Current Research in Green and Sustainable Chemistry 9 (2024) 100428

Contents lists available at ScienceDirect

Current Research in Green and Sustainable Chemistry

journal homepage: www.elsevier.com/journals/current-research-in-green-and-sustainable-chemistry/2666-0865

Advancements of nanotechnological strategies as conventional approach for heavy metal removal from industrial wastewater: Start-of-the-art review

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ARTICLE INFO

Keywords:
Wastewater
Nanotechnology
Nanoparticles
Adsorption
Heavy metals

ABSTRACT

Multi-faceted growth and progression of the healthy and economical society, depends upon access to clean and safe water. Rapidly over-growing population, increased in industrialization, urbanisation, and widespread practices in agricultural have all together been contributing to the production of more rapid wastewater discharge, which has not only polluted or contaminated the water but also have played a role in killing the aquatic life. One class of harmful water pollutants that is frequently found in the environment is heavy metals. Almost every transition metal has the ability to dissolve as ions in water. Heavy metals including Pb, Cd, Hg, As, Se and others can contaminate water supplies. Conventional methods for waste-water treatment have peculiar challenges including economic feasibility, energy consumption, environmental hazards, time spent, etc. To overcome these limitations, nanotechnology have been developed, which has its greater extent of application in water treatment area. Nanoparticles have a greater probability of removing heavy metals from wastewater treatment due to their effective surface characteristics and chemical activity. This review focuses on the numerous treatment procedures that have been developed recently and also been applied practically for eradication of heavy metals from waste-water of various industries.

1. Introduction

Research that has been concluded over the few decades, a variety of anthropogenetic and natural activities have impacted drinking water quality and caused ground water pollution. One of the main cause for hazardous waste-water pollution is the discharge of by various sectors industrial sectors like, oil and gas extraction, iron, food, pharmaceutical, paper and pulp, dye, steel industries etc. [1]. Metal ions which have atomic mass in between 63.5 and 200 and a specific of gravity (g) > 5.0 are considered as ions of heavy metal. Some of those heavy-metal contaminants which are present in water are Cr(III), Pb(II), Hg(II), Ni(II), Cr (VI), Cd(II), Co(II), Cu(II), Ag(I), As(III) and As(V) [2]. Due to the ability to reformulate metal particles into new nanosized from, this technology has experienced massive expansion in the development of the waste-water treatment sector. The term "dwarf" in Greek is the source of the word "Nano". As opposed to the other fields like chemistry, engineering and material science, nano-technology is the matter manipulation intentionally at the size scale of less than 100 nm in one dimension i.e., at the level of Atom and Molecules [3]. Nanotechnology used in waste water treatment. Inorganic [gold nanoparticles (AuNP), silica nanoparticles (Si-NP), quantum dots (QD), carbon nanotubes (CNT)], Organic [artificial macromolecules (dendrimers), micelles, liposomes, polymeric NPs, nano-gels, and layered biopolymer], and Polymer based nanoparticles [chitosan, albumin] are used generally for waste-water treatment as shown in Fig. 1. Industries producing metal ions that later cause water pollution are nuclear plants (Fe, Hg, Cd), Steel manufacturing (As, Hg, Cr, Cu, Pb, Zn, Cd), Textile (Pb, Ni, Zn, Cd, As) and Fertilizers (As, Cr, Zn, Pb, Cd) (see Table 1 [4–15] and Table 2 [16–20]).

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https://doi.org/10.1016/j.crgsc.2024.100428
Received 27 April 2024; Received in revised form 27 May 2024; Accepted 20 July 2024

1.1. *Heavy metals*

The environment and public health have always been threatened by metal-contaminated wastewater that comes from human activity in a variety of sectors, including industrial sectors such as automotive manufacturing, mining, textile industries, radioactive waste etc., and home sewage [22]. Environment is the main target of these heavy metals such asArsenic (As), Mercury (Hg), Chromium (Cr), Lead (Pb) and Iron (Fe), having most severe effectsthat includes instant distress of aquatic habitat, soil deprivation that eventually leads to less crops yield. When the heavy metals from contaminated water reach up the food chain, they cause consequences which are adverse to human, animals and other living being [23].

Even though trace elements are typically found in water bodies, heavy metals such as Cd, Zn, Pb, Fe, Cu, Hg, Ni, Mn, Co, etc. are thought to be the most harmful and toxic substances in wastewater effluent [24]. Because the human body is unable to metabolise certain heavy metals, they build up in bodily tissues and pose a health risk to people [25]. Over-all80 % of the global wastewater is released either treated or untreated to the environment. Growing cities' need for clean water is driving up energy generation and the demand for high-quality treated effluents in industrial expansion [26]. Heavy metals have shown adverse consequences to both the environment and health of living. Heavy metals can be a the source for variety of diseases leading to organ damage in humans, impaired voluntary muscle function, skin irritation, anaemia [27]. Copper may cause liver infections and anaemia [28]. Lead consumption contributes to infant brain damage, muscle impairment and kidney failure Mercury can be the source for nervous and circulatory disorders, arthritis [29]. Copper (Cu) can cause liver damage and hinder enzymatic activities in soil [30]. Chromium may lead to diarrhoea and nausea [31].

1.2. *Nanoparticles for heavy metal removal*

Polychlorinated biphenyls (PCB) [Capacitors, Plastics, Glue, and Transformers etc.], **Azo-dyes** [ponceau, amaranth, Tartrazine, etc.], **Pesticides** [Insecticides, Fungicide, Herbicide,] and **Organic pollutants** [Dioxins] [32]. Being most efficient because of versality of NPs including surface area and reactivity, nanotechnology is excellent treatment method. Nanomaterials being effective in the eradicating process of colorantheavy metal, inorganic and organic compounds present in waste-water. Silver nano particles, nano magnets, Graphene, and nanotubes are the potential nanostructures processed for waste water treatment. Nanomaterials and Nanotechnology are believed to be potent and promising for advanced treatment options [33].

