enables the ease of reuse and recycling of the nanomaterials, a major requirement for real-world application of nanomaterials in water treatment. The synthesis route of the immobilized nanomaterial and dye removal experiments is represented in Fig. 3d.

In another publication, Fe-W BNPs in conjunction with visible light were used to remove MO in water attaining a 98% dye removal [83]. The BNPs displayed bimodal size distribution ranging from 100 to 1000 nm as shown in Fig. 4a and displayed better photocatalyst activity than the monometallic counterparts which were smaller in mean size. The by-products of the degradation process should also be considered. Narendhran et al. [83] investigated the cytotoxicity against mice macrophage cell line (RAW 264.7) of both the pure MO and its by-products after treatment with the Fe-W BNPs. It was observed that the by-products of the degradation process displayed less toxicity rendering them effective candidates for water treatment. The research team also examined the effect of the MO dye or its by-products after BNPs treatment on the germination of Vigna radiata seeds. It was observed that the MO reduced the growth (measured by root length after 5 days of germination) of the seeds considerably while the by-products displayed a much lower toxicity in comparison to the control (seeds germinated under DI water) as shown in Fig. 4b. This study displayed that MO in drinking water (humans) or soil (plants) can detrimental and its removal is imperative.

Uddin and colleagues employed a precipitation technique, illustrated in Fig. 4c, to eliminate MO from water using Co NPs [6]. The optimal adsorption efficiency was observed at neutral pH values, as depicted in Fig. 4d (i). Interestingly, the degradation rate remained consistent as shown in Fig. 4d (ii) regardless of the initial dye concentration, indicating promising results. These findings highlight the effectiveness of the dye removal method across different concentrations, mirroring real-world applications.

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**Fig. 4.** a) Nanoparticle size distributions [83]; b) effects of dyes and by-products on root growth [83]; c) nanoparticle fabrication method [6]; and d) effect of pH and time on dye adsorption rate [6].
3.1.6. Eriochrome Black T

Eriochrome Black T, another anionic dye, is a carcinogenic azo dye commonly used as an indicator in laboratory experiments. It binds well with Mg$^{2+}$ and Ca$^{2+}$ ions, making it a popular indicator during the analysis of hardness in water. The by-products of Eriochrome Black T after chemical reactions are usually disposed in drains, which enables these to be found in water bodies and if untreated well during water treatment they can be found in drinking water. In one publication, Moeinpour and co-workers used Fe-Ni BNP s with 50 nm diameter for the removal of Eriochrome Black T, the mechanism of removal was attributed to adsorption due to oppositely charge species [84]. The adsorption equilibrium was reached which followed a Langmuir model with a high R$^2$ value of over 0.97.

Another research team compiled a review paper solely focused on the application of Zn NPs for Eriochrome Black T removal in water [85]. Abbas et al. used Al NPs to remove Eriochrome Black T from drinking water [86]. Al NPs come from low-cost raw materials which provide a practical and realistic material for real-world applications. About 99% of the dye was removed at an optimum pH and temperature of 7 and 45 °C, respectively. A clear color change (decolorization) was observed which demonstrated the dye degradation process. UV-Visible and X-ray diffraction (XRD) studies were also used as quantitative methods of dye removal measurement and confirm the stability of NPs after treatment. Both adsorption and photocatalysis are well documented mechanisms for dye removal. Another research team reported the photodegradation of Eriochrome Black T using Zn NPs under UV light [87]. Similarly, Ti NPs were used as photocatalyst during the degradation of the dye reaching 82% degradation in 90 min [88]. Several other reports have been published the removal of Eriochrome Black T in water using various types of NPs and nanocomposites including Zn, Ag, Sn, Al, Si, Mo and others, making this dye one of the most studied in the literature [89–95].

Moreover, sensing of dyes in water can improve the quality control of water. A research team developed a latex-capped Ag nanocomposite and used it as an electrochemical sensor for Eriochrome Black T dye [96]. Other publications also reported the development of NP-based dye sensors [11,97]. Many other dyes can be found in water and researchers have reported their removal using NPs as shown in Table 1.

3.1.7. Indigo Carmine

Indigo carmine (IC) is one of the most important synthetic dyes commercially used in the textile denim industry [113]. Estimations suggest 15–20% are lost in the effluents and directly released into the environment as wastewater [114]. IC can cause severe damage to human beings, such as permanent corneal damage, eye and skin irritation, vomiting, and diarrhea [115]. Hence, removing IC dyes from wastewater is fundamental to the environment and human beings. Different water treatment methods for eliminating indigo carmine have been investigated, including adsorption, electrocoagulation, biodegradation, membrane filtration, photocatalysis, ozone, and UV/H$_2$O$_2$ [113]. However, these methods have some drawbacks, like sludge generation, the use of chemicals, or membrane fouling. Nanomaterials-based water treatment technologies, for example, photocatalysis, have been suggested as sustainable alternatives for degrading and mineralizing IC in wastewater. Table 2 compares the efficiencies of photocatalytic indigo carmine degradation.

Aluminum-doped titanium dioxide/zinc ferrite (Al-TiO$_2$/ZnFe$_2$O$_4$) nanocomposite completely mineralized IC in 120 min under visible light irradiation, indicating dye and its intermediates were converted to carbon dioxide and water [114]. The enhanced photocatalytic of Al-TiO$_2$/ZnFe$_2$O$_4$ was attributed to heterojunction formation. Photocatalytic degradation of IC using MgO@g-C$_3$N$_4$ [116] showed a superior degradation ability compared to TiO$_2$@g-C$_3$N$_4$ [117] and ZnO@g-C$_3$N$_4$ [114] under visible light. The application of boron nitride as a photocatalyst for decolorizing IC dye was determined 88% in 60 min [118]. Boron nitride produced good electron-hole pairs under UV light absorption and was recycled and reused for extended periods.

Although the application of nanomaterials for IC degradation has been demonstrated, its application on a complex matrix as real textile wastewater containing detersents, dye, mordants, salts, and auxiliary agents is still a knowledge gap. Therefore, color removal from textile wastewater does not intrinsically mean mineralization or potential wastewater reuse in a close circuit because of recalcitrant by-product accumulation due to insufficient degradation [120]. So, combinations of hybrid technologies may be suitable alternatives for industrial textile wastewater (ITWW) to increase biodegradability and mineralization [120].

