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Review

Advances in the Applications of Nanomaterials for Wastewater Treatment

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Abstract: Freshwater is in limited supply, and the growing population further contributes to its scarcity. The effective treatment of wastewater is essential now more than ever, because waterborne infections significantly contribute to global deaths, and millions of people are deprived of safe drinking water. Current wastewater treatment technologies include preliminary, primary, secondary, and tertiary treatments, which are effective in removing several contaminants; however, contaminants in the nanoscale range are often difficult to eliminate using these steps. Some of these include organic and inorganic pollutants, pharmaceuticals, pathogens and contaminants of emerging concern. The use of nanomaterials is a promising solution to this problem. Nanoparticles have unique properties allowing them to efficiently remove residual contaminants while being cost-effective and environmentally friendly. In this review, the need for novel developments in nanotechnology for wastewater treatment is discussed, as well as key nanomaterials and their corresponding target contaminants, which they are effective against. The nanomaterials of focus in this review are carbon nanotubes, graphene-based nanosheets, fullerenes, silver nanoparticles, copper nanoparticles and iron nanoparticles. Finally, the challenges and prospects of nanoparticle utilisation in the context of wastewater treatment are presented.

Keywords: nanomaterials; wastewater treatment; carbon nanotubes; graphene-based nanoparticles; silver nanoparticles

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1. Introduction

The rapid growth of the world population and climate change, are two key factors that immensely affect the availability of freshwater. In total, 80% of diseases worldwide are directly or indirectly caused by a poor water quality supply, and 19% of global fatalities are attributable to infections caused by pathogenic microorganisms in water [1]. The developing world is mostly at risk; and this compounded by the fact, the cost of analysing the microbial and chemical content of water is high and relatively complex. In addition to having a negative impact on human life, contaminated water also negatively impacts wildlife and the environment [2,3]. Globally, the construction of water pipes connected to lodgings has increased in the last 20 years, but a large portion of the population still do not have access to clean drinking water, comprising approximately 780 million people [4]. In 2010, 690 million people had access to water which was only partially treated [5]. The conservation of water is a strategy used to reduce the amount of water usage, but other solutions are needed because conservation alone is insufficient due to the demands of the ever-growing population. Poor sanitation also puts pressure on the delivery of clean and safe water. Therefore, new innovative and cost-effective ways to treat wastewater are crucial [6]. Only 2.5–3% of the earth's water is freshwater, and of this 3%, about 70% exists in the form of ice, and the remaining 30% is groundwater, which can be difficult to access [7]. By 2050, the global population is predicted to reach 9 billion, and by 2075, 75% of the global population will have an inadequate availability of freshwater [8]. This, again substantiates the importance of novel and scalable wastewater treatment methodologies.

The basic wastewater treatment process usually involves three main steps: primary, secondary and tertiary treatment. These steps are dependent on the size and location of the treatment plant but also, more importantly, the type of raw water that needs to be treated, as is further discussed in Section 2. One of the specific treatment methods adopted in these three treatment steps is separation by sedimentation, as induced by gravity. Boiling, which kills bacteria is also common. However, recalcitrant minerals/metals may not be effectively removed using these methods. Ultraviolet (UV) light is also effective for microbial inactivation, but filtration is usually a pre-requisite step, and few residuals are removed during this treatment. The use of chemicals is another commonly adopted method of purifying water. Coagulants, for example, enable the agglomeration of suspended materials, which can subsequently be separated by filtration. However, few dissolved materials are removed using this method. Other chemicals such as chlorine, bromine, iodine and hydrogen peroxide can be used to kill microbes, but some of these chemicals are immensely toxic and may result in more harm (carcinogenic) to humans and the environment. Reverse osmosis is a well-utilised method for wastewater treatment; however, chemical and bacterial contaminants are not effectively captured by this technology. Often, a combination of these methods is employed to achieve an improved treatment efficiency. It is evident that there are many limitations to these conventional methods. Hence, there is an increased need for new methods, such as nanotechnology, which is capable of addressing these limitations, especially when the contaminants are of a micro- or nanoscale [9].

Nanotechnology can be used to overcome serious environmental problems, such as solid waste management and air and water pollution [10]. The most difficult contaminants to eliminate in wastewater are those in the nanoscale range (1–100 nm), hence the corresponding suitability of nano-based methodologies. Nanotechnologies are extremely advantageous for water remediation not only because of the dimensional domain, but also because of the excellent physicochemical properties of nanomaterials. Nanotechnology research and development, both in water purification and in other applications (energy storage, medicine, clothing and food preservation), are developing rapidly worldwide. In the US, 6 billion dollars are invested in nanotechnology research and development annually [1]. Although nanoparticles can be sourced from natural sources, they can also be synthesized. There is immense research interest in the field of novel nanomaterial synthesis based on materials with desirable properties, particularly for improving the quality of the effluent discharge from various industries. Nanoparticles vary in size, solubility, shape, surface area and charge, and all of these determine their respective chemical, biological and physical characteristics [2]. Nanofiltration (NF), reverse osmosis (RO), microfiltration (MF) and ultrafiltration (UF) are all nano-based methods used for treating wastewater. Of these methods, nanofiltration is predominantly applied, as it is capable of removing salts, minerals, pathogens, anions, cations and total dissolved solids (TDS). The removal of pathogens such as viruses, protozoa and bacteria is another capability of this technology that is particularly important for mitigating waterborne infections in humans and animals [8].