Accomplishing of the detoxification and reclamation of environment, numerous techniques like membrane filtration, adsorption, ion exchange, precipitation, treatments by electrochemical process, biosorption, flotation, evaporation, and oxidation processes are used extensively [34], Nano-based materials such as photocatalysts, nano-adsorbents, nano-metals and nano-membranes are discussed in this evaluationstudywhich are well-known for the advanced breakthroughs in nanotechnologies which are used for the remediation of toxins and other water contaminants [35]. Process by the use of advanced nanotechnology engineering overlays the connection for the way of technical encroachments in advanced water and wastewater treatment technology.

Through the facilitation for recovering and remediation of water, nano-technology holds decent potential to improve water resources' quality, availability, and sustainability over time. This report highlights building potential of nanotechnology in waste-water remediation and discusses most of the latest developments in nanotechnology-mediated remediation systems [36].

2. Methods for heavy-metal removal from waste water

Techniques for removing wastewater are shown by the applications listed in the review that follows. These include magnetic separation, adsorption, photocatalysis, coagulation in wastewater purification, and various forms of nanoporous membranes. The current advancements in nanoscale materials and procedures for treating polluted industrial wastewater and groundwater are highlighted. These advancements focus on addressing issues related to hazardous compounds, metal ions, inorganic and organic solutes, as well as specific pathogenic viruses and bacteria [37]. Comprehensively studying these resource material for wastewater remediation, and their recovery is focussed on by studying advancements in nanofabrication, and smart nanomaterials [38].

2.1. *Nano-porous membranes*

Nano-porous resources exhibit the inclusive applications in the fields of electrocatalysis, energy, and environmental science, nanodevice fabrication, and also in analytical-science [39]. Recently studies on nano-porous membranes for application in waste-water purification [36]. One such example of nano membranes is PEI cross-linked membranes. In a single-salt filtering process, three positively charged nanofiltration membranes were created by PEI cross-linking on the upper layer of a P84 substrate. These membranes exhibit a high rejection rate

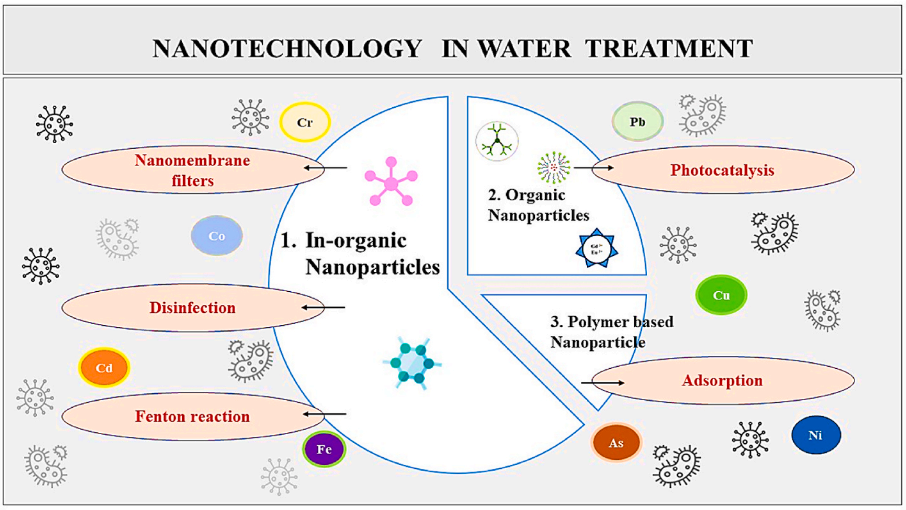

Fig. 1. Different nanoparticles are used for waste-water treatment by different approaches.

Table 1

Types of nanoparticles and their advantages [21].

Sr. no.	Nanoparticle	Diameter	Advantages	References
1	Carbon Black	10–500 nm	Electrical conductivity, High strength, Surface area, protection of plastics and elastomers against UV, Saline electric batteries.	[4]
2	Graphene	500 nm	Light absorption, Extreme strength, electrical conductivity.	[5]
3	Carbon Nanofiber	5–100 nm	Electrical, mechanical properties and frequency shielding.	[6]
4	Fullerenes	50–100 μm	Safe and inert, semiconductor, conductor and superconductor, intensity based light transmission.	[7]
5	Aluminium	2–50 nm	Large surface area, high reactivity, and sensitivity to heat, moisture, and sunshine.	[8]
6	Titanium dioxide (TiO_2)	5–50 nm	Properties of self-cleaning and ability to remove pollutants through the photocatalysis process.	[9]
7	Silver (Ag-NPs)	1–100 nm	Absorbs and scatters light, stable, anti-bacterial, disinfectant and anticancer therapy, as well as used as a vaccine adjuvant, anti-diabetic drug, and a biosensor, and to support bone and wound healing	[10]
8	Gold (Au-NPs)	5–500 nm	Interactive with visible light, reactive. Dark-field microscopy using resonance scattering to identify microbes and their byproducts.	[11]
9	Iron (Fe-NPs)	1-nm	Magnetic resonance imaging, tissue repair, immunoassay, biological fluid detoxification, heat, medication administration, and cell separation	[12]
10	Zinc (Zn-NPs)	40–60 nm, 80–100 nm	Antifungal, Anti-corrosive, UV filtering, Antibacterial.	[13]
11	Copper	40 nm, 60 nm, 80 nm	Very high thermal and electrical conductivity, Ductile, highly flammable solids.	[14]
12	Lead	20–40 nm	High toxicity, reactive, highly stable.	[15]

