Letters in Applied NanoBioScience
Open-Access Journal (ISSN: 2284-6808)

Review
Volume 12, Issue 4, 2023, 125
https://doi.org/10.33263/LIANBS124.125

Nano Adsorbents in Wastewater Treatment: A New Paradigm in Wastewater Management

Pratibha Pandey [1], Fahad Khan [1,*], Shristi Agarwal [1], Manisha Singh [1]

[1] Noida Institute of Engineering and Technology, 19, Knowledge Park-II, Institutional Area, Greater Noida, 201306, India; shukla.pratibha1985@gmail.com(P.P.); fahadintegralian@gmail.com (F.K.); shristidps@gmail.com (S.A.); manisha292singh@gmail.com (M.S.);
* Correspondence: fahadintegralian@gmail.com (F.K.);
Scopus Author ID 57201049984

Received: 4.03.2022; Accepted: 15.04.2022; Published: 18.09.2022

Abstract: Increasing water pollution has urged the need to elucidate more potent techniques for removing contaminants from wastewater 1 and groundwater. Numerous techniques or processes have been explored and designed for water purification. Amongst all other water/wastewater remediation techniques, nanotechnology has gained wider attention in water remediation via numerous mechanisms, such as the adsorption of heavy metals and the removal of pathogens. Nanoadsorbent materials have emerged as a promising solution for solving this crucial environmental issue. Their unique chemical and physical properties, such as higher ranking, quality, and status, promote their application compared to traditional adsorbents. Recent research studies have reported their promising potential in water treatment, including polymeric, carbon, tubezeolites, and metal nanosorbents. Hence, this review mainly aims to provide summarized data presenting all the beneficial aspects of nanosorbents in wastewater/water remediation.

Keywords: nanotechnology; nanoadsorbents; remediation; wastewater; water.

1. Introduction

Water is one of the major constituents of life and a plentiful major resource on Earth; the very first life form originated in the sea. About 3/4th part of the Earth is water, of which approximately 70% of fresh water is being utilized in agriculture, displaying the central role of water in the world economy. A continued supply of clean and fresh water is of utmost importance for human civilization [1]. Water pollution has become a universal problem. Wastewater comprises different pollutants, including heavy metals, nitrates, fluorides, dyes, ammonia, and many other emerging pollutants, which are ultimately toxic to living beings. Accumulating pesticides in the aquatic environment and sedimentation of these pesticides in the soil pose health risks to humans [2]. Non-biodegradable organic dyes impart ecological toxicity and have been a major threat to humankind. One of the best ways to resolve the issue of water scarcity is to reuse wastewater after treatment [3].

Nanotechnology is a boon to mitigate the problems raised due to water pollution. It allows the development of nanomaterials like nanoadsorbents, nano clay, nanocomposites, catalysts, reagents, and many more, which are the most efficient tools discovered till now. Wastewater remediation can be taken to its highest efficiency using these high tech-materials. Nanomaterials are very useful for removing any emerging pollutants like pharmaceuticals, trace elements, and particulate matter in the range of 0.1-651mg/g in wastewater [4]. The clay nanocomposites have shown great efficiency in removing ammonia, nitrate, and bacteria from the wastewater. The adsorption of pharmaceutical compounds using nano adsorbents has gained much popularity owing to their low-cost, high surface area, and effectiveness. ZnO-NPs (zinc oxide nanoparticles) are synthesized with the coating of CTAB surfactant and BMTF (ionic liquid molecules) and are effectively used in the removal of EBT (Eriochrome Black T) from aqueous media [5]. The applications of adsorptive membranes such as polymeric membranes (PMs), polymer-ceramic membranes (PCMs), electro-spinning nanofiber membranes (ENMs), and nano-enhanced membranes (NEMs), have gained momentum in high selectivity and adsorption capacity for heavy metal ions. Adsorptive membranes (AMs) have also demonstrated high effectiveness in heavy metal removal from wastewater owing to their exclusive structural properties [6].

2. Water and its Contaminants

The origin of life is believed to have been associated with the aqueous solutions of oceans. Living organisms have been dependent on various forms of aqueous solutions for their essential biological processes, including blood and digestive juices. Water is also the major constituent of Earth's hydrosphere and is essential for all existing forms of life, even though it provides no calories or organic nutrients [7]. Water can be contaminated in different ways, usually due to human activities known as wastewater. It is produced by household/domestic, industrial activities, etc. Major causes for groundwater contamination include animal feces intrusion or wastewater due to heavy rain, whereas surface water contamination comprises wastewater discharge into natural water sources with increased turbidity and color change [8]. Wastewater consists of 99.9% water, and the remaining 0.1% contains organic matter, microorganisms, and inorganic compounds to be removed. Wastewater also includes storm runoff, as harmful substances wash off roads, parking lots, and rooftops which hold contaminants like oil, fuels, insecticides, herbicides, and residual sediments. Domestic wastewater comprises grease, scum detergents, vegetable materials, and sediments. Industrial wastewater comprises toxic chemicals, organic wastes, metals, increased sediment, radioactive elements, acidic/basic, and high-temperature waste [9]. Figure 1 summarizes all possible water and wastewater contaminants that must be treated before they are released into another body of water so that it does not cause further pollution of water resources.

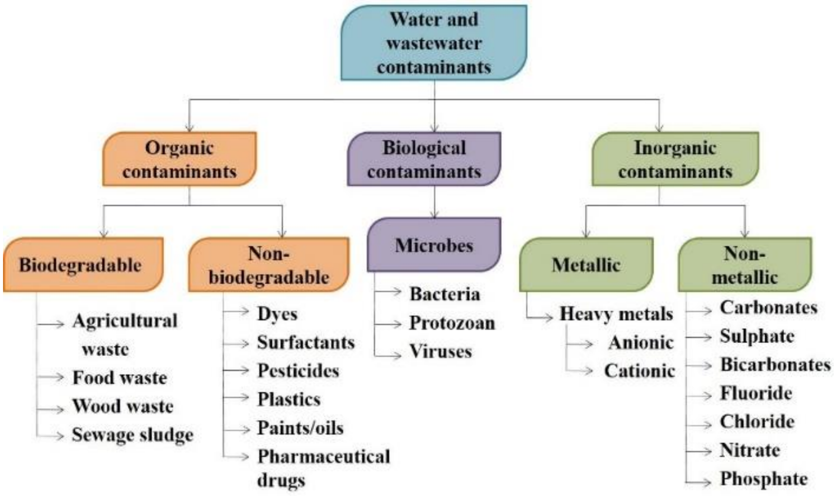

Figure 1. List of water/wastewater contaminants, including biological, organic, and inorganic contaminants.

Based on the radix and nature of wastewater and water contaminants, they have been categorized into inorganic, biological, and organic pollutants. Heavy metals are recognized as the most hazardous contaminants amongst all other water contaminants due to their toxicity and stubborn nature in organisms and lead to food chain increase also, and they are non-degradable like arsenic (As), lead (Pb), nickel (Ni), chromium (Cr), zinc (Zn), etc. They cause damage to the cardiovascular and gastrointestinal tract and CNS, the endocrine glands, kidneys, liver, lungs, and bones. Heavy metal refers to any metallic chemical element with a relatively high density of 5g cm^{-3} and atomic mass (higher than 23) or atomic number (more than 20). These metals are required at the lower concentration for maintaining various physiological and biological activities in living organisms but become toxic at higher levels. The efficient removal of heavy metals is the demand of sustainable development as they may become carcinogenic [10]. Hence, numerous strategies, including bioaccumulation, rhizofilteration, biosorption, biotransformation, volatilization, and bioextraction are employed to remove heavy metals by the biological species.

Recent research has also reported the presence of SARS-CoV-2 (severe acute respiratory syndrome coronavirus 2) in wastewater and water. Face masks and stools of COVID-19 patients were reported as the primary route of coronavirus transmission into water and wastewater. The majority of coronavirus (SARS-CoV-2) often gets rapidly inactivated in water, i.e., human coronavirus 229E survival in water for 7 days at 23 °C and was dependent on water properties, temperature, property of water, organic matter, suspended solids, pH, and disinfectant doses [11]. Other contaminants include endocrine disrupting chemicals such as personal care products, pharmaceuticals, heavy metals and organic pollutants, resulting in environmental pollution. Chronic exposure to endocrine disrupting chemicals can pose numerous adverse effects on the environment and human health, including issues related to thyroid, reproductive system, cancer and Alzheimer and obesity [12].