Here, we present an overview of the advances in the use of nanomaterials for wastewater treatment. The applications of these materials, with an emphasis on the use of carbon nanotubes, graphene-based nanosheets, fullerenes, silver nanoparticles, copper nanoparticles and iron nanoparticles, are elucidated. Silver nanoparticles, copper nanoparticles and iron nanoparticles are the focus of the review due to their unique physicochemical properties, including their extremely small size, high surface-area-to-volume ratio, which can be functionalized/modified, and excellent magnetic properties. In contrast, carbon-based materials such as carbon nanotubes, graphene-based nanosheets and fullerenes are examined in this review due to their unique performance characteristics and the diversity of their carbon-based structures. In addition, it is relatively easy to functionalize the surface properties of carbon-based materials to target a particular water pollutant. The challenges involved in the application of these materials and the need to overcome these problems are discussed. While the present study focuses on the application of the aforementioned nanomaterials for wastewater remediation, some novel applications of other nanomaterials for water remediation are beyond the scope of the study. The interested reader is referred to the comprehensive review by Tang et al. [11] for a detailed understanding of the applications of nanomaterial-enabled photothermal-based solar systems for water disinfection. Furthermore, the mechanism of the thermoplasmonic disinfection of wastewater can also be found elsewhere [12]. Hot electron photocatalysis is another promising method that has been described in Shiraishi et al. [13].

2. Current Wastewater Treatment Technologies

The removal of soils, pathogens, organic materials and toxic chemicals and the necessity to comply with the guidelines and legislation for the safe discharge of wastewater constitute some of the main reasons for wastewater treatment. The type and mixture of waste that ends up in a wastewater treatment plant (WWTP) depend on the source(s). Correspondingly, the technology adopted for the treatment depends on the type of waste. The waste can be municipal waste (from homes, schools, hospitals, restaurants and shops), industrial waste (from factories and pharmaceutical companies), or inflow and infiltration (from sewers and manholes and groundwater and stormwater). The first step in attaining an adequate treatment is the characterisation of the wastewater to identify its specific constituents. Parameters such as the pH, biological oxygen demand (BOD), chemical oxygen demand (COD), alkalinity, hardness, mineral composition, anionic composition and non-ionic composition are important to obtain. Thereafter, the correct technologies can be implemented for treatment. The treatment may be physical, chemical or biological, but a combination of all three is usually applied [14]. The current WWT steps are further explained hereafter.

2.1. Preliminary Treatment

The preliminary treatment can be considered the most important treatment step, as it affects all the other treatment steps. This step removes larger solid material which, if not eliminated, may cause pipe blockages and impede the rest of the treatment process. The incoming wastewater is subjected to metal screens to filter out large items such as plastics, paper, etc. Solid particles, which are smaller and penetrate the screens, are removed by sedimentation. Some of these solids include stones, sand and grit. Collected solids can then be disposed of properly. There are solids which cannot be removed by filtering or settling, such as fats, oils and grease (FOG). These are usually removed by a process known as floatation. Air bubbles are introduced into the water tank, which causes the FOG to float to the surface of the tank so that it can be mechanically skimmed from the tank [14,15].

2.2. Primary Treatment

Primary treatment removes a significant number of suspended solids (Figure 1). This step is carried out in clarifiers, also known as settling tanks. The primary sewage sludge settles at the bottom of the tank and is then removed from the tank by mechanical means. The primary sewage sludge is transported to a different part of the plant, where it is also treated [14]. Primary treatment may also involve the use of coagulants, resulting in a better settlement of suspended solids in the water. The use of coagulants can be expensive, and the corrosive and hazardous properties of some coagulants make them less desirable (e.g., ferric chloride). Coagulants also need to be recovered or reused. This recovery process may increase the cost of the treatment process [16]. Although coagulants are effective in further removing solids, they do not remove endocrine-disrupting compounds (EDCs), which have adverse effects on aquatic and human health. The application of nanotechnology can also target these harmful compounds [17]. Preliminary and primary treatments are very important steps in the WWT process, but they do not remove pathogens, dissolved solids and pharmaceuticals. Thus, further treatment is needed.