3.1.8. Pharmaceutical pollutants

The onset of COVID-19 pandemic in the beginning of year 2020 has drastically escalated the consumption of the pharmaceutical compounds [121]. Subsequently, the discharged of these persistent pharmaceutical residues into aquatic environment has also increased continuously through the sewage systems. According to a report published by World Health Organization (WHO), the increased use and unsafe disposal of pharmaceuticals is ubiquitous and is a major concern worldwide [122]. The trace concentration of pharmaceuticals found in natural water reservoirs is known to cause adverse effects on the environment due to unintentional consumption and assimilation by humans and other organisms. Most of these compounds are low volatile, highly polar and tough to degrade biologically [123,124]. More than 200 antibiotics sulfonamide have been found in water, and 15–20 are still detectable even in drinking water worldwide [122]. The conventional treatment processes for treating wastewater such as filtration, coagulation-flocculation, sedimentation, and chlorination do not completely remove the pharmaceuticals and endocrine disruptors [125]. Generally, the functional groups present in pharmaceuticals (–OH, –COOH, –NH$_2$, SO$_2$, –CONH$_2$, –C–C etc.) have strong interaction affinity, thus allow adsorption on material surfaces via electrostatic interaction, hydrogen bonding, polar-polar interaction, and coordination ability. Carbon based nanomaterials such as activated carbon, multi-wall carbon nanotubes, graphene etc. have been used to adsorb pharmaceuticals and endocrine disruptors effectively. In addition to this advanced oxidation processes such as photocatalysis, Fenton process, ozonation, sulfite radicals are well studied for the removal of pharmaceuticals.

Recently, Rojas-Cervantes and co-workers has synthesized a series of MWCNTs doped with Fe and Cu to removal of paracetamol from

![Table 1](image)

<table>
<thead>
<tr>
<th>Dye name</th>
<th>Nanomaterial</th>
<th>Mechanism of removal</th>
<th>Time to equilibrium</th>
<th>Ref</th>
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<tr>
<td>Methyl red</td>
<td>Fe$_3$O$_4$</td>
<td>Adsorption</td>
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<td>[98]</td>
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<tr>
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<td>Photocatalysis</td>
<td>20 min</td>
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<td>[100]</td>
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<tr>
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<td>Photocatalysis</td>
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<td>[101]</td>
</tr>
<tr>
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<td>Fe$_3$Co$_2$O$_4$</td>
<td>Adsorption</td>
<td>50 min</td>
<td>[102]</td>
</tr>
<tr>
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<td>ZnO$_2$</td>
<td>Adsorption</td>
<td>10 min</td>
<td>[103]</td>
</tr>
<tr>
<td>Congo red</td>
<td>Fe</td>
<td>Adsorption</td>
<td>200 min</td>
<td>[104]</td>
</tr>
<tr>
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<td>ZnO</td>
<td>Adsorption</td>
<td>150 min</td>
<td>[105]</td>
</tr>
<tr>
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<td>ZnO</td>
<td>Adsorption</td>
<td>150 min</td>
<td>[105]</td>
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<tr>
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aqueous solution using a combined process of adsorption and Fenton-like oxidation [126]. The synergic effect between both Fe$^{2+}$/Fe$^{3+}$ and Cu$^+$/Cu$^{2+}$ in Fenton-like reaction results in the 90.2–98.3% oxidation of paracetamol within 5 h of reaction time under mild reaction conditions (neutral pH and 25 °C). The higher rate constant of reaction Cu$^+$/H$_2$O$_2$, with respect to that of Fe$^{2+}$/H$_2$O$_2$ was observed and was attributed to the production of more hydroxyl radicals (OH$^*$) in the case of catalyst with copper.

Similarly, pristine graphene, graphene oxide (GO), reduced graphene oxide (rGO) and their composites have exhibited excellent performance for the removal of pharmaceutical pollutants [127–129]. Januário et al. have demonstrated the use of the activated carbon functionalized with GO for efficient removal of COVID-19 treatment related pharmaceuticals such as chloroquine (CQN) and dipyrone (DIP) from wastewater. The composite shows maximum adsorption capacities of CQN and DIP were 37.65 and 62.43 mg/g in 12 and 18 h, respectively, with copper.

In another report, ZnS NPs synthesized by the green route using S. frutescens plant extract was used for the degradation of various dyes and pharmaceuticals [130]. The ZnS NPs showed more than 96% of degradation of two pharmaceutical drugs sulfisoxazole (SSX) and sulfamethoxazole (SMX) within 2 h. The OH$^*$ radicals produced on the aqueous-catalyst interface were the active oxidizing agents and ones responsible for that higher degradation efficiency. Balarak et al. [131] has synthesized NiO NPs using sol-gel method and used it for the removal of Amoxicillin (AMO) from pharmaceutical wastewater. With the optimum concentration of NPs (0.2 g/L) degradation efficiency of 96% was achieved for 25 mg/L of AMO within 120 min

Numerous studies have been conducted for the removal of pharmaceuticals using heterogeneous TiO$_2$ nano-photocatalyst [132–134]. Zhang and co-workers has investigated the combination of TiO$_2$ along with UV light/chlorine for the degradation of ibuprofen (IBF) [135]. The quenching experiment confirmed the presence of OH$^*$, Cl$^*$, and ClO$^*$ radicals during the degradation experiment. The proposed degradation pathway suggested the hydrogen abstraction from benzene ring of IBP by OH$^*$ and subsequently the formation of chlorine-substituted products when Cl$^*$ reacted with dehydrogenation radical. Further, the proposed pathway was justified with Density functional theory (DFT) studies.

Zhu and coworkers [136] have developed an efficient and stable (wide pH range) iron–nitrogen-carbon (Fe-N-C) using a covalent organic framework as a precursor. The prepared catalyst was highly porous containing homogeneous micropores and was able to activate peroxymonosulfate via a non-radical pathway. It was found that 30 mg/L of Fe-N-C activator with 3 mM PMS was able to degrade 10 mg/L paracetamol (PCT) within 5 min. The quenching and electron paramagnetic resonance (EPR) experiments suggested that the high-valent iron-oxo species are the major reactive oxygen species and the Fe-N site is responsible for activating PMS (Fig. 5i). Also, the singlet oxygen and electron transfer are other two possible pathways in the process of degradation as shown in Fig. 5 (ii, iii).

Similarly, many reports have been published where transitions metals such as Cr, Mn, Fe, Ni, Cu, Co, and Zn was used as dopant to improve the photocatalytic efficiency of TiO$_2$ for the degradation of pharmaceuticals [137–140]. In addition to this noble metal NPs like Au, Ag, Pt, Pd etc. also played a vital role in escalating TiO$_2$ NPs photocatalytic performance under visible light irradiations [141–143].