of four different kinds of heavy metal salts: $PbCl_2$, $Cu(NO_3)_2$, $ZnCl_2$, and $Ni(NO_3)_2$. Rejection percentage of the membrane for these heavy metals is to be found 99.0 %, 96.7 %, 92.0 % and 96.2 % separately [40]. The membrane pore size was personalized by altering the content of P84 (thermal stable at 100°cross-linked membrane) in the casting solutions [41]. Membrane-based separation has several advantages over traditional separation techniques, including being more energy-efficient, having a large separation range, using few or no chemicals, being modular, having gentle operating conditions, and being well-suited for integration with other processes [42]. The categories and strategies for fabrication of numerous nano-porous membranes, first are introduced, and later then the fabricated nano-porous membrane for water pollutants are activated to filter, for example organic chemicals, metallic ions, salt, anions, biological substrates and nanoparticles, that are demonstrated and specified [43]. Material which are utilized for membrane development for filtrationarecellulose-based composite, ion-exchange nanofiltration and carbon nanomaterial which carry out Ultrafiltration, microfiltration, nanofiltration, reverse and forward osmosis for heavy metal removal from wastewater [44]. Newly developed nano-porous materials for rapid, economic friendly, and high-performance purification of water [45]. Mathematic models that will be appropriate are to be established for obtaining the system concentration profiles and integrating the specific transport equations, characteristics for membrane formation, essential assumptions; Wang et al., has defined few methods for fabrication of nano-porous membranes which include; Interfacial polymerization, Phase inversion, Track-etching, and Electrospinning respectively. Generally used polymers for production of these membranes include polypropylene (PP), polyvinylidene fluoride (PVDF), polyether sulfone (PES), cellulose acetate (CA) and polysulfone (PSU). For the treatment; from polluted to fresh water, materials used possess small pore sizes and high reactivity towards impurities present in water. Microfiltration membranes generally have pore sizes between 0.5 μm and 10 μm and operate at comparatively low pressures. The pressure range is from 0.02 MPa to 0.5 MPa [46].The use of an ultra-filtration (UF) membrane with a pre-defined pore size of 0.5–1 μm has become more popular in wastewater treatment. This is owing to its ability to operate at low pressures, use relatively minimal amounts of energy, provide high-quality results, and be easily operated. Transmembrane pressure for ultra-filtration membrane is 1–10 bar [47]. Thin-film composite (TFC) structure for nanofiltration (NF) membranes are made of porous layer created by interfacial polymerization (IP) on a porous substrate, with pore sizes ranging from 0.01 to 0.001 μm [48].Experiments on reverse osmosis performed by Ref. [49] with a NaCl aqueous solution (2000 ppm) show that the performance of membrane Reverse osmosis is enhanced by the inclusion of SiO_2 nanoparticles; with the water permeability of $1.2 \times 10^{-12}\ m^3/m^2sPa$ and salt rejection was $\sim$98 %. Also, it was studied that these membranes showed excellent thermal stability; that is, heat treatment of 95 °C, at180min [49].The provided description of different processes of Nano-membrane filtration is shown in Fig. 2 [50].

Table 2

Technologies of wastewater treatment. Their advantages and disadvantages.

Types of treatment	Advantage	Disadvantage	Reference
1. Nano-porous membranes	Membrane properties could be adjusted. 2. Minimum occupied area. 3. High processing efficiency.	Membrane fouling	[16]
4. Magnetic separation	Less eco-toxicological impact. 5. Fast removal kinetics. 6. Spectrum of wide-ranging micro-pollutants are treated.	They need to be quantified again because they are not measurable.	[17]
7. Adsorption	Efficiency, low cost, no generation of hazardous by-products, eases of design and operation.	Toxicity of spent adsorbent.	[18]
8. Photocatalysis	High/greater degradation rate.	Potent to be harmful because of exposure to carcinogenic UV light.	[19]
9. Coagulation	Process is simple. Good for reclamation of removed pollutants.	Require high dosage. Produce massive sludge and large particles.	[20]

2.1.1. *Phase inversion*

Thermodynamic potential variances, mass and heat-transfer rates, and kinetics of phase formation (fluid dynamics) govern the composite

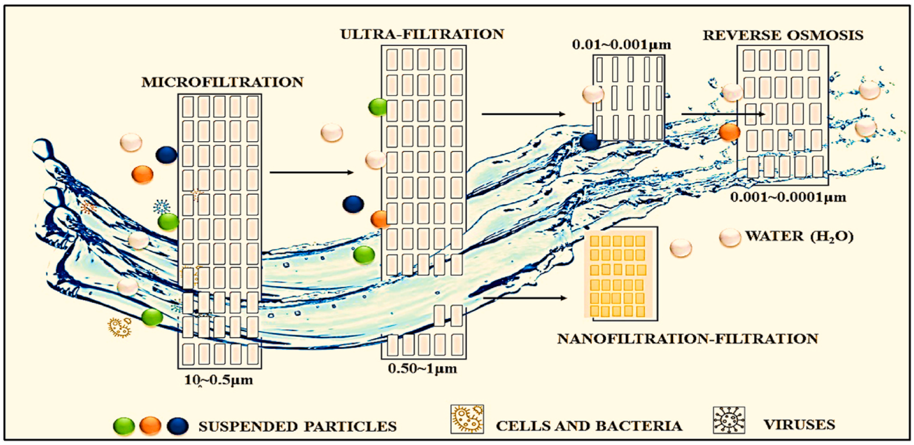

Fig. 2. Schematic illustration of different processes of Nano-membrane filtration for water purification.