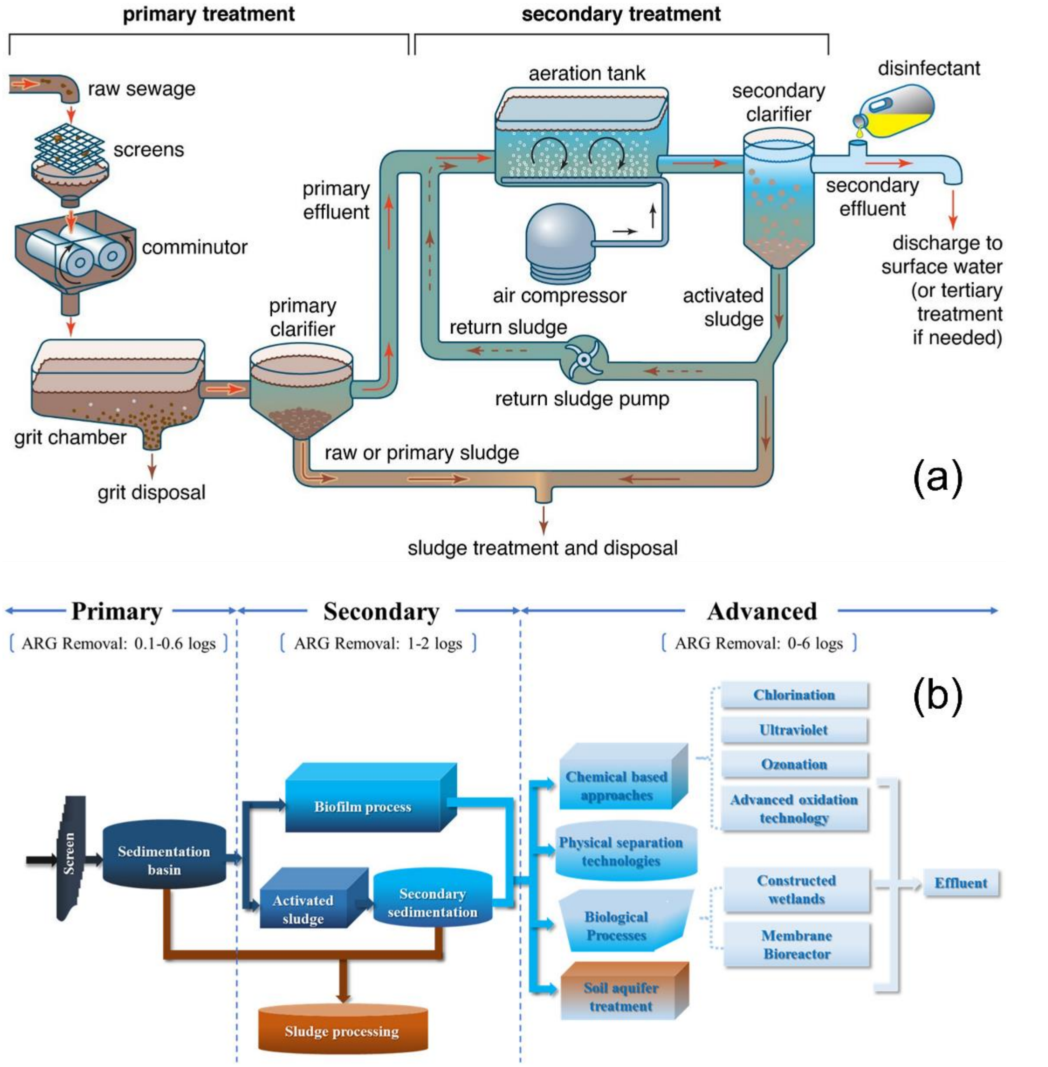

Figure 1. (**a**) Wastewater treatment steps [18], showing (**b**) the removal efficacy of antibiotic resistance genes (ARG) (emerging contaminants) in this step [19].

2.3. Secondary Treatment

By utilising biological treatment, this step targets dissolved solids which cannot be removed by filtration or sedimentation. One example of biological treatment is the use of sequencing batch reactors (SBRs), which involves two or more tanks in series [20]. The primary wastewater is released into the first tank, after which oxygen is supplied (aeration) to the tank by blowers. Oxygen is required by the microorganisms to enable them metabolise and decompose the present organic material. The aeration stage may last for up to 105 min [21]. Subsequent to this phase is the settling step, during which the biomass settles in the tank. The clean water can be separated with the aid of a decant arm. Although this step removes a large portion of organic and inorganic pollutants, pollutants in the nanoscale range remain. Secondary treatment are usually incapable of effectively eliminating contaminants of emerging concern (CEC), such as medicines and domestic cleaning products, which are harmful to the environment when released as effluents [22]. However, Pei et al. [19] highlighted that antibiotic resistance genes (ARGs), a class of emerging contaminants, may be more effectively removed during secondary treatment, as illustrated in Figure 1b.

2.4. Tertiary Treatment

The final stage is the tertiary treatment, and this differs depending on the WWTP. After the treatment steps mentioned above, there are still pollutants and residual toxins in the effluent which must be removed [23,24]. This step removes nutrients, pathogens and odours [25]. In this way, the quality of the discharged effluent is improved and meets stricter standards that are not obtainable through secondary treatment. Most tertiary treatment methods involve the application of physicochemical techniques, such as activated carbon adsorption, additional disinfection and even reverse osmosis [26–28]. It should be mentioned that the advanced oxidation technology, such as photocatalysis and photoelectrocatalysis, outlined as part of the tertiary treatment in Figure 1, are relevant nanotechnological approaches for water remediation due to the use of semiconductor catalysts in the form of nanomaterials.

2.5. Limitations of Current Treatment Steps

Despite the successes of the outlined methods, their large-scale applications are often plagued by a myriad of challenges. For example, chlorination, which is used to remove pathogens, leaves an undesired taste and smell in the water, and a further dechlorination step is often required to prevent this. An alternative to chlorine is ozonation, which is also effective in inactivating pathogens [29,30]. However, this method can be expensive due to the energy costs. Other methods of microorganism removal are ion exchange and ultraviolet (UV) photocatalysis, but these are not very convenient for the complete removal of pathogens. Nanofiltration (NF), reverse osmosis (RO), microfiltration (MF) and ultrafiltration (UF) are highly effective in removing micropollutants but may induce equipment fouling. There is a need for newer technologies that can adequately eliminate newly emerging contaminants. Nanotechnology has been deemed an effective technology in this regard [17].

3. The Use of Nanotechnology for Contaminant Removal

Nanoparticles can be used to improve the quality of an effluent which would otherwise still contain contaminants. The use of nanotechnology to treat wastewater in developing countries may be greatly beneficial, as major infrastructure is not needed, and it can be cost-effective and easy to operate. Nanotechnology for WWT has been utilised for laboratory-scale tests and has been very successful [9,31]. Nanoparticles can adsorb organic and inorganic pollutants from wastewater, which are otherwise difficult to remove. Another advantage of using nanoparticles is that during the manufacturing process, harmful by-products are not released. Their unique properties, including their small size, large surface area, high reactivity, large surface-area-to-volume ratio and high porosity, provide them with these advantages. They also have unique optical properties, such as their transparency and the presence of iridescent films [32]. The large surface area is the most important, as it allows for more active adsorbing sites. Some nanoparticles can also be reused, which is a major sustainable attribute. Magnetic nanoparticles can be collected and separated from the wastewater after treatment and reused many times. These magnetic nanoparticles are capable of removing radionuclides and heavy metals [6].