3. TechniquesUsed in Wastewater and Water Remediation

Several studies have reported numerous chemical and physical wastewater and water purification methods, including chemical precipitation, coagulation/flocculation, ultrafiltration, ion exchange, electrolysis, reverse osmosis, and adsorption. The usage frequency of techniques to be employed depends on various factors, including the amount of sorbent molecules and supportive materials and cost [13]. Further sections comprise the techniques used in the remediation process (Table 1).

Table 1. Table summarizing various water/wastewater remediation techniques with their advantages and limitations.

Techniques used in water/wastewater remediation	**Method**	**Advantages**	**Disadvantages**
Chemical Precipitation	Metal ions are precipitated by adding coagulants which are organic polymers like lime, alum, etc.	Cost-effective Can Remove most metals Easy to operate	Sludge formation Additional cost for sludge disposal
Ion Exchange	The exchange of metal ions with the ions held by electrostatic forces takes place in this process.	Faster removal Highly effective Materials are regenerated	Quite expensive Some ions are not completely removed
Reverse Osmosis	The dissolved solids cause the separation of metal ions at a pressure greater than the internal osmotic pressure	Environment friendly Good quality water	Removal of minerals Time-consuming High cost

Techniques used in water/wastewater remediation	Method	Advantages	Disadvantages
Electrodialysis	The cells of concentrated and dilute salts are formed by the separation of cations and anions through an electrical potential between two electrodes.	High recovery rate Limited pretreatment is required	Membrane fouling occurs High operational cost Energy consumption
Coagulation/ flocculation	Colloidal material is joined into small aggregates called "flocs" by adding a coagulant to the water.	High efficiency Require limited investment	High operational cost Not effective against COD Formation of sludge
Ultrafiltration	Fluid is passed through a semipermeable membrane while the suspended solids retain on the other side of the membrane	Removes a wide range of pollutants Can be regenerated The highest quality water is produced	Ineffective against inorganic pollutants
Adsorption	A Gas or liquid solute is accumulated on the adsorbent surface, forming a molecular or atomic film.	Removes most pollutants High efficiency, cost-effective Easy operation	Requires regeneration difficult to remove adsorbents from treated water

3.1. Chemical precipitation technique used in the water remediation process.

Chemical precipitation is the chemical method of water purification and is one of the most widely used techniques used in water treatment. This technique has been utilized in heavy metal impurities removal from industrial wastewater globally due to its easy process and low cost. Recently, it is also a suitable method for important heavy metals like Ni and Cu [14]. Chemical precipitation involves a chemical reaction between precipitating agents like hydroxides, carbonates, sulfides, and dissolved metal ions in wastewater to form insoluble particles. The chemical precipitation process is followed by physical processes of wastewater treatments such as filtration, coagulation, or sedimentation [15]. The elimination of heavy metals by chemical precipitation techniques includes numerous basic steps as firstly, chemicals such as magnesium hydroxides and soda ash are added to wastewater, followed by physical treatments. In this step, heavy metal ions precipitate as carbonates and hydroxides. Then the precipitated heavy metals get eliminated via several other methods such as gravity separation, magnetic separation, dissolved air flotation, or vortex separation, depending on the water sample and scale of precipitated heavy metals [16]. After that, remaining heavy metals left after previous steps are again precipitated by the addition of some other chemicals such as inorganic or organic sulfides and salt for effective precipitation of even very low concentrations of heavy metals.

3.2. Ion exchange technique used in the water remediation process.

Ion exchange is an ancient technique that was used earlier for the softening of water being used for large-scale industries. Now the ion-exchange technique is an integral part of new industrial and technical processes used for water treatments. Ion-exchange materials of wide varieties are available in the market, including organic and synthesized exchangers [17]. It can be defined as a reversible chemical reaction process in which an ion (from an aqueous solution) gets replaced by a similarly charged ion attached with an exchange site on insoluble and immobile solid materials such as chemically synthesized resins, zeolites, or clay. The most common matrix used for ion exchange is synthetic organic resins, inorganic three-dimensional matrix, and new-generation hybrid materials [18]. Ion exchange resins, especially cation exchange resins procedures, have been reported to be highly effective and efficient for eliminating a large number of heavy metal cations from water and wastewater. However, the elimination of some heavy metals like Pb is a little challenging due to its competitivity against resin's active ion-exchange sites occurring naturally in cation exchange resin, such as aluminosilicate colloids [19]. Hence, the ion exchange method is not completely suitable for eliminating all types of heavy metals present in water and wastewater.

3.3. Reverse osmosis technique used in the water remediation process.

The reverse osmosis technique of water and wastewater remediation is basically a membrane-based filtration method utilized in large industries to eliminate dissolved heavy metal ions and salts in water feedstock [20]. In the reverse osmosis (RO) technique diffusion-controlled process occurs in which the mass transfer of permeates occurs through a dense membrane under a controlled solution diffusion mechanism [21]. The mass transfer due to solvent mobility maintains the solute concentration on both sides of the membrane and leads to the development of a pressure gradient (or osmotic gradient). External pressure is used to reverse the flow of perspicuous solvent and, therefore, is recognized as a reverse osmosis process. It is an extremely efficient method for eliminating all types of dissolved ions and organic impurities from water and wastewater. A remarkable benefit of this technique includes the cost-effective recovery of metals in retentate (concentrated solution of by-product) [22]. The versatility of this technique relies on the reduced concentration of ionic pollutants and organic compounds in water and wastewater, which further makes it stand out from other traditional techniques for heavy metal removal at both large and small-scale water purification [23]. However, the membranes used in reverse osmosis are expensive both to operate and procure; also, the high-pressure demand of this method leads to its high cost of operation and high sensitivity to operating conditions.

3.4. Electrolysis and Flocculation/Coagulation techniques used in the water remediation process.

The electrolysis technique is an electrochemical reaction-dependent technique in which a direct electric current is passed through an ionic material that has been dissolved in a suitable solvent. This further results in a chemical reaction at the electrode, leading to the separation of heavy metal ions from wastewater and water. In this process (electrolytic metal deposition), the metal ions are reduced electrochemically, producing high-purity metals. This process is not only limited to metal separation from wastewater but also the large-scale production of metals, including zinc or copper. A wide range of electrodes can be employed, including graphite, metallic, and semiconductor materials. The appropriate selection of electrodes helps balance the chemical reactivity between the electrolyte and electrode production cost [24].

Coagulation and flocculation are well-known processes used in wastewater or water remediation due to their better turbidity removal efficiency [25]. It is a two-phase process that removes stable colloids in water via forming larger aggregates, followed by a sedimentation process. The first phase is the coagulation process, where coagulant addition in water reduces the repulsive forces between the colloids [26]. The flocculation process is the second phase, which involves bonding destabilized particles leading to floc formation through Van der Waals's force of attraction. Other factors on which the efficiency of the coagulation-flocculation process depends include mixing speed, dosage and type of coagulant, pH and temperature of wastewater, floc settling time, and pollutant concentration in wastewater [27].

Recently, the development of a wider range of nano-flocculants has been reported to be highly efficient in treating water polluted with dyes, heavy metals, and microorganisms (such as bacteria) as they possess a large surface area to volume ratio, which further enhances their adsorption potential and chemical activity towards target contaminants as compared to non-nanomaterial [28]. The toxicity and health hazard possessed by inorganic coagulants is one of the major issues related to the coagulation-flocculation process. In addition, the coagulation-flocculation process involving natural coagulants is not effective in removing chemical oxygen demand (COD) due to their organic properties.