multi-scale process of membrane development. Energy fluctuation and nonsolvent infiltration cause membrane development [51]. Phase domains as well as other organised structures that have representative scales length of 10–100 nm form and at the mesoscale through the time scales of 10–1000ns. At the industrial scale, the membrane typically has hole diameters between 10 and 1000 nm and a thickness of several micrometres (μm). The creation process might take several seconds or even hours [52]. The measuring molecular simulations, such as dissipative particle dynamics (DPD), Monte Carlo (MC) as well as molecular dynamics (MD), represent "bottom-up" in that the system behaviour emerges from a set of particle interaction potentials, in contrast to the model of macroscopic transport and the PF models, representing "top-down" approaches. Because of this, while having far large or even mesoscale spatiotemporal scales, molecular dynamics (MD) simulations dynamic/static properties of membrane systems, Dissipative particle dynamics (DPD) and MC are categorised as molecular-scale simulations [53]. In most cases, Microporous membranes are made by a variation of processes for liquid phase inversion. One of such process requires casting of thin film of homogeneous solution of a polymer is taken in a solvent and immersed in a nonsolvent bath, where it undergoes phase separation of homogenous mixture into a polymer-lean phase and polymer-rich phase [54]. Polymer solutions in phase separation processes are induced through variation in composition such as predominant external conditions. Phases of liquid-solid and liquid-liquid separation are possible in this system-dependent process. When it comes to polymer solutions, there is a difference between particle and molecular solutions; the liquid-liquid phase may separate in response to changes in both the upper and lower solution temperatures [55]. Polyethylene, isotactic poly(4-methyl 1-pentene) (PMP), a semi-crystalline polyolefin with desirable chemical resistance, heat stability, gas permeability, and biosecurity, and syndiotactic polystyrene solutions are among the important fluid-solid transformations that occur at high pressures for high density. The phenomenon of liquid-liquid phase separation has been seen in the dioctyl phthalate (DOP), diphenyl ether (DPE), or DBP system [56], resulting in the formation of a bi-continuous structural membrane. Hybrid membranes which are made by these materials achieved copper (Cu), cadmium (Cd), and chromium (Cr) removal in the range of 10 %–50 % at different water flux.

2.1.2. *Interfacial polymerization*

A chemical process contained at the liquid–air or liquid-liquid interface, considerably aids in the controlled development of the films, fibres and capsules, for use as separation membranes and electrode materials. Current advancements in polymer chemistry and technology have revitalised interfacial polymerization [57]. TFC (thin film composite) Interfacial polymerization (IP), a technique that makes it simple to synthesise an ultrathin selective layer, is used to create membranes. To enable diamine penetration into the support, microporous poly-sulfone membranes are firstly submerged in an aqueous diamine solution, *m*-phenylenediamine (MPD) [58]. The permeated support for infusion comes into contact with trimesoyl chloride (TMC), an organic segment of acyl chloride, after the removal of excess diamine over the surface. A substrate is alternatively dipped into the two of the monomer solutions in the molecular layer-by-layer process (bottom panel). Following each dipping step, the substrate is washed with the appropriate solvents (example: water and hexane). The use of PIP-based NF membrane is typically deemed inappropriate for the removal of divalent cations. For instance, when using Mg^{2+} (MgCl$_2$) as an example, the majority of the documented membranes had a rejection rate of just 70–80 %. The NF270, a well-recognized product, has a Ca^{2+} rejection rate ranging from 40 % to 60 %. After multiple cycles of this type of dip-coating procedure, a thin, flawless film with multiple polyamide layers is produced. According to Cheng et al., in 2021; Rejection percentage for Cu^{2+} wasfound 93.9 %, Mn^{2+}97.9 %, and for Cd^{2+} it was observed to be of 87.7 % [59]. According to Tian et al., rejection against Ni^{2+}and Zn^{2+}was tobe found over 98 % [60].

2.1.3. *Track-etching*

Escalating the MD for purification of water from surfactants, oil, and surfactant-stabilized emulsions was made possible by developments in membrane alteration/modification for omni phobic or Janus surfaces production (membrane interface is normally lyophilic on one side and lyophobic on the other side) [61]. Membrane dimensions and morphology including pore size should be considered and systematically characterised. TeMs have a limited pore size distribution, have a tortuosity of 1, regular pore geometry, a narrow thickness, and the capacity to manage them per unit area. Therefore, considering for an advanced nanofiber technology for membrane distillation (MD), these membranes could be employed as models for the development and validation of Liquid entry pressure (LEP), fouling, high temperature, and theoretical mass. Air gap membrane distillation (AGMD) [62], Sweeping gas membrane distillation (SGMD) [63], Direct contact membrane distillation(DCMD) [64] and Vacuum membrane distillation (VMD) [65] are the four recognized and extensively researched membrane distillation variants. Track-etching of the polyimide (PI) membranes were studied for the enhancement of the fabrication method of nanopore formation process and also in regards of the control over the pore diameter growth. The etching solution is prepared and pretreatment of the Polyimide membrane was performed by soaking in the prepared organic solvent which may include; ACN (acetonitrile), THF (tetrahydrofuran), DMF (dimethylformamide), DMSO (dimethyl sulfoxide), EtOH (ethanol), MeOH(methanol) [66].