In a study by Jiang et al. [33], adsorption and membrane filtration, as nanotechnology-based treatment methods, were examined. Adsorption was preferred over the membrane filtration method, as it was the simplest to use and could treat organic and inorganic pollutants. It is an attractive method for removing organic materials, as well as salts, bases, acids and toxic compounds. The efficiency of adsorption was determined by the pore structure of the adsorbent and the interaction between the adsorbent and the contaminant [34]. The authors also examined carbon-based nanoparticles, graphene-based nanoparticles and carbon nanotubes, all of which had a high performance with regard to the removal of heavy metals and organic pollutants. The hydrophobicity of carbon-based nanoparticles was also tested, and it was realised that the adsorption energy was increased, and the surface area was reduced as loose aggerates were formed. To alleviate this, functional groups or metal oxide particles were added. The authors also remarked that carbon nanoparticles can be reused if the pH is lowered, without a decrease in the adsorption capacity. Membrane filtration (MF, UF and NF) was also examined. The difference between MF, UF and NF is the size of the pores of the membranes. However, the main disadvantage of these processes is the fouling of the membranes. This issue can be overcome via modification (with silica, aluminium, zeolite and titanium oxide). Silver can also be added to prevent biofilm growth and to kill bacteria and viruses [35].

A major challenge affecting many contaminants is the fact that they can be present in very low concentrations, which can be difficult to detect. The advantage of using nanomaterials is that they can concentrate pollutants to a level high enough to allow them to be detected and removed. An example of this is the use of Au-TiO_2 nanoparticles to concentrate low levels of insecticide in wastewater, which can then be removed [36]. New developments on effective sensors for detecting nanosized contaminants are needed, as the problem of the false detection of contaminants and pathogens is predominant in most treatment applications.

4. Types of Nanoparticles for Wastewater Treatment

It is worth mentioning that several parameters should be considered, such as the quality standards of the effluent that are to be met and the efficiency of the nanomaterial, its recyclability, environmental impact and cost, before applying nanotechnology for WWT [37]. Adequate knowledge of the properties, characteristics and functions of different nanoparticles is also important when deciding which type to use for contaminant removal. In this section, the characteristics of carbon nanotubes, graphene-based nanoparticles and silver, copper and iron nanoparticles and their applications to water treatment are discussed.

4.1. Carbon Nanotubes

Carbon nanotubes (CNTs) are comprised of graphene sheets rolled into a cylindrical tube shape, which is shown in Figure 2, referred to as a single-walled carbon nanotube (SWCNT). It is important to mention that this is not the procedure for fabricating CNTs but only indicates a general representation of CNTs. Multiple layers of graphene sheets are referred to as multi-walled carbon nanotubes (MWCNTs). The fabrication methods for CNTs and MWCNTs (including chemical vapour deposition, laser ablation, arc discharge, and electrophoretic deposition) are extensively covered in the literature [38,39].

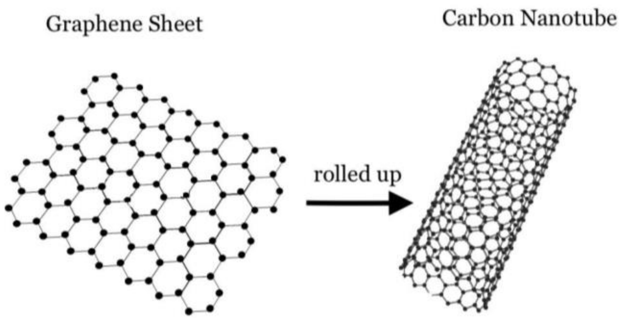

Figure 2. Graphene sheet rolled up to form a single-walled CNT [40].

Table 1 describes a comparison between SWCNTs and MWCNTs. While SWCNTs are usually present in stiff rope-like bundles (resulting from their small diameter/surface area and increased van der Waals forces), MWCNTs can be present in an agglomerated needle-like structures [41]. SWCNTs tend to be in the diameter range of 0.7–3 nm, whereas MWCNTS may possess a diameter of 10–200 nm [41,42].

Table 1. Comparison between SWCNTs and MWCNTs [43].

Property	SWCNT	MWCNT
Bulk synthesis	Difficult	Easy
Graphene layer	Single	Multiple
Purity	Poor	High
Thermal conductivity (W/(m K))	6000	2000
Specific gravity (g/cm^3)	0.8	1.8
Electrical conductivity (S/cm)	10^2–10^6	10^3–10^5
Electron mobility (cm^2/(Vs))	~10^5	10^4–10^5
Thermal stability in air (°C)	>600	>600

CNT is one of the allotropes of carbon and was discovered approximately three decades ago. It is one of the lightest and toughest materials on earth and possesses hydrophobic properties [44]. To attract water functional groups that are hydrophilic, they are coated on the top of each nanotube. The water flows into the CNT but is pushed out very quickly as it is repelled by the tube walls. The pollutants are caught on the top of the CNT by the functional groups, leaving only clean water to flow out [40,45]. CNTs are chemically stable and have mesopores, distinguishing them from traditional adsorbents such as clay, zeolites, metal oxides, activated carbon and polymers. The unique thermal, chemical, electrical and mechanical properties of CNTs sets them apart, as they are able to remove many impurities from aqueous solutions [43]. CNTs are becoming very popular not only for wastewater purification but also for energy storage, space applications and electronics [34]. Organic material is typically adsorbed on the external and internal portions of open-ended CNTs. Inorganic pollutants can also be adsorbed on the external side through the addition of certain functional groups. Polycyclic aromatic hydrocarbons (PAHs), which are persistent organic pollutants, can be adsorbed in the interstitial channel of the CNT [45]. The ease of functionalization, large surface area, high aspect ratio and fast water transport are features that make CNTs an evolving nanomaterial. They can be used on their own as a filter, or they can be implemented in existing membranes to improve the performance.

Another feature of CNTs that renders their use highly attractive is their antifouling properties, disinfection capacity, permeability and strength, as enabled by their sp^2 chemical bonds. CNTs can be synthesized by photoablation, chemical vapour deposition or arc discharge and can be free-standing or mixed. Free-standing CNTs can be split into vertically-aligned CNTs, where water flows very quickly through their inner section, and those manufactured as bucky-paper members, where their arrangement is random, leading to a large 3D network with a high surface area. CNT membranes can supersede or possibly improve the performance of NF, RO, MF, UF and forward osmosis (FO). The hydrophobic hollow section indicates that little external energy is required to move the water molecules through the CNT [46], which greatly reduces the cost.