3.5. Ultrafiltration and adsorption techniques used in the water remediation process.

This is a filtration process that can separate dissolved tiny suspended particles and macromolecules (having size in the colloidal range) from a fluid or liquid feed by using a selectively permeable membrane with a range of pore size (between 1 and 100 nm) [29]. It can be defined as pressure-driven membrane transport process where the molecules with higher molecular weights (macrosolutes) are concentrated on one side of the membrane, whereas small-sized molecules (such as microsolutes or solvents) move freely through the selected membrane. An ultrafiltration membrane technique is also used to retain larger solutes using lower operating pressure of up to 10 bars compared to the RO (reverse osmosis) membrane process [30]. It removes turbidity, colloidal particles, DOM (dissolved organic matter), toxic substances, and microorganisms from pure drinking water. The usage of various nanoparticles such as CNTs (carbon nanotubes), clays, graphene, zeolites, carbon molecular sieve, or metallic oxide has remarkably enhanced the performance of the ultrafiltration technique [31]. However, the applications of membrane technologies can be affected by several types of fouling, such as inorganic fouling, colloidal and particulate fouling, biofouling, and organic fouling. Another important issue is oily wastewater, which can harm sea life and cause a major environmental catastrophe. Recently, research proved that ultrafiltration with enhanced morphology and mechanical strength is the most effective technology for oily wastewater treatment [32].

Another method used for the treatment of water and wastewater is adsorption. It is a surface phenomenon commonly used in the removal of inorganic and organic contaminants that is mainly dependent on the interaction between a porous solid adsorbent and an adsorbable solute formed by the physical bonds (van der Waals) or chemical bonds (covalent bond) [33]. The solute molecules get concentrated on the surface of the adsorbent by the attractive forces between them. In this process, a large specific surface area is preferable for providing large adsorption capacity. Adsorption is preferred over other wastewater treatment technologies because of its cost-effectiveness, better efficacy, versatility, simple operation, and ability to remove all types of contaminants [34]. Activated charcoal is commonly used for removing pollutants from wastewater and adsorbing contaminants from drinking water sources, such as groundwater, rivers, lakes, and reservoirs; however, it is quite expensive [35]. Recently, research was done on adsorbents based on nanoparticles i.e., nanoadsorbents, and it was found that they have considerably higher adsorption rate due to their large surface area and are eco-friendly, reusable, high adsorbing, cost-effective, and even removed dye from the solution. Their higher ranking, status, and quality enhanced their application in different fields compared to other adsorbents [36]. Also, the adsorption of contaminants using nanomaterials proved one of the best approaches for advanced sewage treatment procedures. Altogether, all the summarized techniques are highly effective in water purification and pollutant elimination with a limitation of usage of expensive equipment and time-consuming. Also, they require chemical inputs, some of which are hazardous and toxic. However, associated negative consequences with these techniques have resulted in several studies to elucidate more efficient, cost-effective, and eco-friendly techniques for wastewater remediation. Adsorption can be further classified into two categories depending on the concentration and nature of force between adsorbent and adsorbate molecules. Positive adsorption can be defined as adsorption in which adsorbate concentration is more on the surface of the adsorbent than its concentration in the bulk phase via van der force of attraction. Hence, it is also known as Vander Waal's adsorption, and these forces are easiest to be separated [37]. It can be easily reversed by heating or decreasing the pressure. In negative adsorption, adsorbate concentration is less than its concentration in bulk. Chemisorption (or chemical Adsorption) involves chemical bond formation between adsorbent and adsorbate. This type of adsorption is also called Langmuir adsorption. It is much stronger than physisorption and cannot be easily reversed. It may further be categorized as activated adsorption (needs catalytically active adsorbent) or exchange adsorption (charge attraction between adsorbent and adsorbate) [38].

4. Nanoadsorbents Used in the Wastewater/water Remediation Process

The main interaction force controlling adsorption is the affinity between the adsorbent and the adsorbate. The process of adsorption increases with the increase in adsorbent surface area. The adsorbent is an important factor in determining the adsorption method's versatility, efficiency, and economics [39]. Although commercial activated carbons, zeolites, commercial activated alumina, silica gels, ion-exchange resins, and other adsorbents are highly successful in removing heavy metal ions and other types of pollutants, they do have some limitations. Some of them are quite expensive, some require pretreatment and another problem is their disposal and regeneration. In recent years, adsorbents such as magnetic adsorbents, Saudi natural clay, and nanoadsorbents have been used to eliminate contaminants as they have overcome these limitations [40].

Nanomaterials are materials with nanoscale dimensions (ranging from 1-100 nm) exhibit the potential to be used in removing a variety of toxic metals, especially heavy metals. Nanoparticles are preferred over other adsorbents due to their multiple sorption sites, high specific surface area, low-temperature modification, porosity, surface functionalities, short intraparticle diffusion distance, and ion binding capabilities [41]. Along with these, other physicochemical properties, such as shape, size, chemical composition, crystal structure, physicochemical stability, surface energy, surface area, and surface roughness, also affect the properties and efficiency of nanosorbent materials. It was found that nanomaterials can be made more reactive on decreasing size, thereby increasing the surface area relative to volume. Also, surface charge greatly influences the toxicity of nanoparticles as it regulates numerous aspects of nanomaterials, including colloidal behavior, selective adsorption of nanoparticles, blood-brain barrier integrity, plasma protein binding, and transmembrane permeability. Crystalline structure and composition also play a vital role in the toxicity of nanoparticles, along with surface coating and surface roughness [42].

Based on these physicochemical properties, numerous types of nanomaterials have been synthesized in recent times. Some of them are carbon nanotubes, metal nanoparticles, nanowires, polymeric nanoparticles, and many more. Some factors, including intrinsic compositions, innate surface properties, external nanosorbent materials functionalization, and sizes, may also affect these physicochemical properties. Properties and behavior of nanosorbent materials, including large surface area, high absorptive capacity, high chemical activity, and high surface binding energy, were explained by the distribution and nature of active sites on the surface of these materials [43]. Recently, surface modification of these materials was carried out to enhance their properties like adsorption capacity, efficiency, and stability to eliminate a wide variety of heavy metal pollutants. They successfully improved the performance of nano adsorbents by modifying their surface using various methods.

4.1. Synthesis of nanosorbents materials.

Either the bottom-up approach or the top-down approach generally synthesizes nanosorbent materials. The type of approach employed depends on the advantages it has over the other; the top-down approach is a conventional process in which the size of bulk material is reduced to the nanoscale through erosion of particle size by mechanical alloying, micromechanical, electrochemical, sonochemical exfoliation, acidic dilution(oxidation), high energy ball milling and reactive milling, while in bottom-up approach the nonabsorbent materials are synthesized by atomic layer deposition atom on the atom, the molecule on a molecule by arch discharge method, unzipping of carbon nanotubes, reduction of graphene oxide, sol-gel method, chemical and physical vapor deposition [44]. The bottom-up approach to nanosorbent material synthesis is the most modern approach, but it has two major drawbacks: one is that chemical purification is required during the nanofabrication process, and the other is that large-scale production is not cost-effective or feasible. Nonetheless, it is the most popular method used in this age. Similarly, the top-down approach also has its limitations, such as damage to the surface and crystallographic structures during particle size reduction. However, the top-down approach still plays a significant role in the synthesis of nanoparticles [45]. Apart from chemical and physical methods, the nanoparticles can be synthesized by the green approach, including biological methods using plant extracts, microorganisms (such as actinomycetes, bacteria, fungi, and algae), enzymes, biomolecules, and bioreduction [46].

4.2. Classification of nanosorbent materials and their applications.

A wider range of nanomaterials are synthesized and applied in various fields and treatments in modern times, such as nanowires, nanotubes, nanobots, nanoparticles, quantum dots, etc. nanomaterials are being used in water, and wastewater treatment for effective removal of heavy metals and other harmful pollutants due to their unique properties major of which is high absorption [47]. In recent years, CNMs (carbon nanomaterials) such as carbon nanotubes, graphene, and derivatives, fullerenes, carbon nanofibers, nanodiamonds, nanoporous carbon, graphitic carbon nitride have been extensively utilized as adsorbents because of their easy modification, high chemical stability, extraordinary surface properties, large specific surface area, controlled structural varieties, ease of regeneration, porosity and low density. A recent study shows that when modified, several nano adsorbent materials showed improved adequacy and adsorption capacity for eradicating pollutants from water and wastewater such as silica-shell coating onto Fe_3O_4 particles [48]. A study shows that iron oxide magnetic nanomaterials have displayed significant efficacy in wastewater treatment at a larger scale and have therefore emerged as one of the most promising materials for heavy metal treatment from water and wastewater. Numerous experiments have also shown significant pollutant removal efficiency of iron oxide nanomaterials in water and wastewater. For example, Fe_3O_4 hollow nanospheres were shown to be highly effective sorbents for red dye [49]. The nanosorbent material should be non-toxic or at least toxic and should be highly sensitive to eradicate very low concentrations of contaminant. It should also have a very high sorption capacity. The nanosorbent material should possess a surface that can be very easily reactivated whenever needed. Various modification techniques for nanomaterials make them useful for water and wastewater treatment [50]. The further section has summarized several generally used and recently discovered nanomaterials in wastewater treatments, such as CNTs (carbon-based nanoadsorbents or carbon nanotubes), metal-based nanoadsorbents, polymeric nanoadsorbants, and zeolites (Figure 2).