2.1.4. Electrospinning

Having the low-cost compensations, easy operation of equipment's and because of its high-efficiency, the process of electrospinning is very much convenient. The electro-spun nanofibers generated are very significant nanomaterials, possessing many notable benefits such as a substantial specific surface area, adjustable pore structure and high porosity, good permeability, and alterable functionalized surface [67]. Furthermore, nanofibers have the capability to be arranged in layers to create textiles and can be produced by the process of electrospinning. Electrospun nanofibrous membranes (ENFMs) possess the characteristics of nanofibers, but their membranous structure allows for convenient handling and recycling (A [68]). As a result, ENFMs have been researched extensively in variety of sectors, as well as electronic information, biological medicine and new energy. ENFMs have garnered a lot of interest in recent decades in the field of environment pollution control and restoration [69]. Because of limited pore size, highly porous structure, and distribution, specific surface area, compatibility with inorganic, easy alterations, good flexibility, and easy separation for recycling, which are consider as excellent adsorbents nanofibers are becoming more and more important. Electrospinning process can create nanostructures with special qualities like high surface area and porosity, for creating polymeric nanofibers it has been presented as one of the most effective method [70]. Nanofibers have been created using solvent thermal synthesis, phase separation, self-assembly, and template technique. The benefits of electrospinning are minimal cost, basic equipment, ease of use, and great efficiency. Three types of electro spun nanofibrous membranes (ENFMs), including hybrid polymer (organic/inorganic), material composite ENFMs organic polymer ENFMs, and inorganic ENFMs are main ENFMs. Nanofibrous membranes have been created by electrospinning organic polymers and inorganic materials. These membranes are used as adsorbents to remove heavy metal ions from wastewater. Certain natural polymers include abundant functional groups that exhibit a strong attraction to metals. These polymers may be readily transformed into membranes via the process of electrospinning. These membranes are capable of effectively removing heavy metals from water by adsorption [71]. According to Salehi et al., adsorption capacities of Cu^{2+}, Pb^{2+}, and Ag^{+} ions filtered from waste water have been increased by this method of removal from 27.8 mg/g, 49.5 mg/g, and 78.0 mg/g, to 39.7 mg/g, 98.1 mg/g, and 102.4 mg/g after phosphorylation and amination of crosslinked PAN nanofibers. The interwoven fibrous architectures of electrospun nanofibers have successfully overcome the recovery difficulties associated with nanomaterials [72]. In the study investigated by Esfahani et al., in 2021; removal of selected heavy metals by electrospunpolyacrylic acid (PAA), polyallylamine hydrochloride (PAH) and modified laminated ultrafiltration (UF) membranes (PAA/PAH-UF).In synthetic metal solutions, the PAA/PAH-UF membrane exhibited 38–85 % higher removal efficiency after being compared to original membrane. Lesser amount removal of Pb^{2+} compared to Cd^{2+} and Cu^{2+} was observed due to the larger ionic radius of Pb^{2+} resulting in less availability of $–COO^{-}$ for Pb^{2+} [73].

2.2. Magnetic separation

The remarkable properties and wide range uses of magnetic nanoparticles including the treatment of wastewater have expanded the vision for advanced research in nanoparticle research. The discharge of heavy metals and other pollutants in water sources/resources is problematic owing to the ongoing negative/harmful impacts on the ecosystem [74]. Further, in the applications for waste-water treatment, amino-functionalized (aminated) magnetic nanoparticles, which are designed by fixing magnetic nanoparticles with amino-functional groups and perform better than initial magnetic nanoparticles [75]. Because of the susceptibility to be separated magnetically and again processed without changing their structure or effectiveness, respectively and also the fact that their magnetic qualities are obligatory for the efficient, environmentally friendly and responsible removal of impurities from the waste-water [76]. The key focal areas that need to be assessed and considered are the synthesis of nanoparticles and the future prospects for amino-functionalized magnetic nanoparticles. Magnetic nanoparticles with amino functionalization for the purpose of water purification. Integrating magnetic nanoparticles with amino functional groups by grafting producing magnetic nanoparticles that have been functionalized with amino groups [77] as shown in Fig. 3 [78]. Notable approaches have been examined for the elimination of metals, organic pollutants, and pathogens from polluted water. Furthermore provided taken-in-point consideration are; impact of variables such as ion selectivity, pH, contact time, dosage of magnetic nanoparticles, and recyclability [77]. Despite the relatively small surface area of approx. 59 m2 g^{-1}, Fe3O4 nanoparticles, dissolved completely in water and efficiently eliminated metal ions of Pb(II) almost 90%within time duration of few minutes only through the strong electrostatic attraction between the heavy metal ions in wastewater and negatively charged magnetite surface of magnetic ion nanoparticle of iron [79]. In order to enhance the distance between particles, magnetite nanoparticles were coated with Polymer organo disulfide (PTMT) to create porous core-shell magnetic microspheres. The PTMT shell, with its uneven and rough surface, offered many thiol groups that served as the main binding sites for heavy metals [80]. With the surface area, upgraded magnetic microspheres reached the high adsorption capacities of 603 mg/g for Hg(II), 533 mg/g for Pb(II), and 216 mg/g for Cd(II). This modified design gave the Fe_3O_4 nanoparticles, capacity to attach with and remove Ag(I) by coating them with Ag + -imprinted thiourea-chitosan. The ion imprinted magnetic polymers scavenged 90 % Ag(I) from the wastewater with the initial silver content up to 2157mg/L^{-1}. Amine groups from the thiourea fractions providing strong metal binding sites by coordination. Because the amine groups produced in an acidic rich environment suppress up taking of Ag(I)via electrostatic repulsion, while the hydroxide precipitation of Ag(I) in the commonly used media could inhibit the formation of metal/resin composite, these adsorbents are able to complete the Ag (I) adsorption capacity of 532mg/g^{-1} [81].

2.3. Adsorption

Fundamentally, nanoparticles (NPs) are equivalent variations of their bulk counterparts. NPs usually are more or less 100 nm in at least one of the dimensions. Owing in their areas, large specific surface area with fewer surface imperfections, because of which they have very unique physical, chemical, magnetic, biological, optical, and electrical, characteristics [82]. All of these properties makes them exceptional adsorbents and lot more effective in case of huge range of pollutants [83]. In order to be more qualified in the category of NPs, the particle has to lie within the size range of 1–100 nm. The size is considered of extremely importance for a particle to be considered as NPs as it defines the adsorption capability and versatility. The numerous pollutants which are found in water today, categorised into three categories generally, viz., Inorganic and Organic pollutants [84] as shown in Fig. 4 [85].