There is a need of the hour to find multifunctional and safe materials that can be used for the removal of various dyes and pharmaceuticals from water bodies. The conventional treatment methods are not able to
nanomaterials in water treatment. Researchers have certainly showed research concerning the cost of producing the nanomaterials, methods of fields. Reducing the number of processing steps, energy consumption, of these pharmaceuticals in water systems and re-examine the current reuse is required. Galangash et al. [145] reported the removal of Black 5 towards such as filtration and centrifugation by the use of magnetic from small molecules at the periphery, advancing inward to ascertain desired number of generations, whereas convergent synthesis initiates from small molecules at the periphery, advancing inward to ascertain the ultimate number of generations according to dendron size [12,63]. Researchers have combined dendrimers with magnetic NPs to enhance the rate of dye removal and to eliminate separation steps afterwards such as filtration and centrifugation by the use of magnetic fields. Reducing the number of processing steps, energy consumption, environmental impact, and energy requirements in the purification process increases the likelihood of global adoption of dendrimers and nanomaterials in water treatment. Researchers have certainly showed the effectiveness and efficiency of such material in lab-scale but more research concerning the cost of producing the nanomaterials, methods of synthesis and the separation of the nanomaterials afterwards to enable re-use is required. Galangash et al. [145] reported the removal of Black 5 (RB5) and Acid Red 114 (AR114) dyes from an aqueous solution using magnetic polyhydroxyl modified NPs (Fe₃O₄@SiO₂-TRIS). Another team used magnetic dendrimers to remove MB and MO dyes, achieving best adsorption values of 96 and 21 mg/g, respectively, at pH values of 3 and 11, respectively [146]. The aforementioned article demonstrated the effect of pH on the adsorption process and consideration must be taken on the means used to alter the pH. The use of harsh chemicals could be detrimental to the environment and may require removal steps. Ideally, particles that can still perform satisfactorily at any pH level are ideal however, there is usually an optimum pH level with respect to degradation/adsorption rate.

Another article investigated the use of poly(propylene imine) (PPI) dendrimer in eliminating textile dyes (Direct red 23, Direct red 80, Acid Green 25 and Acid Blue 7) from water solutions [147]. The research explores the impact of operational factors like dendrimer density, dye concentration, salt composition, and pH on dye elimination. The findings demonstrate that acidic pH promotes dye adsorption by the dendrimer, while higher dye concentration and salt content hinder the percentage of dye removal. The study proposes that dendrimers, with their eco-friendly characteristics and strong adsorption capability, present a promising solution for treating colored textile wastewater and effectively removing dyes.

Another research team conducted an investigation on the effectiveness of the PPI dendrimer for removing Direct Red 80 and Acid Green 25 dyes from water [148]. However, their specific focus was on studying the thermodynamic properties of the dye and its impact on the adsorption process. The research examined the impact of temperature on dye removal and studied adsorption isotherms (Langmuir and Freundlich) and kinetics (pseudo-first-order and pseudo-second-order) at different temperatures. Thermodynamic parameters were calculated, indicating that the adsorption process with PPI dendrimer as an eco-friendly material was spontaneous. These findings suggest that PPI dendrimer can be a suitable adsorbent for effectively eliminating dyes from colored textile wastewater across varying temperatures. The optimal pH for dye removal was observed at pH 2, the pH was altered by using an acid (H₂SO₄) or a base (NaOH). UV-Visible spectroscopy was employed for adsorption studies due to its advantages, including accuracy, cost-effectiveness, high throughput, and rapid results. The shifts observed in absorbance maxima or wavelengths indicate alterations in the chemical composition, specifically related to the process of adsorption.

Duan and research team synthesised a porous PAMAM dendrimer gel adsorbent that could purify water via filtration of MO and tartrazine (TTZ) dyes [7]. Adsorption was completed in a space of only 15 min with adsorption rates 680 mg/g for MO and 690 mg/g for TTZ. The microstructure of the dendrimers is shown in Fig. 6a and b showing spherical dendritic structures that resembles uniform tree-branch-like structures. The team discovered that the dendrimer was good at adsorbing anionic dyes (MO and TTZ) but not as good at removing cationic dyes like MB and MV as shown in Fig. 6c. The aqueous swelling behavior of freeze-dried PAMAM dendrimer gel was investigated; the PAMAM gel exhibited a rapid swelling rate, reaching equilibrium within 10 min, and demonstrated a high swelling ratio of 645%. This exceptional swelling property is believed to enhance the transport of dye molecules in water. The PAMAM gel displayed a consistently positive surface charge across a wide pH range (3–10), thanks to the abundance of amine groups present. Notably, as the solution pH decreased, the Zeta potential value showed a significant increase, which can be attributed to the progressive protonation of the amine groups. Taking into account the findings mentioned above, it can be inferred that the PAMAM gel, enriched with a high concentration of amines, possesses a porous microstructure, a large surface area, and remarkable swelling properties. As a result, it holds great potential as a highly effective adsorbent for anionic dyes. Furthermore, the dendrimers showed excellent sustainability as it could be recycled via a filtration process. Eskandarian et al. [149] investigate the application of MWCNTs-PPI dendrimer in the removal of dyes in single and multiple dye water solutions. Direct Blue 86 and Direct Red 23 were used as model dyes and the pH was adjusted by H₂SO₄ and NaOH solutions. The chemical structures and the effect of pH on the stability of the dyes are shown in Fig. 6d. The microstructure of the dendrimers before and after dye adsorption is shown in Fig. 6e and 3.
proposal is to implement personal, home-based, and office-based water purifiers that utilize these nanomaterials, preferably in an immobilized form to prevent their release into the water system. For instance, water bottles equipped with nanomaterials and, if necessary, a light source can be used to treat water before consumption, effectively addressing dye contamination. Additionally, these nanomaterials have the capability to eliminate pathogens (as described in Section 2.3) and remove heavy metals (as described in Section 2.2), making tap water a more efficient and safer option after most contaminants have been removed.