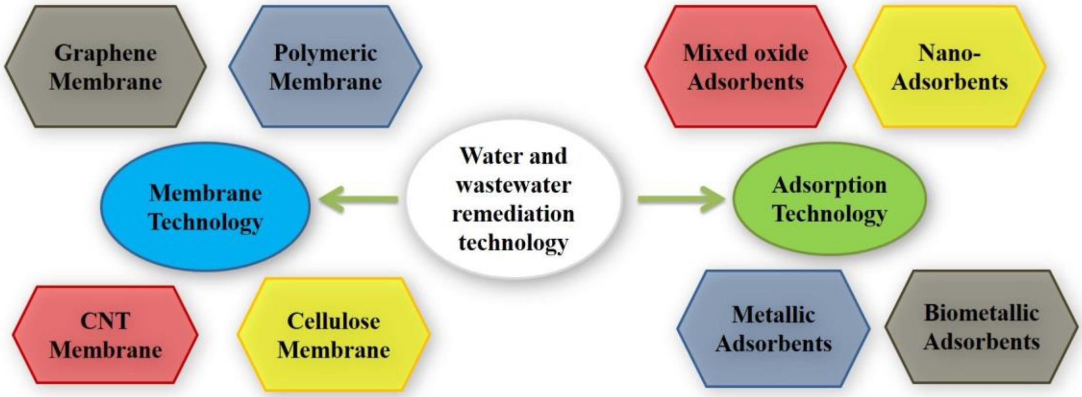

Figure 2. List of water/wastewater remediation technologies.

4.2.1.CNTs (carbon-based nanoadsorbents or carbon nanotubes).

Carbon nanotubes can be considered cylindrical nanostructures of carbon, and on the basis of their synthesis, they can be further classified under two broad categories, including single-walled CNTs and multi-walled CNTs. CNTs can be compared with rolled graphene sheets and can be synthesized with laser ablation method, arc discharge method, pyrolysis method, CVD method, etc. CNTs have hydrophobic properties, which can cause particle accumulation in an aqueous solution, stabilizing it to obviate the reduction in surface activities [51]. Besides this, carbon nanotubes have high adsorption sites, high surface area, and tunable surface chemistry. CNTs are unique since they possess various distinctive potentials such as permeability, adsorption capability, morphology, and physicochemical properties. In CNTs the EDA (electron donor-acceptor) interactions have been reported to be a major adsorption mechanism. The surface affinity of CNTs can also be modulated to a wider range of contaminants in wastewater/water remediation and surface fictionalization. The adsorption capacity can be highly increased by fictionalizing CNTs with hydroxyl, carboxyl, and carbonyl groups which are generally added by oxidation of CNTs using acids such as HNO_3, H_2SO_4, HCl, H_2O_2, $KMnO_4$, and NaOCl. CNTs also possess antimicrobial properties and cause oxidative stress in bacteria, leading to cell wall removal [52]. Carbon nanotubes functionalized with silver nanoparticles displayed a tremendous ability to inactivate microorganisms. CNTs have numerous advantages over traditional adsorbents like activated carbon; however, their usage in large-scale wastewater treatment is a very costlier process.

4.2.2. Metal and non-metal based nanoadsorbents.

Metal and non-metal nano oxides (more active adsorbents) can be considered n efficient replacement for activated carbon used in eradicating heavy material and radioactive elements.

Furthermore, nanometal oxides with high surface area comprise a small intraparticle diffusion distance, which can be easily compressed without any change in surface area. In recent years, membrane technology has utilized a wider range of metal nanoparticles in wastewater treatment [53]. This subsection briefly describes some potential metal and non-metal oxide nanoparticles with their applications in water/wastewater remediation, including nano-silver and nano-titanium dioxide, zero valent nano-iron, and magnetic nanoparticles [54] (Table 2).

Table 2. Nanoadsorbents used in water/wastewater treatment processes.

Nanoadsorbents	Alternative approach	Advantages	Disadvantages	Applications
Nano-TiO_2 and nano-silver	Activation through modification of TiO_2 by visible light	Long-lasting, high chemical stability Nano-silver: less toxic, bactericidal	Demand ultraviolet activation Nano-silver: limited durability	Removal of organic pollutants Antibiofouling surfaces, water decontamination
Nano-zero valent iron	Stabilized by entrapment in polymeric matrices	High reactivity	Requires stabilization	Groundwater purification
Magnetic nanoparticles	Improving osmosis	Easy restoration by a magnetic field	Requires stabilization	Groundwater purification

Silver nanoparticles (AgNPs) and their various nanocomposite materials have been largely used as catalysts and disinfectants for water and wastewater treatment for a long time [55]. A recent study showed the potential efficacy of adsorbent of silver and titanium oxides-doped activated carbon in removing total phenols from pharmaceutical effluents, and a green approach was used to synthesize this adsorbent using Shea butter leaves extracts. Further, the adsorbent was bio-synthesized via reducing Ti $(NO_3).4H_2O$ and $AgNO_3$ into their oxides and their subsequent doping on activated carbon [56]. Moreover, metal nanoparticles having antimicrobial activity are used to counteract biofouling due to their bactericidal properties which silver is one of the most commonly preferred bactericides in fouling reduction. Membranes infused with silver nanoparticles have been reported to be highly effective against two bacterial strains viz. *P. mendocina* KR1 and *E. coli* K12 are generally present in wastewater [57]. Additionally, silver nanocomposites have also displayed significant potential in removing viral contamination from wastewater. Recent studies have projected the significant potential of $Al2O_3$ and ZrO_2 PES (polyethersulfone) in wastewater filtration. TiO_2 nanoparticles have been extensively utilized as photocatalysts due to their high stability, photocatalytic activity, and low cost. It is also extensively being utilized as an antifogging agent due to its non-toxic nature and photo-induced super-hydrophobicity, thereby performing a key role in environmental decontamination [58]. Another type of nanopowder called titanate nanoflowers also displayed significant potential in heavy metal ions removal, such as Cd^{2+}, Zn^{2+}, Ni^{2+}, etc., and are efficiently removed by titanate nanoflowers due to their specific and large surface area [59].

4.2.3.ZnO and magnetic nanoparticles.

Studies have shown the potential of ZnO nanoparticles in removing total coliforms from the municipal wastewater treatment plant. Aggregating ZnO nanoparticles in the cytoplasm and cell membrane of bacteria inhibited bacterial growth. Basically, ZnO nanoparticles easily penetrate the cytoplasm and cell membrane of bacteria, and H_2O_2 secretion increases with increasing penetration time, thereby increasing toxic effects on bacteria [60]. Magnetic nanoparticles (MNPs) are widely employed for wastewater treatment processes, such as flocculation, emulsification, adsorption, filtration, and photocatalytic activities, due to their magnetic properties, which make treatment easy and unique. The major advantage of preferring magnetic nanoparticles is that these nanoparticles directly interact with contaminants and also, and the loaded particles can be removed effectively using magnetic field [61]. In a study, magnetite (Fe_3O_4) has also been used to eradicate groundwater contaminants viz. arsenic. Iron oxide magnetic nanoparticles are prepared as an amino-functionalized magnetite nanoparticle using the solvothermal reaction method and thereafter grafted on HPG (hyperbranched polyglycerol). Obtained MNP-HPG is separated using a magnetic field and is characterized before being used in adsorption experiments. Research findings clearly show that HPG-MNPs displayed strong re-disperse properties and magnetic response, which strongly validated their potential as an efficient adsorbent for removing heavy metals using a simple separation procedure [62]. Synthesized nanoparticles get easily collected by utilizing an external magnetic field from wastewater in a very short span of time and can further be easily reused after regeneration. Figure 2 explains various surface functionalization methods, and table 2 shows their characters and potential uses along with the synthesis method.