The mechanism of adsorption follows following four steps, i.e. A) The contaminating molecules/solute transferred by the solution to the adsorbent's border layer. B) Diffusion happens from the adsorbent's peripheral surface to its boundary layer. C) Diffusion happens from the adsorbent's external surface to its boundary/peripheral layer. D) The sorbate's adsorption into the solid phase [86]. The adsorption process is ultimately determined by the adsorbent selection. A good adsorbent will have a high adsorption capacity, a fast adsorption rate, and be easy to separate or recover [87]. Most adsorbents used to remove heavy-metal contaminants from water are granular or nano-powdery materials, such as activated carbon, natural zeolites, biomaterial, graphene, and nano-metal particles. Granular adsorption materials can be easily produced, segregated, functionalized, and regenerate; however, their adsorption capabilities and rates are generally modest [87]. Hydrotalcites also known as Layered Double Hydroxides (LDHs) with general

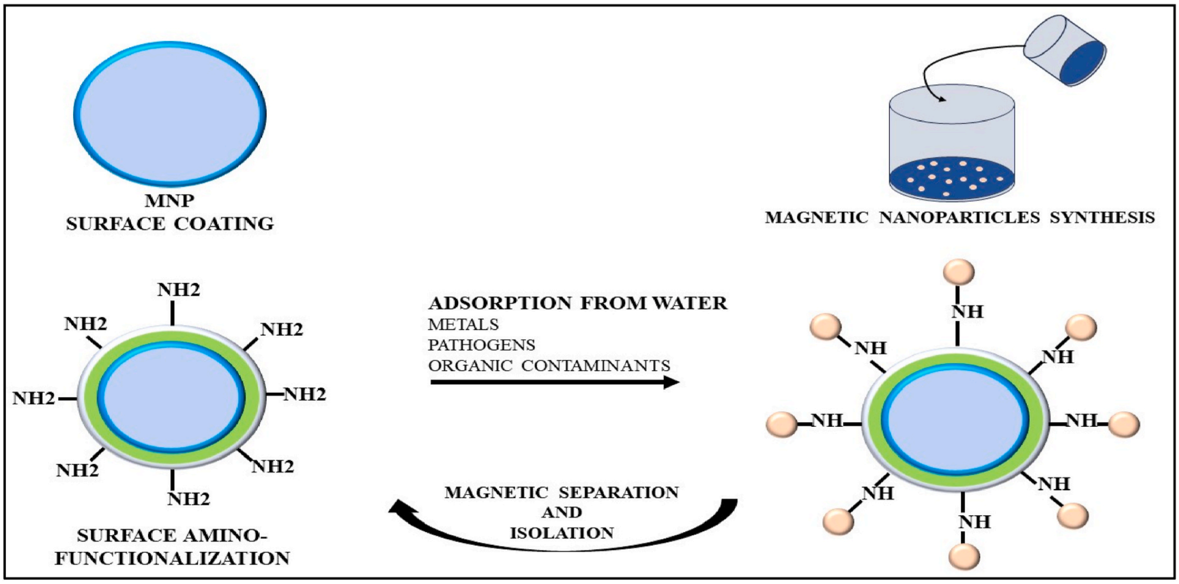

Fig. 3. The use of magnetic nanoparticles as nano-adsorbent for micro-pollutant removal.

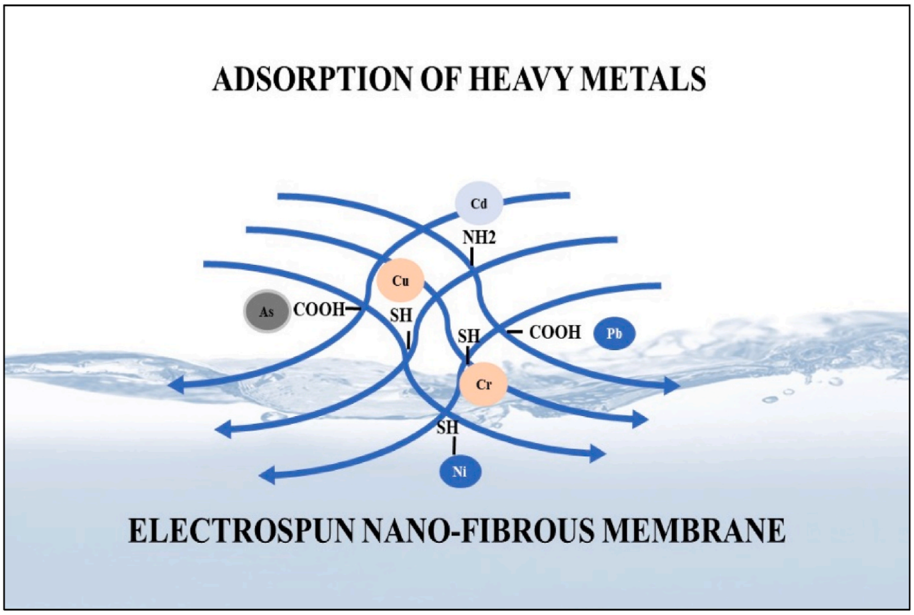

Fig. 4. High solids concentrations in water, high temperatures, and the majority of neutral solute particles result in the maximum rate of adsorption. Prefiguration by adsorption was introduced in this way.

formula $[M^{2+}_{1\text{-}x}M^{3+}_{x}(OH)2]^{x\ +}\ [A_{x/n}]^{n-}.mH_2O$. Along with high surface area/small size, these possesses significant catalytic properties including atomic level distribution in the nanosheet of metal ions uniformly, acid-base bifunctionality, compositional diversity, and can be used as a catalyst for various important reactions occurring in the environment e. g. the greenhouse gas emission control. CO_2being feared greenhouse gas can reduce by the use of mixed-oxide catalyst based of LDHs [88]. At the present time, there is lack of reviews on the characteristics of adsorption, interaction in mechanism, and application of LDHs-based nanomaterials in the removal of heavy metals.