3.2. Removal of heavy metals using nanoparticles and dendrimers

Heavy metals such as Pb, Cd, and Ni exert toxic effects on both drinking and wastewater. In the absence of proper purification measures, industries release these heavy metals into aquatic environments, posing a risk to both wastewater and potential drinking water sources. Fish inhabiting these environments undergo significant disruptions to their physiological and metabolic processes, reproductive capabilities, and immune systems due to the presence of heavy metals. Additionally, human consumption of water contaminated with heavy metals has been associated with the development of diseases, including cancer. A published report presents alarming statistics, revealing the widespread occurrence of heavy metals in drinking water across multiple countries globally [150]. Nanomaterials have garnered considerable attention in the literature regarding heavy metal removal due to their nano-size. The small size and high surface area of nanoparticles enable them to readily react with and adsorb heavy metal ions, even at low nanoparticle concentrations, providing efficient and rapid removal.

Vázquez-Guerrero and co-workers combined Fe NPs with cellulose nanofibers and used the resulting nanocomposite to remove Cd(II) and Pb(II) from water [151]. The cellulose nanofibers were extracted from Moringa oleifera via three different methods namely the pulping Kraft process, acid hydrolysis and ultrasonication. The adsorption of Cd and Pb by the Fe NPs on the surfaces of the cellulose was attributed as the purification method which followed a pseudo-second-order kinetic model for both Cd and Pb ions. Scanning electron microscopy (SEM) reviewed clear differences in morphology before and after adoption of Cd and Pb. Fourier transform infrared (FTIR) also confirmed the adsorption of heavy metal ions as evidenced by a decrease in transmittance in signature bonds such as -OH and -CH groups. The Zeta potential of the nanocomposite was $-23 \text{ mV}$ which favors the adsorption of the positively charged heavy metals, Cd$^{2+}$ and Pb$^{2+}$ ions. The adsorption kinetics of both heavy metals were different but both reached equilibrium at 150 min as shown in Fig. 7a. The process of adsorption of Pb and Cd in the first phase (linear region) of the graphs in Fig. 7a was described to occur at the surface of the cellulose, where the transfer of substances and the diffusion of the adsorbed Cd and Pb take place. Additionally, the second phase is characterized by a sluggish rate of adsorption due to the slow movement of ions and surface-related phenomena. This indicates that the rate-limiting step and the type of adsorption governing the system. The adsorbent’s surface offers numerous vacant bonding sites for the metal ions, facilitating easy adsorption. As the adsorption process progresses, the concentration of metal ions and available sites decreases, resulting in a slower adsorption rate once the system reaches equilibrium.

Faraghal et al. [8] used Fe NPs coated with Chitosan/Xylan for the simultaneous removal of Pb(II), Salicylic acid and Congo red (CR) dye which were selected strategically to represent some of the three main water contaminates namely heavy metals, pharmaceuticals and azo dyes in that order. The ability of one nanomaterial tackling several contaminants of diverse chemistries and origin demonstrates the power of nanotechnology in water treatment and paves way for its wide use in water treatment on international levels. The adsorption of contaminates was attributed to chemical chelation for Pb(II) and physical interaction for Salicylic acid and CR dye. The pH influenced the optimal adsorption efficiency of each of the three species, the recorded optimal pH for Pb, Salicylic acid and CR dye were 5.5, 4.0 and 6.1, in that order. Changes in absorption efficiencies of the species were observed when all three
Fig. 7. a) Heavy metal adsorption kinetics [151]; b-c) effect of pH on single and ternary systems [57]; d) heavy metal adsorption mechanism onto nanocomposite [8]; and e) nanocomposite fabrication method [153].
contaminates (ternary system) were present at the same time due to a competition between Pb, Salicylic acid and CR dye over the active sites as shown in Fig. 7b. The dynamics of the competition for active sites was also pH dependent as shown in Fig. 7b and c. The nanocomposite could still adsorb all three contaminants in a ternary system simultaneously which shows great potential for this nanomaterial in real-world applications. The adsorption mechanism is represented in Fig. 7d. Moreover, the nanocomposites displayed great recyclability particularly, HCl solution can clean the nanocomposites to remove adsorbed Pb ions and NaOH solution can remove CR and Salicylic acid after water treatment. Yadav et al. [152] recovered Fe NPs from water contaminated with heavy metals with a purity of at least 90%. The research team went a step further and used the recovered Fe NPs to treat the water by removing metals including Cd, Co, Cr, Pb, Al, Cu, Mn, Ni and Zn.

Moreover, Kumar et al. synthesised hexagonal boron nitride-iron composite nanosheets with many pores and surface functional groups for the adsorption of Cr, MB dye, As and acid orange (AO) dye [153]. This report also represented the potential of nanomaterials in the simultaneous removal of various pollutants which can come from diverse sources. The adsorption kinetics of all pollutants exemplified Freundlich isotherm model and a pseudo-second-order dynamics. The magnetic hybrid aerogels were synthesised following the procedure shown in Fig. 6e that involved thermal poly-condensation, pyrolysis, ultra-sonication and freeze drying. Similarly, another publication reported the application of Fe NPs in the removal of Cd and Ni heavy metals in water [154]. The Fe NPs was synthesised from Fe ions reacted with clove and green coffee extracts as reducing agents. The Fe NPs attained adsorption rates of up to 78 mg/g. The resulting pyramidal Fe NPs are shown in Fig. 8a. Interestingly, the Fe NPs also displayed excellent antimicrobial activity against some of the world most known pathogens.
pathogenic microbes including S. aureus and E. coli as shown in Fig. 8b. A schematic of the mechanism of antibacterial activity is shown in Fig. 8c which involved DNA damage, enzyme inactivation, cell membrane perforation, and cell damage from reactive oxygen species.

Fe has been combined with various elements, including Cu, to further enhance its exceptional properties in heavy metal removal, antibacterial activity, dye removal, and adsorbent capabilities. One notable instance is the work of Ye and their research team, who produced Cu-Fe BNP s and successfully employed them for the removal of hexavalent chromium from water [155]. Cr comes in many forms, some of which are extremely poisonous while others are non-toxic to the human body. The reduction of Cr$^{6+}$ to its non-toxic counterparts such as Cr$^{3+}$ and/or its composites like Cr(OH)$_2$ and Cr$_2$Fe$_3$ (OH)$_3$ leads to cleaner water and was demonstrated. Cr(III) is a well-known supplement sold off-the-shelf for glucose metabolism, weight management and antioxidant properties and hence its presence in water is not poisonous. The Fe nanocomposites can be easily recovered after use using magnets. The mechanism of Cr removal was described by an initial adsorption phase onto the BNP s followed by internal electron transfer. The adsorption rate was plotted against time and the resulting curve followed a typical pseudo-second-order curve.