4.2.4.Zeolites and other nanosorbents.

Zeolites are microporous, aluminosilicate minerals made of silicon, aluminum, and oxygen, which contain cavities and channels, also referred to as molecular sieves, where cations, water and/or small molecules may reside. The common structure of zeolites is formed by tetrahedrally linking the silica and aluminum atoms with each other through shared oxygen atoms. Zeolites can be natural or synthetic materials. Natural zeolites have shown exceptional ion exchange and sorption properties. Hence, they are more effective in removing metal cations from wastewaters as compared to other commonly used cation exchange materials, such as organic resins. Numerous studies have also confirmed the efficiency of high-silica zeolites in removing organic micro-pollutants (OMPs) from water [63]. Normal-sized zeolite is on a macro scale. Still, zeolites on the nanoscale with sizes ranging from 10-500 nm have shown extraordinary performance in water/wastewater treatments due to their high surface area, cost-effective production, stability in water, and, most importantly, their compatibility with the natural environment [64]. Some studies also suggested that Z-NZVI (zeolite-supported nanoscale zero-valent iron) synthesized from a simplified liquid phase reduction of iron salts exhibited greater potential for treating impaired soil and water as it adsorbs As (III), Pb (II), and Cd (II). Zeolites contain electrostatic pores where nanoparticles such as silver ions can be incorporated and then exchanged with other cations. On studying the different materials containing nano-silver, including zeolites, it was found that silver shows antimicrobial properties as it inhibits the growth of microbes.

Moreover, ceramic water filters containing silver were also developed by potters for water purification [65]. The presence of pathogenic bacteria in groundwater was a major concern for those who depend on it. So, a cation resin-silver nanoparticle filter was developed to disinfect groundwater. It is a cost-effective filter and was successful in removing the targeted bacteria. However, Tiwari et al. stated that nano-zeolites, which he prepared by laser-induced fragmentation on a microscale, can be used in sequencing batch reactors for both wastewater and water treatment [66]. The only problem with zeolites was the reduction of the active surface due to the immobilization of nano-silver particles. In addition, other nanoadsorbents like nanometals and zeolites are cost-effective and show compatibility with the ongoing water remediation techniques as they can be implemented in beads and pellets as fixed adsorbents. Whereas nanometals and CNTs are produced for numerous applications, polymeric adsorbents have recently gained wider attention. They have shown extraordinary performance by eliminating both organic and inorganic compounds in just one step. They have also been used for removing dyes from wastewater. The main disadvantage of using these nanoadsorbents is their high production cost and the technical demand for improving the polymeric dendrimers. In terms of ecotoxicity, nanoadsorbent materials like nonometals, CNTs, and zeolites are classified as non-toxic on the basis of their origin and composition. However, the potential toxicity, chemical stabilizers, and surface modifications can be affected by the size and shape of these nanoadsorbents. An experiment was conducted in which nanoparticles from the treated water were inserted in rats, and the results showed vital organ damage and DNA damage in these experimental animals. Furthermore, with the new advancements in known nanomaterials, the ecotoxicity has to be re-evaluated, so a general assessment could not be given regarding their potential toxicity [67].

The nanoadsorbents other than those discussed above have shown high efficiency in removing toxic dyes from impaired water. Presently, a versatile bi-functionalized iron oxide nanoadsorbent has been synthesized for the extraction of toxic dyes present in wastewater. It was successful in removing them as they combined iron oxide nanoparticles with carboxymethyl-β-cyclodextrin polymer. Different techniques such as Fourier transform infrared spectroscopy, X-ray diffraction, SEM (scanning electron microscopy), TEM (transmission electron microscopy) were used to characterize the structure of these nanoadsorbents. The catalytic activity of this nanoadsorbent was monitored by UV-Vis spectroscopy in an aqueous environment [68]. Apart from these, nano-hydroxyapatite and nano-clay minerals have great potential to eliminate organic and inorganic pollutants. The advantages associated with these materials are their low cost, high surface area, and high stability; hence it is considered an ideal nanosorbent. It can act as both hydrophilic and hydrophobic material, which helps it to interact with organic and inorganic contaminants. Its efficiency can be improved by using humic acid, which gets adsorbed on the surface of the hydroxyapatite. Nano-hydroxyapatite-humic acid complex has shown better results as compared to nano-hydroxyapatite in heavy metal removal from wastewater. The excessive use of harmful drugs is a major concern as they are difficult to remove from water and pose a serious threat to aquatic life [69]. In order to resolve this situation, sustainable green nanoadsorbents were engineered, which were successful in removing these pharmaceutical contaminants. Also, the discharge of industrial waste and other human activities can devastate the entire biosphere. To prevent this, researchers synthesized iron-oxide-based nanosorbent, which have the potential to remove organic and inorganic pollutants as well as biological contaminants [70]. Similarly, magnesium and zinc oxide nanosorbents were found to be effective in treating industrial wastewater. The nanoadsorbents gained attention as they are cost-effective, environment friendly, and exhibit great potential in water remediation as compared to traditional adsorbents. Their larger surface area leads to high adsorption capacity and maximum removal of contaminants in less time [71]. The presence of another heavy metal, lead, in water can cause long-term damage to humans, including kidney damage and increased risk of high blood pressure. Researchers fabricated silicon dioxide/titanium dioxide (SiO_2/TiO_2) nanofibrous membranes capable of removing lead from wastewater [72]. Another nanoadsorbent, silver/iron oxide nanocomposites, was synthesized to efficiently remove radioiodine released in water due to nuclear power plant disasters. Sadak et al. prepared another nanoadsorbent, namely ferric oxide (Fe_3O_4) magnetic nanoparticles conjugated with polyacrylic acid, which was highly efficient in removing toxic heavy metals at a certain pH [73]. Likewise, calcium oxide/ferric oxide (CaO/Fe_2O_3) nanocomposites were used to remove chromium from wastewater. Another nanoadsorbent used for water and wastewater remediation is magnetic Fe_3O_4/CeO_2 nanocomposite, which effectively removes the anionic dye of Acid Black 210 by adsorbing it from an aqueous medium. Its efficiency improved after modifying the nanocomposite with organic and inorganic molecules and organic polymers. It means more active functional groups will be formed on the surface leading to its weak coagulation and high stability; hence it is considered one of the best magnetic nanoadsorbents. Moreover, it can be easily removed from water/wastewater by applying an external magnetic field.

4.2.4. Limitations of nanoadsorbent materials.

Nanoadsorbents have shown excellent performance in the remediation of water and wastewater. So far, numerous studies have indicated that they are best suited for the treatment of water due to their unique physicochemical properties, but they have some disadvantages. One of them is the ecotoxicity caused by the nanomaterials present in the treated water [74], which can destroy aquatic life. Another restriction includes their high cost and maintenance, e.g., CNTs, which are highly efficient nanoadsorbents but are quite expensive. The cost-effectiveness of nanomaterials is an important factor and can be improved by the long-term use of nanomaterials. For example, photocatalysis, another method applied in the purification of water, has the ability to is another method applied in the purification of water that can maintain its activity through the restoration of nano adsorbent materials [75]. Some studies have reported the undesirable effects of nanomaterials due to the addition of substances in water for its purification. The example includes chlorination, in which chlorine is added to water in order to get rid of pathogens, but it was observed that it produced cancer-causing by-products [76]. Also, due to the small size of nanoparticles, they can enter the lymph and blood through epithelial and endothelial barriers and then move further into our brain, heart, liver, and other organs and tissues. Once these factors are removed, nanotechnology will provide the desired outcomes like high-quality water and low-cost treatments.