CNTs have been used to remove pollutants such as dyes, pharmaceuticals and herbicides from water. The oxygen groups on the CNT surface facilitate adsorption processes via chemisorption, physisorption and electrostatic interaction. Balarak et al. used SWCNTs to remove AB29 dye, which is an acid dye [47]. Their study revealed that the mechanism of the adsorption of AB29 dye by SWCNT occurred mainly via London dispersion force, $\pi - \pi$ electrostatic interaction, hydrogen bonding and the hydrophobic effect. Approximately 99.4% of the dye was removed using SWCNT with the optimal conditions of 0.12 g/L, an initial concentration of 10 mg/L, a pH of 3 and a contact time of 75 min.

A major challenge of CNTs is their hydrophobic nature, which causes them to undergo agglomeration in water, and due to massive Van der Waals forces, the adsorptive surface area is severely reduced. To increase the adsorption capacity of CNTs, functionalization with polymers and amorphization, with many defects, have been exploited. For instance, a reported study on the removal of Methyl Orange and Rhodamine B using a CNT revealed that the short-term temperature treatment (200 °C for 30 min) of Ferrocene and ammonium chloride (analytically pure) could result in an appreciable hydrophilicity [48]. However, the adsorption capacity was still low with 21.39 mg/g and 25.5 mg/g in the case of Methyl orange and Rhodamine B, respectively.

The use of carboxylic-acid-modified CNTs as a linking skeleton for metal–organic-frameworks has been reported for methylene blue dye removal. The functionalized CNT-MOF was wrapped in a gelatine and crosslinked to increase the chemical stability. The CNT provided a greater surface area for a greater adsorption, and the adsorption capacity of 106 mg/g of methylene blue was achieved under the conditions of a 289K and 100 mg/L initial dye concentration. The adsorption isotherm and kinetics suggested a chemisorption mechanism with an activated energy of 83.33 kJ/mol, and the adsorbent could be reused six times [49]. Another study on methylene blue removal using a polyethylene terephthalate nanofiber-MWCNT adsorbent revealed a physisorption mechanism with a very low maximum adsorption capacity of 7.047 mg/g [50]. Heavy metal removal has been achieved using polymer-metal-organic-framework-CNT composites. A recent study on the removal of arsenic-spiked water with two adsorbents, Zn-BDC@chitosan/CNT and Zn-BDC@chitosan/graphene oxide (GO), revealed that the graphene oxide-metal-organic-framework-chitosan outperformed the CNT analogue because of the GO higher specific surface area and active sites [51]. This shows not only that MOF and polymers are necessary to increase interactions with the adsorbate, but also that the surface functional groups and specific surface area of the CNTs are vital for achieving a good adsorption capacity. Furthermore, CNT-grafted poly[(sodium methacrylate)-*co*-2-(methacryloyloxy)ethyl acetoacetate] has been used to remove high concentrations of lead (II) from water. The synthesized material possesses both acid and basic functional groups. The maximum adsorption reached 1178 mg/g, and an adsorbent dose of 2.5 g/L could reduce Pb^{2+} from 1000 ppb to 2 ppb, which was significantly higher than the values described in most of the reported studies in the literature [52]. A similar study on polymer-grafted CNTs reported that the material could remove Pb^{2+} with a relatively lower capacity [53,54].

The studies conducted revealed that chemisorption dominates in terms of the removal capacity of CNTs for most pollutants, and the pseudo-second-order kinetics can effectively describe the mechanism of adsorption. The pH value is the most critical parameter that influences the CNT adsorption capacity, especially for divalent metals. However, the low dispersion of CNTs and their high agglomeration and hydrophobic nature present serious challenges that ultimately result in a lower adsorption capacity compared to GO and active carbons. The grafting of CNTs on polymers and their crosslinking with mainly glutaraldehyde to increase their mechanical and chemical strength are noteworthy endeavours. The polymer grafting contributed to a greater capacity and reusability of most reported CNT-modified adsorbents. However, with the exception of natural polymers, synthesis is usually complex and time consuming. A natural method which seems to be especially appealing is the use of biological self-assembly microorganism-CNT composites. This is a form of natural crosslinking with microorganisms such as fungi, bacteria, even algae and can be achieved at the lower temperature of 30 °C. This idea has been used for porous carbon derived from starch, and it showed a higher surface area and higher adsorption capacity than porous carbon alone [55]. Table 2 shows some reported CNTs, along with their target pollutants, optimal conditions and adsorption capacities.

Table 2. Reported studies on CNTs' application for the removal of wastewater contaminants.

Adsorbents	pH	Contact Time (min)	Adsorbent Dosage (g)	Target Pollutant	Adsorption Capacity (mg/g)	Adsorption Mechanism	Ref.
Chitin/magnetite/MWCNT	2.0	45	0.05	Cr(VI)	11.3	Chemisorption	[56]
Zero-valent iron/MWCNT	8.0	60	4 *	Arsenate	250	Complexation mechanism	[57]
Zero-valent iron/MWCNT	7.0	90	4 *	Arsenite	200	Complexation mechanism	[57]
CNT-sediments	10.0	300	10 **	Cd(II)	1.482	Physisorption	[58]

Table 2. *Cont.*

Adsorbents	pH	Contact Time (min)	Adsorbent Dosage (g)	Target Pollutant	Adsorption Capacity (mg/g)	Adsorption Mechanism	Ref.
PES/1% MWCNTs-NH2	7.0	10	0.1	Pb(II)	272	Chemisorption	[53]
Ion-imprinted polymers/MWCNT	6.0	15	0.02	Pb(II)	83.20	Chemisorption	[54]
MWCNT	6.0	-	0.3	Pb(II)	97.08	Physisorption	[59]
MWCNT	6.0	-	0.3	Cu(II)	24.49	Physisorption	[59]
MWCNT	11.0	-	0.3	Cd(II)	10.86	Physisorption	[59]
Oxidized-MWCNTs	5.5	120	0.02	Cu(II)	14.00	Chemisorption	[60]
Zn-BDC@CT/GO	4.0	20	0.01	Arsenic	128.20	Chemisorption	[51]
F-CNTs@MOF@Gel	9.0	2000	0.02	Methyelene blue	106.50	Physisorption	[49]
SWCNT	3	75	0.12	Acid Blue 92	86.91	-	[47]
PET-NF-MWCNT	8	120	0.008	Methylene blue	7.047	Chemisorption	[50]

Note: * is in g/L, ** is in percentage (%).