Fe NPs have shown great potential in heavy metal removal and is deemed one of the most reported nanomaterials in the literature of heavy metal removal for water treatment. However, Fe is not the only material looked at by researchers, other publications have also reported the application of Ag, Zn and Cu NPs in heavy metal removal. Fatima and co-workers reported the use of Fe-Zn BNP s for the removal of Cr and fluorescein in water [156]. Additionally, Guevara-Bernal and research group used coffee husk and lignin modified with Ag NPs for the removal of Pb(II), Cd(II), Cr(III), and Cu(II) ions in water [157]. The impregnation method was used to synthesise the nanocomposite which involved mixing the coffee husk and lignin with AgNO$_3$ as a precursor for Ag NP synthesis and NaBH$_4$ as a reducing agent (a typical wet-chemistry technique of synthesizing Ag NPs). In addition to heavy metal removal, the modified Ag NPs also displayed antifungal activity against Candida albicans, Candida parapsilosis, Candida glabrata, Candida krusei and Candida guilliermondii. Although not investigated in their study, Ag also has excellent antibacterial and antiviral activity against a diverse collection of pathogens [158–165]. In fact, Ag is used in many commercial products as an antimicrobial agent and is the most used in these applications. The coffee husk and lignin alone also possess heavy metal adsorption properties but these properties are significantly enhanced by the presence of Ag NPs. Others also reported common products such as bananas, sunflower, corn cob and limestone as good adsorbents of heavy metals and these agents can also be enhanced with nanomaterials [166,167]. Mg NPs have also been explored in heavy metal removal. Mg has the added advantage of being biocompatible and biodegradable, making it easier to manage not to mention its much lower cost and much higher abundance than Ag. Siciliano et al. [168] utilized Fe-Mg BNP s for the removal of Pb from water, attaining over 90% removal in 30 min. XRD characterisation were used during adsorption analysis. The Fe-Mg BNP s displayed better adsorption characteristics than commercial monometallic Fe. In another publication, Ag NPs immobilized onto sulfonated polyethylene sulfone via an electro-spinning method displayed great adsorption properties of Pb and Cd in water [169]. Immobilization enables the ease of recycling of the NPs after water treatment leading to shorter lead times and lower chances of NP contamination modifiers for treatment. The nanocomposites were washed using NaOH and distilled water as a recycling method and could be re-used for 10 cycles without significant decrease in adsorption efficiency. These nanomaterials displayed great practicality and potential for real-world application owing to the ease of recycling and good number of re-use cycles. The nanocomposites also displayed a high tensile strength of 5.4 MPa and an elongation of 70%, demonstrating their durability in flowing water with high pressures such would be the case in real-world applications. Hydrogen bonding played a significant role in strong interactions between OH (water) and S═O groups. Sulphonate groups often act as acceptors in hydrogen bonding. The removal efficiency of Cd(II) and Pb(II) through adsorption is facilitated by electrostatic interactions between the positively charged metal ions and the negatively charged absorbent surface. The adsorption capacity decreases as the pH increases due to repulsive forces between the cations and the adsorbent. Cd(II) adsorption occurs rapidly, reaching 80% within 20 min and 100% equilibrium adsorption in 40 min. Pb(II) adsorption was slower with 100% equilibrium adsorption in 60 min. Mahmoud et al. [170] used Cu NPs for the removal of Pb, Ni, and Cd in water. It was found that the rate of removal was highest for Pb followed by Cd and lastly Ni with each species reaching equilibrium with an hour. The adsorption rate of the heavy metals fitted Freundlich models well, with $R^2$ values of over 0.97.

This section emphasizes the widespread utilization of Fe NPs and their composites, such as Fe-cellulose, in the removal of heavy metals. Fe is a cost-effective material that is readily available and possesses numerous advantageous properties. It exhibits high adsorption capacity for a wide range of pollutants and also exhibits antibacterial activity against waterborne pathogens. These qualities make it a favorable choice over scarce and expensive materials like Ag or Pd. It is important to note that NPs are highly reactive, resulting in competition with other salts and metals present in real water for pollutant adsorption. Therefore, the most effective stage for removing heavy metals occurs when the water is nearly clean, after other salts and dyes have already been removed in previous stages. Additionally, most publications are based on batch processes conducted in controlled environments, utilizing deionized water and adding heavy metals separately. An interesting study described the use of Fe NPs in a real wastewater sample obtained from an industrial site in Beni-Suef, Egypt [154]. Initially, the effluent contained Cd$^{2+}$ metal ions at a concentration of 5.50 mg/L. Remarkably, even in the presence of high levels of competing ions, the Fe NPs exhibited an impressive removal efficiency of up to 98% for Cd$^{2+}$ metal ions.

Dendrimers are also used for heavy metal removal and some examples are presented in Table 3. Gajjar et al. [171] synthesised hydroxyl-terminated triazine-based dendrimers of different generations (G1(OH)8, G2(OH)32, and G3(OH)128) using a divergent method. The hydroxyl-terminated dendrimers were evaluated as adsorbents for the removal of Cu$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ ions from water, with sorption behavior studied in relation to pH and generation number. The results indicated that G3(OH)128 exhibited the highest sorption capacity, which increased with higher generation number and pH. A review by Sajid et al. [172] summarized the top 5 reasons why dendrimers are excellent heavy metal removers of heavy metals. As adsorbents for the removal of heavy metals, dendrimers have various advantages. They are unusual macro-molecules due to their highly branched and changeable structure with accessible internal cavities and a functionalized surface. Second, their enormous surface area and extensive network of peripheral functional groups lead to strong heavy metal collecting capacities. Third, the