5. Conclusion

There are numerous wastewater/water remediation techniques; however, adsorption has emerged as the most potent and widely used technique/process. The adsorption technique can efficiently reduce numerous classes of pollutants (both inorganic and organic) with limited or no formation of poisonous by-products(s) or intermediates. Therefore, these materials are applicable in removing pollutants from the water source. Recent studies have also projected that nanoadsorbent materials have been gaining wider recognition in water remediation, having unique potential in the adsorption process. In comparison, nanoadsorbent's properties increase their application and have become more beneficial in numerous fields than traditional adsorbents. Hence, nanoadsorbent materials can be considered next-generation adsorbents useful in environmental purification and pollutant control in water/wastewater. Further studies are needed to be done with these nanoadsorbent materials, including surface adaptations and chemical stabilization for improving their application in water/wastewater.

Funding

This research received no external funding.

Acknowledgments

The authors are grateful to the NIET, Greater Noida, for providing support to write this review.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Yousefi, M.; Ghoochani, M.; Hossein Mahvi, A. Health risk assessment to fluoride in drinking water of rural residents living in the Poldasht city, Northwest of Iran. *Ecotoxicology and Environmental Safety* **2018**, *148*, 426-430, https://doi.org/10.1016/j.ecoenv.2017.10.057.
2. Mahboob, S.; Niazi, F.; AlGhanim, K.; Sultana, S.; Al-Misned, F.; Ahmed, Z. Health risks associated with pesticide residues in water, sediments and the muscle tissues of Catla catla at Head Balloki on the River Ravi. *Environmental monitoring and assessment* **2015**, *187*, https://doi.org/10.1007/s10661-015-4285-0.
3. Meena, V.; Dotaniya, M.L.; Saha, J.K.; Das, H.; Patra, A.K. Impact of Lead Contamination on Agroecosystem and Human Health. In: *Lead in Plants and the Environment*. Gupta, D.K.; Chatterjee, S.; Walther, C. Eds.; Springer International Publishing: Cham, **2020**; pp. 67-82, https://doi.org/10.1007/978-3-030-21638-2_4.
4. Chen, Y. Chapter 8 - Photodegradation of pharmaceutical waste by nanomaterials as photocatalysts. In: *Nano-Materials as Photocatalysts for Degradation of Environmental Pollutants*. Singh, P.; Borthakur, A.; Mishra, P.K.; Tiwary, D. Eds.; Elsevier: **2020**; pp. 143-152, https://doi.org/10.1016/B978-0-12-818598-8.00008-0.
5. Kaur, Y.; Jasrotia, T.; Kumar, R.; Chaudhary, G.R.; Chaudhary, S. Adsorptive removal of eriochrome black T (EBT) dye by using surface active low cost zinc oxide nanoparticles: A comparative overview. *Chemosphere* **2021**, *278*, https://doi.org/10.1016/j.chemosphere.2021.130366.
6. Vo, T.S.; Hossain, M.M.; Jeong, H.M.; Kim, K. Heavy metal removal applications using adsorptive membranes. *Nano Convergence* **2020**, *7*, https://doi.org/10.1186/s40580-020-00245-4.
7. Nestola, F.; Smyth, J. Diamonds and water in the deep Earth: A new scenario. *International Geology Review* **2015**, *58*, 1-14, https://doi.org/10.1080/00206814.2015.1056758.
8. Baba, A.; Tayfur, G. Groundwater contamination and its effect on health in Turkey. *Environmental monitoring and assessment* **2011**, *183*, 77-94, https://doi.org/10.1007/s10661-011-1907-z.
9. Rout, P.R.; Shahid, M.K.; Dash, R.R.; Bhunia, P.; Liu, D.; Varjani, S.; Zhang, T.C.; Surampalli, R.Y. Nutrient removal from domestic wastewater: A comprehensive review on conventional and advanced technologies. *Journal of environmental management* **2021**, *296*, https://doi.org/10.1016/j.jenvman.2021.113246.
10. Joseph, L.; Jun, B.-M.; Flora, J.R.V.; Park, C.M.; Yoon, Y. Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere* **2019**, *229*, 142-159, https://doi.org/10.1016/j.chemosphere.2019.04.198.
11. Zhang, D.; Ling, H.; Huang, X.; Li, J.; Li, W.; Yi, C.; Zhang, T.; Jiang, Y.; He, Y.; Deng, S.; Zhang, X.; Wang, X.; Liu, Y.; Li, G.; Qu, J. Potential spreading risks and disinfection challenges of medical wastewater by the presence of Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2) viral RNA in septic tanks of Fangcang Hospital. *The Science of the total environment* **2020**, *741*, https://doi.org/10.1016/j.scitotenv.2020.140445.
12. Kasonga, T.K.; Coetzee, M.A.A.; Kamika, I.; Ngole-Jeme, V.M.; Benteke Momba, M.N. Endocrine-disruptive chemicals as contaminants of emerging concern in wastewater and surface water: A review. *Journal of environmental management* **2021**, *277*, https://doi.org/10.1016/j.jenvman.2020.111485.
13. Crini, G.; Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters* **2019**, *17*, 145-155, https://doi.org/10.1007/s10311-018-0785-9.
14. Santhosh, C.; Velmurugan, V.; Jacob, G.; Jeong, S.K.; Grace, A.N.; Bhatnagar, A. Role of nanomaterials in water treatment applications: A review. *Chemical Engineering Journal* **2016**, *306*, 1116-1137, https://doi.org/10.1016/j.cej.2016.08.053.
15. Rajasulochana, P.; Preethy, V. Comparison on efficiency of various techniques in treatment of waste and sewage water – A comprehensive review. *Resource-Efficient Technologies* **2016**, *2*, 175-184, https://doi.org/10.1016/j.reffit.2016.09.004.
16. Wang, C.; Wang, Z.; Wei, X.; Li, X. A numerical study and flotation experiments of bicyclone column flotation for treating of produced water from ASP flooding. *Journal of Water Process Engineering* **2019**, *32*, https://doi.org/10.1016/j.jwpe.2019.100972.
17. Grzegorzek, M.; Majewska-Nowak, K.; Ahmed, A.E. Removal of fluoride from multicomponent water solutions with the use of monovalent selective ion-exchange membranes. *Science of The Total Environment* **2020**, *722*, https://doi.org/10.1016/j.scitotenv.2020.137681.