4.2. Graphene-Based Nanoparticles

Graphene-based nanosheets (GBN), which are flexible and transparent, consist of three nanosheets which are all similar in structure, namely graphene, graphene oxide (GO) and reduced graphene oxide (rGO), as shown in Figure 3 [61]. GBN has become popular in the fields of optics, mechanics, electrics and, of course, environmental remediation. The final properties of GBNs depend on the route through which they are manufactured.

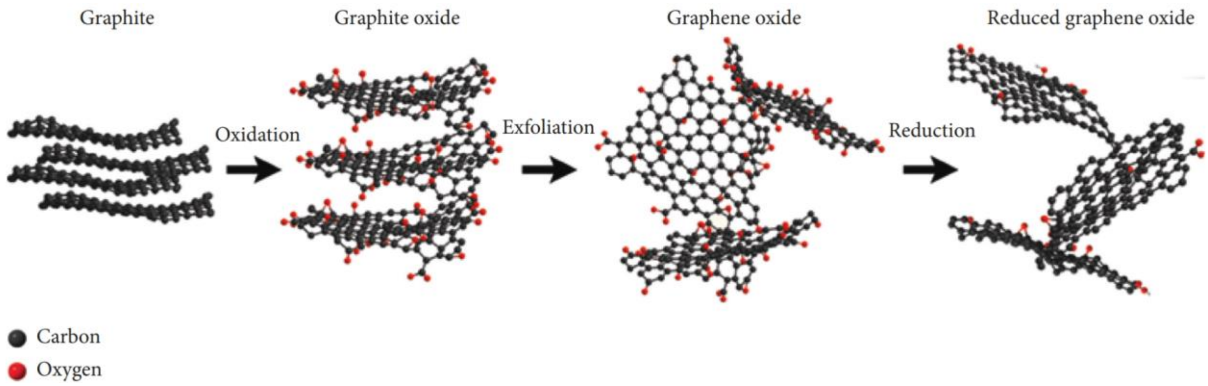

Figure 3. Structure of graphene, graphene oxide and reduced graphene oxide [62].

GO and rGO have surface-oxygen-containing groups (OCGs), chips on their surface, defined edges and structural wrinkles, which make them attractive for water decontamination. Studies have shown that these two materials significantly reduce the amount of organic waste and metallic ions in polluted aqueous solutions. GBNs have a higher adsorption capacity than CNTs, as well as resins and activated carbon, making them a popular choice for pollution control. Graphene can be manufactured using graphite as a raw material. The graphene is peeled off the graphite flakes by a process called mechanical exfoliation until a monolayer of graphene is obtained. Mechanical exfoliation cannot be used for the mass production of graphene and, therefore, it has only been used in laboratory-scale research. Monolayer graphene is very popular because of its high thermal conductivity, high electrical conductivity, flexibility and high resistance. Liquid exfoliation is another method used to produce graphene, and this method can produce it on a large scale but yields a less pure form than chemical exfoliation [62]. GO can be manufactured by fuming different chemicals as oxidizing agents. Traditionally, HNO_3 and $KClO_3$ have been used, but these release NO_x and ClO_2, which are very toxic gases. Thus, they were replaced with H_3PO_4. rGO can be obtained by applying reducing agents to GO and is manufactured as an alternative to graphene. It is highly desirable for water purification due to its functional groups (e.g., C-OH, C-O-C, C=O) and its structure of wrinkles and cracks, which increase the surface area. Chemical reduction using borohydrides, hydrazine and acidic/alkaline reductions are the main production routes for GO. Thermal reduction and microbiological reduction can also be used [63].

The defined edges and defects of GBNs, which are produced during processing, are key attributes that make them useful for water decontamination, as they provide a large surface area (2630 m^2/g) [64]. Due to the sp^2 aromatic structure of GBN, they are chemically stable in acid and alkaline conditions, making them suitable for use in WWTPs. GO and rGO are low in cost and have many adsorption sites that can adsorb PAHs, dyes, organic pollutants and antibiotics, all of which can be difficult to remove using the current wastewater treatment technologies. Graphene can also adsorb organic material, but the adsorption capacity depends on the pH, the temperature, the natural organic matter and the ionic strength. GO has been heavily relied on for the removal of different dyes, including methylene blue and methyl violet. It also has hydrophilic and hydrophobic properties, making it efficient in separating contaminants from wastewater [65,66]. The key attributes that make GO a promising method for the removal of several wastewater contaminants are its large theoretical specific surface, high negative charge density, surface hydrophobic interaction, hydrophilicity and ease of synthesis from readily available natural graphite using exfoliation or chemical oxidation methods [67,68].