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Heavy metals</th>
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<tbody>
<tr>
<td>CNT dendrimer</td>
<td>Pb$^{2+}$, Cu$^{2+}$</td>
</tr>
<tr>
<td>PAMAM dendrimer</td>
<td>Pb$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, As$^{3+}$</td>
</tr>
<tr>
<td>Triazole dendrimers</td>
<td>Pb$^{2+}$, Hg$^{2+}$, Ni$^{2+}$</td>
</tr>
<tr>
<td>Fe(3O)2SiO2(PAMAM Dendrimer)</td>
<td>Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$</td>
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<tr>
<td>PAMAM dendrimer</td>
<td>Cu$^{2+}$</td>
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<tr>
<td>PAMAM dendrimer</td>
<td>Ni$^{2+}$</td>
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<tr>
<td>Si-PAMAM dendrimer</td>
<td>Ni$^{2+}$, Cr$^{2+}$</td>
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<tr>
<td>PAMAM dendrimer</td>
<td>Pb$^{2+}$, Ni$^{2+}$</td>
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<tr>
<td>amine-functionalized Fe NPs</td>
<td>Pb$^{2+}$, Cd$^{2+}$</td>
</tr>
<tr>
<td>PAMAM-CNT dendrimer</td>
<td>Zn$^{2+}$, Cd$^{2+}$, As$^{3+}$</td>
</tr>
<tr>
<td>PAMAM-cellulose dendrimer</td>
<td>Zn$^{2+}$, Fe$^{3+}$</td>
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<tr>
<td>Si- PAMAM dendrimer</td>
<td>Cd$^{2+}$</td>
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<tr>
<td>Si- PAMAM dendrimer</td>
<td>Zn$^{2+}$, Co$^{2+}$</td>
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presence of several specialized functional groups enables good selectivity that may be modified based on the target heavy metal. Fourth, specific changes to dendrimer cores, inside cells, and outer end groups can have a considerable impact on their physicochemical properties and adsorption applications. Finally, grafting dendrimers onto high area supports improves their selectivity and adsorption capability. Another research team fabricated PAMAM dendrimer-modified magnetic NPs for the adsorption of Sudan red dyes from natural waters at remarkable parts-per-billion concentrations [173]. Exhibited excellent adsorption capacity and a linear relationship with Sudan dye concentrations ranging from 0.02 to 300 μg/L, with high correlation coefficients (>0.996). The method demonstrated high sensitivity, with detection limits ranging from 1.8 to 5.5 ng/L, and good precision (<3.0%).

3.3. Antibacterial effects

The presence of microorganisms in water is crucial when discussing drinking water and wastewater treatment. Bacteria and fungi are the two primary types of pathogenic microorganisms. Research efforts have primarily focused on bacteria and the use of nanomaterials as antibacterial agents. Nanomaterials have shown promising potential as they can achieve better effectiveness at lower concentrations compared to conventional antibiotics. Furthermore, nanomaterials have the ability to combat antibiotic-resistant germs, making them highly valuable in this regard. Therefore, NPs can mitigate biofouling in polymeric membrane water treatment [187]. In the literature, Escherichia coli and Pseudomonas aeruginosa are the most commonly used model pathogens. In antibacterial studies, either the growth inhibition zone method or the plate-counting method is used to assess the antibacterial activity of nanomaterials. Furthermore, the nanomaterials can either be in pure form or attached to an immobilizing agent such as polymers, CNTs or silicon wafers for ease of recycling the NPs after water treatment. There are several ways to attain NP immobilisation for water treatment namely: i) polymerization which involves adding NPs to monomers to form a polymer-NP composite, ii) dip coating which involves dipping the membrane or holding material into a colloidal of NPs, grafting polymerization which involves bonding NPs to the polymer surface during polymerization, and III) interfacial polymerization which involves the polymers of reactive monomers or prepolymers interacting with immiscible phases to form a polymeric film. These methods are summarized in Fig. 9a-d.

Anand et al. [188] synthesised Zn NPs using plant extract mediated reduction method for antibacterial activity in water. The ‘green’ NPs displayed antibacterial activity against Pseudomonas aeruginosa and Staphylococcus aureus which was measured via the disk diffusion method. Polyphenolic and amide functional groups of plant extracts were found on the surfaces of the Zn NPs as recorded by FTIR studies. In a different review paper focused on Co-Fe BNP, its was recorded using evidence from multiple sources that having multiple elements/metals to form hybrid or composite materials was advantageous for antibacterial, photocatalytic and heavy metal adsorption activities [3]. In a different publication, Fe-Zn BNP were displayed biocidal activity against E.coli, S. aureus, B. subtilis and P. aeruginosa during waste water treatment [189]. The BNPs also displayed photocatalytic activity which demonstrates their potential to simultaneously kill pathogens and degrade dyes in wastewater treatment. Another publication reported the use of Cu NPs as antibacterial agents in water treatment [9]. The nanomaterials could kill several pathogenic bacteria including S.aureus, B.subtilis, E.coli, P. aeruginosa, and C.albicans. The Cu NPs could also remove Co, Ni, Pb, Cd, and Cr (VI) heavy metals simultaneously [9]. Furthermore, real contaminated water was used and the Cu NPs could still hold-up their efficiency thereby demonstrating the potential application of these nanomaterials in real-world applications. The researchers also investigated the effectiveness of the Cu NPs for the degradation and treatment of tanning wastewater, a highly toxic effluent from the leather industry. The experiments were conducted under both dark and sunlit conditions, utilizing varying concentrations of Cu NPs as shown in for different time intervals (Fig. 2e). Notably, this study presents the first known report on utilizing Cu NPs for the decolorization and treatment of crude tanning wastewater.

4. Recycling and disposal of nanomaterials

Nanomaterials have shown great potential in wastewater and drinking water treatment. They can be used to kill pathogens in water (Section 2.3), preventing many diseases. They can also be used as adsorbing agents to trap organic matter, ions, and heavy metals (Section 2.2), preventing contamination. Additionally, they are effective in degrading harmful and carcinogenic dyes such as MO (section 2.1.5), thanks to their catalytic activity and excellent optical properties. However, the use of nanomaterials in water treatment requires a recycling or disposal plan after use. Ideally, the NPs should be reused multiple times without leaching into the water, as leaching can lead to secondary contamination, commonly referred to as nanowaste. To ensure...
sustainability, the separation of NPs from the water is a necessary step that demands careful attention. Several strategies have been employed to remove nanomaterials or recycle after water treatment, including filtration, flocculation, magnetic fields, aqueous dispersion techniques, antisolvent technique by using CO₂, centrifugation, liquid evaporation, coagulation technique, microemulsion process, microbiological process, incineration and immobilization.

Nanowaste can be classified in 5 classes based on their origin as shown in Table 4 [190]. Engineered nanoparticles from other industries such as drug delivery, textile, packaging, sensors, electronics, paints, cosmetics (e.g., sunscreen) and others can become a water contaminant and requires removal. Engineered nanoparticles (ENPs) are so widespread that no single disposal method is sufficient for all species. Organizations such as universities and companies often outsource the disposal of ENPs, which is risky as nanowaste requires special handling. Industrial products, waste treatment plants, and laboratories contribute to the accumulation of ENP in recycling centers, incinerators, landfills, and sewage treatment plants, with various risks of release into the environment. Incorporation can remove certain carbon-based ENPs at high temperatures, but recycling ENP-containing materials raises concerns about worker health, environmental impact, and product contamination. Existing methods for testing and detecting nanoscale contaminants in wastewater streams are inadequate.