18. Hao, Z.; Yin, H.; Wang, L.; Meng, Y. Wear behavior of seven artificial resin teeth assessed with three-dimensional measurements. *The Journal of prosthetic dentistry* **2014**, *112*, 1507-1512, https://doi.org/10.1016/j.prosdent.2014.04.030.
19. Singh, B.K.; Tomar, R.; Kumar, S.; Jain, A.; Tomar, B.S.; Manchanda, V.K. Sorption of 137Cs, 133Ba and 154Eu by synthesized sodium aluminosilicate (Na-AS). *Journal of Hazardous Materials* **2010**, *178*, 771-776, https://doi.org/10.1016/j.jhazmat.2010.02.007.
20. Maddah, H.; Chogle, A. Biofouling in reverse osmosis: phenomena, monitoring, controlling and remediation. *Applied Water Science* **2017**, *7*, 2637-2651, https://doi.org/10.1007/s13201-016-0493-1.
21. Chang, H.; Hu, R.; Zou, Y.; Quan, X.; Zhong, N.; Zhao, S.; Sun, Y. Highly efficient reverse osmosis concentrate remediation by microalgae for biolipid production assisted with electrooxidation. *Water research* **2020**, *174*, https://doi.org/10.1016/j.watres.2020.115642.
22. Huang, J.; Qi, F.; Zeng, G.; Shi, L.; Li, X.; Gu, Y.; Shi, Y. Repeating recovery and reuse of SDS micelles from MEUF retentate containing Cd2+ by acidification UF. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2017**, *520*, 361-368, https://doi.org/10.1016/j.colsurfa.2017.02.001.
23. Zhao, D.L.; Japip, S.; Zhang, Y.; Weber, M.; Maletzko, C.; Chung, T.-S. Emerging thin-film nanocomposite (TFN) membranes for reverse osmosis: A review. *Water research* **2020**, *173*, https://doi.org/10.1016/j.watres.2020.115557.
24. Liang, D.; He, W.; Li, C.; Wang, F.; Crittenden, J.C.; Feng, Y. Remediation of nitrate contamination by membrane hydrogenotrophic denitrifying biofilm integrated in microbial electrolysis cell. *Water research* **2021**, *188*, https://doi.org/10.1016/j.watres.2020.116498.
25. Wang, C.; Alpatova, A.; McPhedran, K.N.; Gamal El-Din, M. Coagulation/flocculation process with polyaluminum chloride for the remediation of oil sands process-affected water: Performance and mechanism study. *Journal of Environmental Management* **2015**, *160*, 254-262, https://doi.org/10.1016/j.jenvman.2015.06.025.
26. Othmani, B.; Rasteiro, M.G.; Khadhraoui, M. Toward green technology: a review on some efficient model plant-based coagulants/flocculants for freshwater and wastewater remediation. *Clean Technologies and Environmental Policy* **2020**, *22*, 1025-1040, https://doi.org/10.1007/s10098-020-01858-3.
27. Ma, J.; Fu, K.; Fu, X.; Guan, Q.; Ding, L.; Shi, J.; Zhu, G.; Zhang, X.; Zhang, S.; Jiang, L. Flocculation properties and kinetic investigation of polyacrylamide with different cationic monomer content for high turbid water purification. *Separation and Purification Technology* **2017**, *182*, 134-143, https://doi.org/10.1016/j.seppur.2017.03.048.
28. Jumadi, J.; Kamari, A.; Hargreaves, J.S.J.; Yusof, N. A review of nano-based materials used as flocculants for water treatment. *International Journal of Environmental Science and Technology* **2020**, *17*, 3571-3594, https://doi.org/10.1007/s13762-020-02723-y.
29. Bhattacharya, P.; Mukherjee, D.; Deb, N.; Swarnakar, S.; Banerjee, S. Application of green synthesized ZnO nanoparticle coated ceramic ultrafiltration membrane for remediation of pharmaceutical components from synthetic water: Reusability assay of treated water on seed germination. *Journal of Environmental Chemical Engineering* **2020**, *8*, https://doi.org/10.1016/j.jece.2020.103803.
30. Emadzadeh, D.; Matsuura, T.; Ghanbari, M.; Ismail, A.F. Hybrid forward osmosis/ultrafiltration membrane bag for water purification. *Desalination* **2019**, *468*, https://doi.org/10.1016/j.desal.2019.114071.
31. Li, X.; Ma, L.; Zhang, H.; Wang, S.; Jiang, Z.; Guo, R.; Wu, H.; Cao, X.; Yang, J.; Wang, B. Synergistic effect of combining carbon nanotubes and graphene oxide in mixed matrix membranes for efficient CO2 separation. *Journal of Membrane Science* **2015**, *479*, 1-10, https://doi.org/10.1016/j.memsci.2015.01.014.
32. Ahmad, T.; Guria, C.; Mandal, A. A review of oily wastewater treatment using ultrafiltration membrane: A parametric study to enhance the membrane performance. *Journal of Water Process Engineering* **2020**, *36*, https://doi.org/10.1016/j.jwpe.2020.101289.
33. Ali, I.; Gupta, V.K. Advances in water treatment by adsorption technology. *Nature Protocols* **2006**, *1*, 2661-2667, https://doi.org/10.1038/nprot.2006.370.
34. Dotto, G.L.; McKay, G. Current scenario and challenges in adsorption for water treatment. *Journal of Environmental Chemical Engineering* **2020**, *8*, https://doi.org/10.1016/j.jece.2020.103988.
35. Crini, G.; Lichtfouse, E.; Wilson, L.D.; Morin-Crini, N. Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters* **2019**, *17*, 195-213, https://doi.org/10.1007/s10311-018-0786-8.
36. Sharma, Y.C.; Srivastava, V.; Singh, V.K.; Kaul, S.N.; Weng, C.H. Nano-adsorbents for the removal of metallic pollutants from water and wastewater. *Environmental Technology* **2009**, *30*, 583-609, https://doi.org/10.1080/09593330902838080.
37. Shooto, N.D.; Thabede, P.M.; Naidoo, E.B. Simultaneous adsorptive study of toxic metal ions in quaternary system from aqueous solution using low cost black cumin seeds (Nigella sativa) adsorbents. *South African Journal of Chemical Engineering* **2019**, *30*, 15-27, https://doi.org/10.1016/j.sajce.2019.07.002.
38. Syers, J.K.; Browman, M.G.; Smillie, G.W.; Corey, R.B. Phosphate Sorption by Soils Evaluated by the Langmuir Adsorption Equation. *Soil Science Society of America Journal* **1973**, *37*, 358-363, https://doi.org/10.2136/sssaj1973.03615995003700030015x.

39. Jain, A.; Kumari, S.; Agarwal, S.; Khan, S. Water purification via novel nano-adsorbents and their regeneration strategies. *Process Safety and Environmental Protection* **2021**, *152*, 441-454, https://doi.org/10.1016/j.psep.2021.06.031.
40. Pandey, S. A comprehensive review on recent developments in bentonite-based materials used as adsorbents for wastewater treatment. *Journal of Molecular Liquids* **2017**, *241*, 1091-1113, https://doi.org/10.1016/j.molliq.2017.06.115.
41. Singh, N.B.; Nagpal, G.; Agrawal, S.; Rachna. Water purification by using Adsorbents: A Review. *Environmental Technology & Innovation* **2018**, *11*, 187-240, https://doi.org/10.1016/j.eti.2018.05.006.
42. Lu, H.; Wang, J.; Stoller, M.; Wang, T.; Bao, Y.; Hao, H. An Overview of Nanomaterials for Water and Wastewater Treatment. *Advances in Materials Science and Engineering* **2016**, *2016*, https://doi.org/10.1155/2016/4964828.
43. Neyaz, N.; Siddiqui, W.; Nair, K.K. Application of surface functionalized iron oxide nanomaterials as a nanosorbents in extraction of toxic heavy metals from ground water: A review. *Int. J. Environ. Sci.* **2014**, *4*, 472-483.
44. Saleh, T.A. Protocols for synthesis of nanomaterials, polymers, and green materials as adsorbents for water treatment technologies. *Environmental Technology & Innovation* **2021**, *24*, https://doi.org/10.1016/j.eti.2021.101821.
45. Yadav, T.P.; Yadav, R.M.; Singh, D.P. Mechanical milling: a top down approach for the synthesis of nanomaterials and nanocomposites. *Nanosci Nanotechnol*. **2012**, *2*, 22-48, https://doi.org/10.5923/j.nn.20120203.01.
46. Nadaroglu, H.; GÜNGÖR, A.A.; Selvi, İ.N. Synthesis of nanoparticles by green synthesis method. *Int. J. Innov. Res. Rev.* **2017**, *1*, 6-9.
47. Sharma, R.; Kumar, D. Nanoadsorbents: An Approach Towards Wastewater Treatment. In:*Nanotechnology for Sustainable Water Resources*. 2nd ed.; Mishra, A.K.; Hussain, C.M. Eds.; Scrivener Publishing LLC: Beverly, MA, **2018**; pp. 371-405, https://doi.org/10.1002/9781119323655.ch12.
48. Reza, R.T.; Martínez Pérez, C.A.; Rodríguez González, C.A.; Romero, H.M.; García Casillas, P.E. Effect of the polymeric coating over Fe3O4 particles used for magnetic separation. *Central European Journal of Chemistry* **2010**, *8*, 1041-1046, https://doi.org/10.2478/s11532-010-0073-4.
49. Dave, P.N.; Chopda, L.V. Application of Iron Oxide Nanomaterials for the Removal of Heavy Metals. *Journal of Nanotechnology* **2014**, *2014*, https://doi.org/10.1155/2014/398569.
50. Leonel, A.G.; Mansur, A.A.P.; Mansur, H.S. Advanced Functional Nanostructures based on Magnetic Iron Oxide Nanomaterials for Water Remediation: A Review. *Water research* **2021**, *190*, https://doi.org/10.1016/j.watres.2020.116693.
51. Das, R.; Ali, M.E.; Hamid, S.B.A.; Ramakrishna, S.; Chowdhury, Z.Z. Carbon nanotube membranes for water purification: A bright future in water desalination. *Desalination* **2014**, *336*, 97-109, https://doi.org/10.1016/j.desal.2013.12.026.
52. Das, R.; Leo, B.F.; Murphy, F. The Toxic Truth About Carbon Nanotubes in Water Purification: a Perspective View. *Nanoscale Research Letters* **2018**, *13*, https://doi.org/10.1186/s11671-018-2589-z.
53. Anjum, M.; Miandad, R.; Waqas, M.; Gehany, F.; Barakat, M.A. Remediation of wastewater using various nanomaterials. *Arabian Journal of Chemistry* **2019**, *12*, 4897-4919, https://doi.org/10.1016/j.arabjc.2016.10.004.
54. Chauhan, A.; Sillu, D.; Agnihotri, S. Removal of Pharmaceutical Contaminants in Wastewater Using Nanomaterials: A Comprehensive Review. *Current drug metabolism* **2019**, *20*, 483-505, https://doi.org/10.2174/1389200220666181127104812.
55. Beyene, H.D.; Werkneh, A.A.; Bezabh, H.K.; Ambaye, T.G. Synthesis paradigm and applications of silver nanoparticles (AgNPs), a review. *Sustainable Materials and Technologies* **2017**, *13*, 18-23, https://doi.org/10.1016/j.susmat.2017.08.001.
56. Mustapha, S.I.; Aderibigbe, F.A.; Adewoye, T.L.; Mohammed, I.A.; Odey, T.O. Silver and titanium oxides for the removal of phenols from pharmaceutical wastewater. *Materials Today: Proceedings* **2021**, *38*, 816-822,https://doi.org/10.1016/j.matpr.2020.04.669.
57. Zodrow, K.; Brunet, L.; Mahendra, S.; Li, D.; Zhang, A.; Li, Q.; Alvarez, P.J.J. Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal. *Water research* **2009**, *43*, 715-723, https://doi.org/10.1016/j.watres.2008.11.014.
58. Barahimi, V.; Taheri, R.A.; Mazaheri, A.; Moghimi, H. Fabrication of a novel antifouling TiO2/CPTES/metformin-PES nanocomposite membrane for removal of various organic pollutants and heavy metal ions from wastewater. *Chemical Papers* **2020**, *74*, 3545-3556, https://doi.org/10.1007/s11696-020-01178-2.
59. Huang, J.; Cao, Y.; Liu, Z.; Deng, Z.; Tang, F.; Wang, W. Efficient removal of heavy metal ions from water system by titanate nanoflowers. *Chemical Engineering Journal* **2012**, *180*, 75-80, https://doi.org/10.1016/j.cej.2011.11.005.
60. Murcia, J.J.; Hernández Niño, J.S.; Rojas, H.; Brijaldo, M.H.; Martín-Gómez, A.N.; Sánchez-Cid, P.; Navío, J.A.; Hidalgo, M.C.; Jaramillo-Paez, C. ZnO/Ag3PO4 and ZnO–Malachite as Effective Photocatalysts for the