Yang et al. [69] conducted a study on the adsorption capacity of polar and non-polar compounds by colloidal GO. They realised a strong adsorption affinity of GO for all the tested compounds. rGO adsorbed non-polar aromatic organic compounds, such as PAHs and nitroaromatic compounds, better than GO. This reinforces the importance of wastewater characterisation before the administration of the most effective nanomaterial for its treatment. GO, which has oxidative debris on the surface, can reduce the adsorption performance by blocking the adsorption sites. A sample of GO without oxidative debris was tested; it was more effective in absorbing 1-nitropyrene compared to raw GO by 75%. The conditions of the solution in which the GBNs are placed play a role in the adsorption. The adsorption of antibiotics (doxycycline, tetracycline and oxytetracycline) by GO was also tested and yielded adsorption capacities of 398.4, 212.3 and 313.5 mg/g, respectively. When the pH was decreased, the adsorption capacity increased, and for rGO, the adsorption capacity increased with the increase in pH [69]. Generally, GO-based materials present a higher sorption capacity, even for trace metals. This makes them appealing; however, the high cost of their synthesis and different forms of complex functionalization limits their large scale application. Table 3 presents the recent reported studies on the use of GO-based nanomaterials for wastewater treatment.

Table 3. Application of GO-based nanomaterials for the removal of wastewater contaminants.

Adsorbent	pH	Contact Time (min)	Adsorbent Dose (g)	Initial Concentration (mg/L)	Target Pollutant	Maximum Adsorption Capacity (mg/g)	No. of Reuse	Ref.
GO-Citrate	7	5	0.006	50	MB	222.22	5	[70]
GO-Citrate	6	1	0.0024	150	Cu(II)	270.27	5	[70]
Clay/GO/Fe_2O_3	11	-	0.100	1	MB	19.99	-	[71]
Alginate@MOF-rGO	7	720	0.001	10	Tetracycline	43.76	6	[72]
Alginate@MOF-rGO	7	720	0.001	10	Ciprofloxacin	40.76	6	[72]
ZnO/C-foam/GQDs/Alginate	6	30	0.001	5	MB	92.048	5	[73]
ZnO/C-foam/GQDs/Alginate	6	30	0.001	5	Pb(II)	135.624	5	[73]
SGO/cellulose acetate	6	30	0.005	300	MB	239.8	6	[74]
LDH/rGO/PAA-NC	6.3	18.50	0.02	110	Tetracycline	887.5	5	[75]
G/CS/GQD	5	150	-	30	Tetracycline	-	8	[76]
GO-Fe_3O_4	6	5	0.01	350	MB	212.54	5	[77]
GO-Chitosan	7	20	0.002	10	Cu(II)	58.5	-	[78]
UT-mGO	3	15	0.01	0.1	Indigotin blue dye	-	-	[79]
rGO aerogel	6	120	0.001	300	Antimony (II) and (V)	168.58 and 206.72	10	[80]

Note: LDH is layered double hydroxide, MB is methylene blue, UT is deep eutectic solvent, GQD is graphene quantum dots, PAA is poly acrylic acid.

4.3. Fullerenes

Fullerenes are very important carbon-based materials that have been tested for the treatment of water and wastewater. These materials are obtained through the very slow condensation of vaporized carbon [81]. They were discovered when experiments were conducted to understand how long-chain molecules can be formed in the circumstellar and interstellar spaces in the presence of a laser beam [82]. This carbon structure is very similar to graphite but has rolled-up layers and can take the form of tubular, spherical, and ring-like geometric shapes. The difference between graphite and fullerenes is that while graphite has a hexagonal carbon atomic structure, the latter has pentagonal and hexagonal carbon rings [83]. Normally, the slow condensation of carbon vapor results in spherical fullerenes. However, the use of a catalyst during synthesis can yield tubular or ring-like structures. Fullerenes are usually represented as C_{20+n}, and the C_{60} spherical family has been widely explored because of its unique sp2 hybridization and mechanical strength [84]. It can withstand high pressures of up to 3000 psi without deformation and has a bulk modulus of 668 GPa, which makes it harder than diamond [85]. Moreover, it has a high dielectric constant of 4, high affinity fir electrons, large surface-to-volume ratio and a high refractive index. It is also hydrophobic i.e., insoluble, or slightly soluble in water, although it can dissolve in benzene, toluene and carbon disulphide [86]. Additionally, it is the only carbon allotrope that can be dissolved at room temperature, making its synthesis straightforward.

To increase the solubility of nC_{60}, it must be functionalized, as this is obtainable through the use of carbon nanotubes. The incorporation of carboxyl, hydroxyl, epoxy groups and heteroatoms increases the material's capacity to bind organic molecules in an aqueous medium via covalent or non-covalent bonding. These characteristics make C_{60} a suitable material for environmental applications. It has been reported that under specific conditions, C_{60} is not cytotoxic or harmful [87], and it has a neutral biological consequence [88,89]. Water-soluble C_{60} and its derivates have been investigated for their antibacterial activities, and they were found to be toxic to *Escherichia Coli* and *Bacillus subtilis*, hindering their survival under low salt concentrations [90]. Their effectiveness against fungal spores has also been demonstrated [91], as shown in Figure 4E,F. Another study on the biodegradation of sewage sludge using C_{60} via anaerobic digestion indicated no significant effect on the anaerobic community's structure or performance [92]. An in vitro analysis suggested that C_{60} is not harmful to humans and animals; however, there is an observable, serious toxicity to animals in vivo [93]. This cytotoxicity normally arises from surface-modified C_{60}. In general, C_{60} fullerenes are not cytotoxic and can be deployed as adsorbents in water treatment, as fillers in a membrane and even in electrochemical treatment.

Glyphosate, a herbicide used for weed control, is a notable source of water pollution with little or no regulation in many countries. The theoretical elucidation of the adsorption of glyphosate on C_{60} in a vacuum or water reveals that it occurs in at least three different forms, with adsorption energy minima of -0.575 (-0.431) eV, -0.480 (-0.372) eV and -0.451 (-0.402) eV, respectively [94]. However, the effect of the ionic state of glyphosate should be considered carefully, since it can reduce adsorption. Another study demonstrated that the solid-state mixing of $ZnFe_2O_4$ and fullerene CNT yielded magnetic fullerene nanoparticles capable of removing heavy metals (Hg(II), Cd(II), Sn(II), and Pb(II)) from aqueous solution [95]. The addition of $ZnFe_2O_4$ improved the adsorption capacity of the fullerene by about 25%, and the adsorbent could be reused after chemical treatment with either EDTA or HNO_3.