2.4. Photocatalysis

The study of the synthesis, modification, and mechanism of a material that, when a catalyst participates in a chemical reaction, can boost-up or enhance the pace of the reaction along while maintaining its original structure is recognized as catalysis [89]. The process presents a high-water treatment/recovery rate, no/very less residues are produced, might be considered economical, and require modest pressure and temperature conditions [90]. Because of the necessity for a catalyst, a lesser amount of activation energy than a typical normal reaction is required; the reaction will proceed more rapidly than a reaction without a catalyst. Activation energy (Ea) is the minimum amount of energy required for a reaction to take place, as described by Ref. [91]. The catalyst creates a different, lower-activation-energy pathway than the typical reaction pathway, which speeds up the rate of reaction [89]. Nevertheless, the results and the overall involved thermodynamics are the same [92]. Types of Photocatalyst; Metal-Doped Photocatalyst, Supported Material Photocatalyst, and Coupling Heterojunction Photocatalyst [93]. The majority of studies have focused on TiO_2, the most common kind of photocatalyst. Nevertheless, its broad energy gap only reacts to UV light. Currently, there is a significant amount of ongoing research on the use of photocatalysis for treating organic wastes, splitting water to produce hydrogen and oxygen, and fixing nitrogen. Photocatalysis, being independent of any energy input other than light, generates active species with excellent redox capabilities and does not result in any extra pollution. Using it for redox in water treatment is quite practical. Out of all the heavy metal ions, the treatment of Cr(VI) ions has been extensively researched. Several studies have been conducted on the photocatalytic reduction of Cr(VI) employing catalysts based on CdS, ZnO, TiO_2, and ZnS.

In the semiconductor, the electron excitation (e−) in valence band eventually moves to the conduction band, leaving gaps (h+) in the valence band behind. Separation of these electrons and gaps is produced by photogeneration [94]. In order to directly reduce limited heavy metal ions, photo-generated electrons are used frequently as a reductant and the heterogeneous photocatalyst in the framework of photocatalytic activity of TiO_2, was shown in Fig. 5 [95]. Extensively used photocatalysts include transitioned Metal-oxides (MO) and Semi-conductors. Due to this, because of the void/gap energy area they have, which prevents any form of energy levels from being available for encouragement of recombination of gap and electron produced by photoactivation in the solid [96].

The void regions, which ranges from top of the occupied VB (valence band) to bottommost of the VC band (vacant conduction) is termed as the Band gap [97]. In 2005, Tuprakay et al. achieved the effective photoreduction of Cr(VI). For 32 h, photocatalysis was carried out using immobilized TiO_2 at 171 W/m^2 ofUV light intensity [98]. Another example of such process was done by Li et al., in 2022, where they took As(III) solutions of 1000 μg/L (7.8 pH) which was placed in container and irradiation under UV-light was done for the time duration of 6 h. Arsenic (As) removal effectiveness was found to be 80–86 %. They further elaborated the research by showing that without any loss of efficiency the process can be repeated thrice [99]. After 65–70 min of irradiation using TiO_2, Chen et al. found that heavy metal ions including Pb(II), Ag(I), Hg(II), Fe(III), and Cr(VI) may be reduced by a photocatalytic process. The experiment showed removal effectiveness of 27.2 %, 99.7 %, 70 %, 100 % and 79.1 % respectively. A stimulating class of particular inorganic fillers for waste-water treatment is the one that has abilities to photodegrade impurities. Photocatalysis is an eminent and great choice for an efficient and long-lasting oxidation process when it comes to waste-water treatment because of its simple, rapid, energy-efficient, and environmentally beneficial procedure [100]. Graphitic carbon nitride (g-C3N4), TiO_2, gels-modified TiO_2 or Graphene coated membranes are just such examples of materials employed in the photo-degradation of contaminants and toxins, including under visible-light irradiation [101]. Photocatalytic removal of heavy metals has shown positive results in many researches in consideration for treating wastewater. Currently, the use of photocatalytic technology for the elimination of different heavy metal components has been widely researched, but it has not yet been implemented on a commercial scale.

2.5. *Coagulation*

A novel coagulation theory created by Langelier and Ludwig and also identified two different methods for the elimination of colloidal impurities (a) The double layer compression mechanism enables the particles to agglomerate and precipitate by overcoming the repulsive forces [102]; and (b) Precipitate enmeshment is the process because of which metal physically precipitates entangle tiny particles as they are form and settle [102]. The treated samples are characterized for the colour, TSS (Total suspended solids), and turbidity, whereby the percentage (%) removal is calculated. Lae-Mar and Healey, suggested the words "coagulation" and "Flocculation" based on [103], have successfully, theoretically developed and substantiated these two mechanisms. The treated sample was assessed for colour, TSS, and turbidity. The following formula is used to determine the % removal. Using coagulation, filtration, and disinfection in an integrated or multiple barrier water treatment process design, microbiological particles can be managed. Coagulation is necessary to guarantee that particles adhere to the filter medium and, as a result, the microbiological particulates may be efficiently eliminated, allowing for the achievement of the desired results for water treatment [103]. For TiO2 NPs destabilization; three different coagulants: iron sulphate (FeSO4), iron chloride (FeCl3), and alum [Al2 (SO4)3] in source waters [104,105]. Water contamination was increased with arsenic (As) residues. As(V) elimination with the use of polyacrylamide co-coagulant and ferric chloride coagulant by using different process as shown in Fig. 6 [106].

The removal efficiency percent for As(V) will be calculated by formulation given, *i.e.*, Percent removal efficiency (%) $(Cn)=(Ci)-(CfCi)\times 100$.

Where; *Ci* initial values of each contaminant, Cf is final values of each contaminant, and C_n is the response parameter according to Ref. [104].