Removal of Enteropathogenic Bacteria, Dyestuffs, and Heavy Metals from Municipal and Industrial Wastewater. *Water* **2021**, *13*, https://doi.org/10.3390/w13162264.
61. Pinto, M.; Ramalho, P.S.F.; Moreira, N.F.F.; Gonçalves, A.G.; Nunes, O.C.; Pereira, M.F.R.; Soares, O.S.G.P. Application of magnetic nanoparticles for water purification. *Environmental Advances* **2020**, *2*, https://doi.org/10.1016/j.envadv.2020.100010.
62. Bui, T.Q.; Ton, S.N.-C.; Duong, A.T.; Tran, H.T. Size-dependent magnetic responsiveness of magnetite nanoparticles synthesised by co-precipitation and solvothermal methods. *Journal of Science: Advanced Materials and Devices* **2018**, *3*, 107-112, https://doi.org/10.1016/j.jsamd.2017.11.002.
63. Obaid, S.S.; Gaikwad, D.K.; Sayyed, M.I.; Al-Rashdi, K.; Pawar, P.P. Heavy metal ions removal from waste water bythe natural zeolites. *Materials Today: Proceedings* **2018**, *5*, 17930-17934,https://doi.org/10.1016/j.matpr.2018.06.122.
64. Wasielewski, S.; Rott, E.; Minke, R.; Steinmetz, H. Evaluation of Different Clinoptilolite Zeolites as Adsorbent for Ammonium Removal from Highly Concentrated Synthetic Wastewater. *Water* **2018**, *10*, https://doi.org/10.3390/w10050584.
65. Shepard, Z.J.; Lux, E.M.; Oyanedel-Craver, V.A. Performance of silver nanoparticle-impregnated ovoid ceramic water filters. *Environmental Science: Nano* **2020**, *7*, 1772-1780, https://doi.org/10.1039/D0EN00115E.
66. Cervantes-Avilés, P.; Keller, A.A. Incidence of metal-based nanoparticles in the conventional wastewater treatment process. *Water research* **2021**, *189*, https://doi.org/10.1016/j.watres.2020.116603.
67. Ghosh, S.; Ghosh, I.; Chakrabarti, M.; Mukherjee, A. Genotoxicity and biocompatibility of superparamagnetic iron oxide nanoparticles: Influence of surface modification on biodistribution, retention, DNA damage and oxidative stress. *Food and Chemical Toxicology* **2020**, *136*, https://doi.org/10.1016/j.fct.2019.110989.
68. Baig, U.; Uddin, M.K.; Gondal, M.A. Removal of hazardous azo dye from water using synthetic nano adsorbent: Facile synthesis, characterization, adsorption, regeneration and design of experiments. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2020**, *584*, https://doi.org/10.1016/j.colsurfa.2019.124031.
69. El-Sayed, M.E.A. Nanoadsorbents for water and wastewater remediation. *Science of The Total Environment* **2020**, *739*, https://doi.org/10.1016/j.scitotenv.2020.139903.
70. Xu, P.; Zeng, G.M.; Huang, D.L.; Feng, C.L.; Hu, S.; Zhao, M.H.; Lai, C.; Wei, Z.; Huang, C.; Xie, G.X.; Liu, Z.F. Use of iron oxide nanomaterials in wastewater treatment: A review. *Science of The Total Environment* **2012**, *424*, 1-10, https://doi.org/10.1016/j.scitotenv.2012.02.023.
71. Chandra Joshi, N.; Singh, A. Adsorptive performances and characterisations of biologically synthesised zinc oxide based nanosorbent (ZOBN). *Groundwater for Sustainable Development* **2020**, *10*, https://doi.org/10.1016/j.gsd.2019.100325.
72. Mercante, L.A.; Andre, R.S.; Schneider, R.; Mattoso, L.H.C.; Correa, D.S. Free-standing SiO2/TiO2–MoS2 composite nanofibrous membranes as nanoadsorbents for efficient Pb(ii) removal. *New Journal of Chemistry* **2020**, *44*, 13030-13035, https://doi.org/10.1039/D0NJ02561E.
73. Sadak, O.; Hackney, R.; Sundramoorthy, A.K.; Yilmaz, G.; Gunasekaran, S. Azo dye-functionalized magnetic Fe3O4/polyacrylic acid nanoadsorbent for removal of lead (II) ions. *Environmental Nanotechnology, Monitoring & Management* **2020**, *14*, https://doi.org/10.1016/j.enmm.2020.100380.
74. Yaqoob, A.A.; Parveen, T.; Umar, K.; Mohamad Ibrahim, M.N. Role of Nanomaterials in the Treatment of Wastewater: A Review. *Water* **2020**, *12*, https://doi.org/10.3390/w12020495.
75. Zhu, Y.; Liu, X.; Hu, Y.; Wang, R.; Chen, M.; Wu, J.; Wang, Y.; Kang, S.; Sun, Y.; Zhu, M. Behavior, remediation effect and toxicity of nanomaterials in water environments. *Environmental Research* **2019**, *174*, 54-60, https://doi.org/10.1016/j.envres.2019.04.014.
76. Srivastav, A.L.; Patel, N.; Chaudhary, V.K. Disinfection by-products in drinking water: Occurrence, toxicity and abatement. *Environmental Pollution* **2020**, *267*, https://doi.org/10.1016/j.envpol.2020.115474.