There are multiple approaches available for recycling or disposing of nanomaterials, which can originate from various sources, including intentional addition during water treatment for purposes like dye or heavy metal removal, as well as nanowaste derived from products such as sunscreens and electronics. These can be classified as physical/thermal and chemical methods.

4.1. Physical methods of recycling/disposing nanomaterials

The utilization of magnetic fields as a physical technique to separate nanomaterials from water has gained significant interest in the literature. This method has gained recognition due to its simplicity, affordability, high efficiency, repeatability, low power requirements, and its applicability in both batch processes and large-scale (industrial) operations. Differential magnetic catch and release (DMCR) is an alternative approach for magnetic separation in which a variable magnetic flux is applied perpendicular to the flow direction in an open tubular capillary, allowing for the trapping and controlled release of NPs. Grass et al. [10] placed magnets on the outside of a colloidal containing Co NPs and could separate the NPs from the water in under 20 s as demonstrated in Fig. 10 a. This required no external power source and the Co NPs can be recycled by simply draining out the water after a few cycles of magnetic separation and adding new water to be treated. Zhang and co-workers used the sol-immobilization method to immobilize Al-Cd-Mn nanoparticles for photocatalytic dye removal in water using visible light [200]. The valuable trimetallic NPs could remove 96% and 98% of Brilliant blue and Brilliant green dyes respectively within 90 min and could be recycled via a simple centrifugation process and ready for re-use. Gargari and co-workers used silica/polyvinyl imidazole core-shell NPs to remove samarium and dysprosium ions from water [201]. The core-shell NPs were recovered via centrifugation at 14,000 rpm for 20 min. The core-shell NPs were then put in ethanol and washed three times to remove the chemicals on the surfaces of NPs. The NPs were then dried in an oven at 50 °C until a constant mass was achieved which denoted that all the liquid and impurities were removed.

An alternative, cost-effective, and highly efficient approach for the recovery and reutilization of nanomaterials after water treatment involves their immobilization on a solid structure like a polymer, ceramic, or metal. This method allows the water to pass through the material, enabling the nanomaterials to interact with specific substances present in the water, such as degrading dyes or removing heavy metals. Consequently, the water becomes clean without any nanomaterials leaching into it. Immobilization, which has been a groundbreaking technique in biotechnology, offers the ability to reuse enzymes and catalysts for multiple cycles, thereby reducing costs and power consumption associated with separating the substrate and enzyme. In another publication, Ti NPs immobilized onto borosilicate glass and other antibacterial agents against E.coli in water [202]. In a different publication Ti and Zn NPs were immobilized on solid targets for the degradation of methyl red dye in water [203]. Similarly, Alumihumus and co-workers used the sol-immobilization method to immobilize metallic NPs [204].

Some commonly used procedures of recovering nanomaterials after use involve traditional filtration and drying. In another publication, CuO NPs used as catalysts were recycled after use via an aging process that took 1 h, followed by filtering, washing several times with DI water and hence making it easier, faster and more efficient for the magnet to attract the NPs for separation. This method also enables the recycling to be more efficient (higher percentage of recycled NPs) owing to the agglomeration of NPs. This method was demonstrated by Leshuk and co-workers who used polymer floculates combined with magnets to separate NPs from water as shown in Fig. 10b [192]. First the magnetic NPs are intentionally added to water for treatment, UV light is applied to the water for photocatalysis. After the water treatment, the rest of the procedure is the recycling phase whereby a polymer floculant is added which causes the bundling of NPs. Finally, a magnetic field is applied at the bottom of the reaction vessel that causes the solid material to sink and stick to the bottom, enabling the collection of the treated water without the leaching of nanomaterials. In another report, Ag-Si-Fe antibacterial hybrid NPs could be recycled 12 times via the magnetic separation method [193]. These NPs can be utilized to eliminate waterborne pathogens, including antibiotic-resistant bacteria, and can be reused for multiple cycles. The number of reuse cycles can be further enhanced by reviving the performance of the NPs after retrieval through chemical methods (e.g., adding chemicals) or physical methods (e.g., Pulsed Laser Ablation in Liquid [194-198]). Although magnetic separation has a lot of advantages discussed here, they can only be applied to particles that possess magnetic properties. However, researchers can get around this by doping the key magnetic material with materials such as Fe as demonstrated by this research team [193] who coated Ag with Fe to induce magnetic properties. For instance, Pd is not considered a magnetic material but when combined with Fe, the resulting BNPs are magnetic [199].

The centrifugation process is a commonly employed physical technique for separating nanomaterials from water, widely utilized in research labs. This method utilizes high-speed spinning to segregate NPs from the liquid medium based on size, density, and sedimentation rate. It facilitates the isolation and purification of NPs by inducing them to sediment and form distinct layers or bands in a tube or rotor. Rajesh and colleagues developed trimetallic Al-Cd-Mn nanoparticles for photocatalytic dye removal in water using visible light [200]. The valuable trimetallic NPs could remove 96% and 98% of Brilliant blue and Brilliant green dyes respectively within 90 min and could be recycled via simple centrifugation process and ready for re-use. Gargari and co-workers used silica/polyvinyl imidazole core-shell NPs to remove samarium and dysprosium ions from water [201]. The core-shell NPs were recovered via centrifugation at 14,000 rpm for 20 min. The core-shell NPs were then put in ethanol and washed three times to remove the chemicals on the surfaces of NPs. The NPs were then dried in an oven at 50 °C until a constant mass was achieved which denoted that all the liquid and impurities were removed.

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Some commonly used procedures of recovering nanomaterials after use involve traditional filtration and drying. In another publication, CuO NPs used as catalysts were recycled after use via an aging process that took 1 h, followed by filtering, washing several times with DI water and
drying in vacuum at 80 °C [205].