Trimercaptotriazine sodium salt 15 % (TMT-15)reacts with heavy metals and formvirtually insoluble heavy metal-TMT solid compound which is extremely stable and is easy to separate, was used by Zheng et al., in their research. It was considered efficient for Cu^{2+} removal and

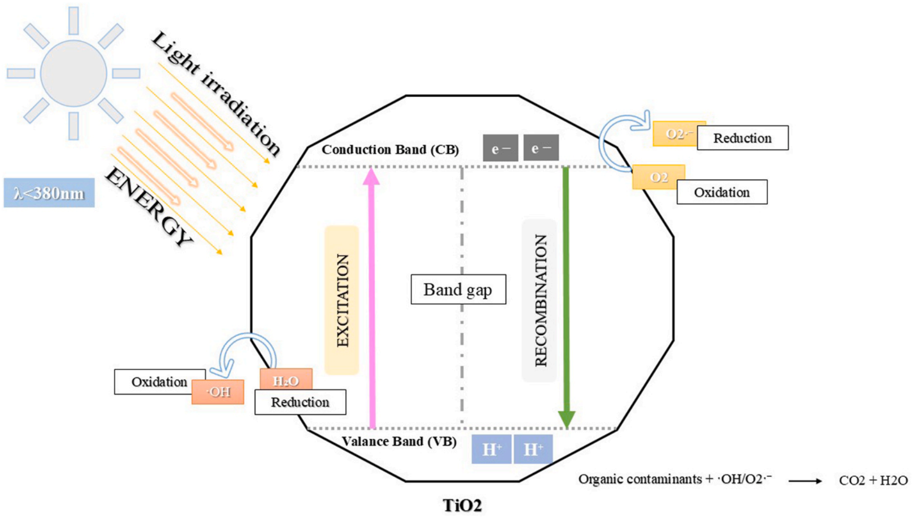

Fig. 5. Heterogeneous photocatalyst in the framework of photocatalytic activity.

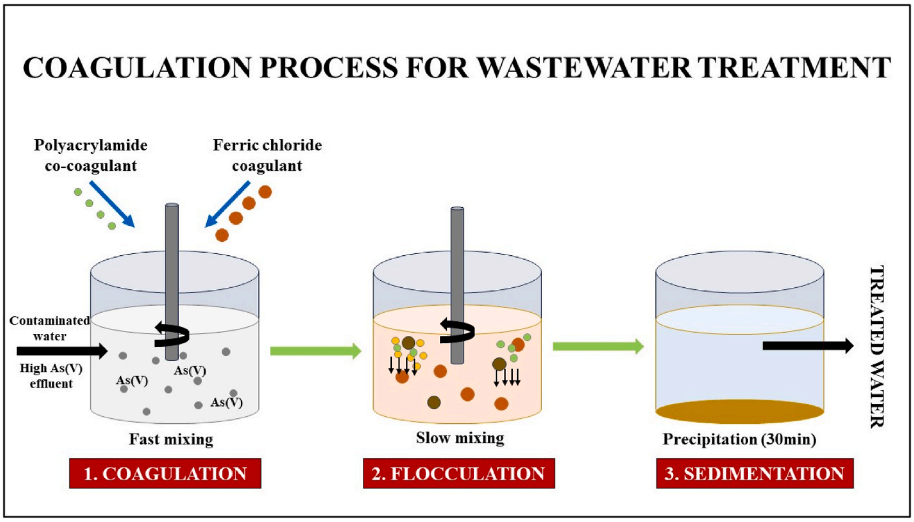

Fig. 6. As(V) elimination with the use of polyacrylamide co-coagulant and ferric chloride coagulant by using the coagulation-flocculation and sedimentation process.

showed the highest efficiency removal of 98 % at concentration of 30 mL/L, followed by Ni^{2+} removal efficiency with much lower efficiency of appx 53 % [107]. The three-stage treatment procedure, when operated under ideal circumstances, was able to extract 99.72 % Cu and 99.7 % Ni from metal-EDTA electroplating effluent [108]. Maximum decrease for Lead (88 %), Cadmium (96 %), Arsenic (23 %), Manganese (96 %) Iron (90 %), and Zinc (48 %) was observedusing*moringa* leaf powder as the coagulant [109]. Highly porous nanoparticles of Fe2O3 were used in water treatment by Mahmoudabadi et al., and maximum COD elimination for alcohol vinasse was found at a quantity of 3000 ppm. Fe^{2+} and hydroperoxyl radicals ($HO^{2}\cdot$) in the solution can be produced when the Fe^{3+}reacts with H_2O_2. The generated hydroxyl radical target the organic substrate RH. Resulting in a decrease in the efficiency of COD removal since H_2O_2 is consumed. Indeed, the occurrence of radical scavenging reactions with the excess iron indicates the existence of an appropriate dose of α-Fe2O3 nanoparticles [110].

3. Conclusion

Significant aspects that lead to the increase in contamination of waste-water sources are commercialization, industrialization, growth in population. It is extremely important to be ensured of hygienic and clean water to the community. Ensuring the safe and clean, there are more accessible and practiced treatments throughout the whole world. Many of the researchers found that the nanotechnology is an efficient and successful way to enhance wastewater treatment. Nanoparticles that are widely used for treatment are titanium dioxide nanoparticle, silver nanoparticle, iron nanoparticle, gold nanoparticle, carbonaceous nanoparticle etc. Different types of processing methods used for water treatment are explained in this review, such as Membrane filtration (Nano-porous membrane), Magnetic separation, Adsorption, Photocatalysis and Coagulation. Nanoparticle based treatment ensure cost-effective, ecofriendly, time and energy saving approaches when compared to the traditional and conventional methods of waste water treatment.

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

Data will be made available on request.

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