4.2. Chemical methods of recycling/disposing nanomaterials

Cloud point extraction (CPE) is a liquid-liquid extraction process in which a surfactant is added to create micelles that, at a specified temperature, separate target analytes (NPs) from an aqueous solution, allowing for easy recovery. In a variety of applications, CPE provides simplicity, cost-effectiveness, and efficient concentration of hydrophobic or amphiphilic chemicals. Nazar et al. [206], used CPE using non-ionic surfactants Triton X-114/Triton X-100 to recycle Ag and Pd NPs. The CPE procedure is shown in Fig. 10c. The Au NPs migrated to the top liquid portion which was surfactant rich, enabling easy separation. UV-Visible analysis was used to study the nanomaterials before and after extraction as shown in Fig. 10d (insert shows the spectra CPE). A slight red shift of the Au plasmon peak from 527 nm before separation and 541 nm after CPE demonstrates a slight agglomeration of the NPs. The absence of new peaks or massive shifts in absorbance demonstrates chemical stability after separation. The 541 nm peak was absent for the bottom fluid which was surfactant-poor region, which demonstrated the absence of the Ag NPs in this region. Similarly, Chao et al. [207] used Triton X-114-based CPE to extract Ag NPs and its ions from antibacterial products found in water. In this report, inductively coupled plasma mass spectrometry was used instead of UV-Vis to quantify the concentration of NPs in the surfactant-rich phase. The extraction efficiency reached its maximum within 10 min and then stabilized, leading to the selection of 30 min as a conservative extraction time. The recovery rates of Ag NPs in antibacterial products ranged from 72% to 103% during the CPE procedure, whereas the extraction efficiencies of Ag⁺ ions ranged from 1% to 10%. TEM, SEM/EDX, and UV-Vis were used to identify possible coextracted Ag NPs. The same research group also published another paper in which Ag NPs were recycled from water via CPE and reported that the addition of 35 mM NaNO₃ or 10 mM Na₂S₂O₃ significantly improved the phase separation and the extraction efficiency of Ag NPs [208]. Moreover, another group used Triton-X114-based CPE to separate Ag and hybrid AgI NPs which were recovered after incubation at 40 °C for 10 min followed by centrifugation [209].

Crystal growth is also another viable chemical technique used to recovered nanomaterials. In another report, Sn NPs were recovered via by adding NaOH as a mineralizer to form an amorphous Sn compound which could be recycled by dissolving the formed solid in an acid [210]. In another report another chemical-based recovery technique was used to recover ZnO NPs [211]. Reagents including HCl and a phosphine oxide were mixed with the ZnO-containing substrate for 30 min followed by the recovery of ZnO NPs via an ethanolic precipitation step. One of the major disadvantages of chemical routes in comparison to physical routes of separation is the requirement of additional chemicals which themselves might be harmful and require separation from water. Physical techniques such as filtration, magnetic separation and coagulation does not require potentially harmful chemicals and tends to
involve a smaller number of processing steps, which is admired for large-scale applications. Physical techniques are also easier to automate and implement artificial intelligence based on sensor feedback enabling a more sustainable environment utilizing fewer human resources in such hazardous environments. Another research team could recycle Fe-based nanocomposites that were used to remove heavy metals and carcinogenic dyes from water by cleaning the nanocomposites with HCl and NaOH after water treatment [8]. The nanocomposites could be used again after cleaning for many cycles.

5. Recommendations and conclusion

Many reports discuss the risk of nanowaste and concerns to the environment [212–216] however, less publications discuss solutions. Encouraging researchers to transition their focus from problem discussion to the publication of practical solutions, as outlined in Section 4, is crucial for exploiting the widespread adoption and acceptance of nanomaterials in global water treatment. Given the extensive use of nanomaterials in various major industries, there is an urgent need for innovative, easily implementable, cost-effective, and energy-efficient nanomaterial recycling techniques. Moreover, public awareness of the presence of nanomaterials in everyday items such as paint, cosmetics, and sunscreens, as well as the impact of textile dyes in water, remains limited. Reviews like these play a vital role in raising awareness among researchers, policymakers, and startups, providing insights for potential products to address these issues. Consider, for example, washing machines equipped to degrade textile dyes before releasing wastewater, offering a substantial positive impact on global water quality. Ground-breaking inventions could include water bottles or dispensers with integrated UV light and immobilized nanomaterials for disinfection, heavy metal removal, and polymer elimination. Additionally, the development of machines capable of degrading dyes in industrial waste (paint, textiles, etc.) before disposal could significantly reduce the risk of untreated dyes reaching ecosystems and, ultimately, impacting human health.

This comprehensive review analysis has shown the crucial role of nanomaterials and dendraimers, in water treatment applications. An investigation into the use of nanomaterials in various applications such as dye removal, antibacterial effects, photocatalysis, heavy metal removal and nanowaste removal has demonstrated their significant potential to combat water pollution. The need for nanomaterials that can be recycled without leaching into the water has been emphasized, along with the use of nanoparticle immobilization, magnetic flocculation, and cloud point extraction as promising recycling techniques. The practicality of this research has been demonstrated with the use of industrial effluents in real-life scenarios for water treatment analysis. The use of Fe and C nanomaterials is prevalent in the literature of water treatment technologies, Environ. Sci. Technol. 49 (2015) 5277–5287, https://doi.org/10.1021/ES506351R/ASSET/IMAGES/MEDIUM/ES-2014-06351R_0006. GIF.

Researchers should also focus attention on the cost of fabrication of nanomaterials and if this cost is justifiable for real-world applications, especially those requiring large scale systems. For example, an average sized water treatment plant processes about 18–36 billion liters of water per year and academic and industrial researchers must examine and consider answers to the following questions:

1. What are the current methods of producing the required nanomaterials to meet the required concentration of NPs?
2. What mass of nanomaterials are required per year per power plant?
3. What are the best and most practical nanomaterial recycling methods?
4. How do we measure NP contamination from the water treatment process?
5. How do we deal with possibly inducing nanowaste into the water during NP treatment?
6. At what stage of the water treatment should nanomaterials be best incorporated?
7. Weather treated water follow zero discharge of hazardous chemicals (ZDHC) wastewater guidelines?
8. What is the typical cycle assessment (LCA) of nanomaterials in water treatment?

These are a few of the important questions that the literature and research community are yet to agree upon. There is a need to move forward from lab-scale proven pollutant removal methods, as evidenced in this review paper, to real-world application.

CRedit authorship contribution statement

Mayur Mahkesana: Formal analysis, Investigation, Writing – original draft. Anesu Nyabadza: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. Ajay Kumar: Validation, Visualization, Writing – review & editing. Anoush Plouze: Visualization, Writing – review & editing. Dermot Brabazon: Conceptualization, Formal analysis, Funding acquisition, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. Irving Ramirez: Formal analysis, Visualization, Writing – original draft. Mercedes Vazquez: Conceptualization, Funding acquisition, Writing – review & editing. Satheesh Krishnamurthy: Formal analysis, Validation, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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