Recent developments in the application of this nanomaterial have featured the utilisation of C_{60} and TiO_2 for the degradation of a wide variety of pollutants, as well as the application of computational methods (such as density functional theory, DFT) to elucidate the molecular interactions between C_{60} and TiO_2. Qi et al. [96] demonstrated that the modified C_{60}-aTiO_2 nanocomposite possessed an enhanced dye degradation activity against methylene blue. A photocatalytic mechanism was proposed using DFT, and it was realised that incorporating C_{60} into the TiO_2 surface introduced an additional doping site, resulting in an improved performance. The application of water-soluble fullerol for the activation of TiO_2 under visible light was demonstrated to be a viable route for inducing the reduction of toxic Cr^{VI} to less toxic Cr^{III} in water [97]. Given the ease of synthesis of this class of nanomaterials and their enhanced visible light activity, the application of fullerene nanomaterials for water and wastewater treatment is expected to grow in the coming years.

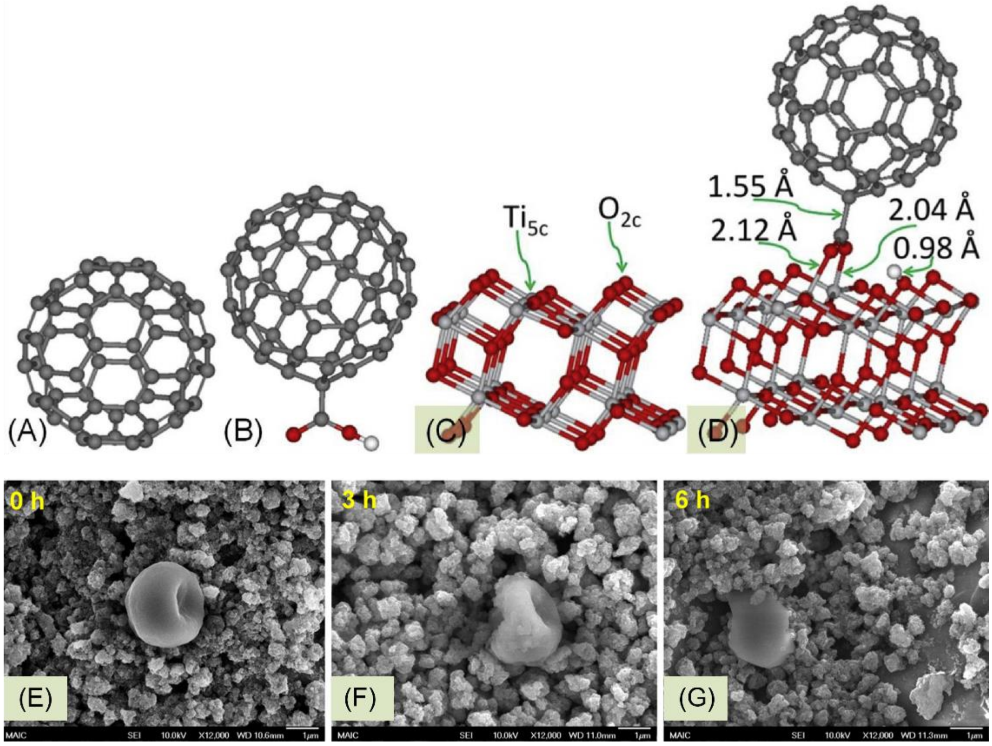

Figure 4. Optimised structures of (**A**) C_{60}, (**B**) C_{60}-COOH, (**C**) clean a-TiO_2 and (**D**) C_{60}-COOH@a-TiO_2, obtained via DFT computations [96]. Morphological changes in *Aspergillus niger* spores before inactivation (**E**) and after being inactivated by C_{60}/TiO_2 for (**F**) 3 h and (**G**) 6 h, respectively [91].

4.4. Silver Nanoparticles

The overuse, incorrect use and incorrect disposal of antibiotics has led to the rapid growth of antibiotic resistance. WWTPs are said to be a reservoir for antibiotic-resistant bacteria, as they are not killed before their release into the environment. This increased resistance is a great concern for the future development of new antibiotic drugs [98]. For many decades, silver nanoparticles have been known to have excellent antimicrobial properties. While they are extremely toxic to bacteria such as *E. coli*, they are only slightly toxic to animal cells at a certain concentrations. Silver has been and is still used for drinking water disinfection. Silver nanoparticles can be manufactured by inert gas condensation (IGC) [99], where temperatures above 2000 °C are used. The temperature can be varied to change the size of the nanoparticles.

Another method used to manufacture silver nanoparticles is co-condensation, where the use of higher temperatures leads to larger particle sizes and a narrower distribution [100]. When grown using the ICG method, the average particle size is 75 nm, whereas an average particle size of 15 nm can be achieved when the co-condensation method is applied [101]. As the co-condensation method produces smaller particles (with an increased surface area), it is a viable synthesis route, as smaller particle sizes possess better adsorption properties. In addition to these methods, chemical reduction, microemulsion, UV-initiated photoreduction and micro-assisted synthesis can be applied for the synthesis of silver nanoparticles. The interested reader may refer to the extensive review by Iravani et al. [102], which discusses several synthesis methods. In the study by Baker et al. [101], the antimicrobial effect of silver nanoparticles was tested using *E. coli*. The nanoparticles were mixed with *E. coli* and spread on agar plates. Plates containing silver nanoparticles were also used, and the *E. coli* was spread on these plates. Figure 5 shows the colony-forming unit (CFU) on each of the plates using different methods. Increasing the concentration of silver led to increasing antibacterial behaviour. Similar antimicrobial properties have been reported in the following studies [103,104].

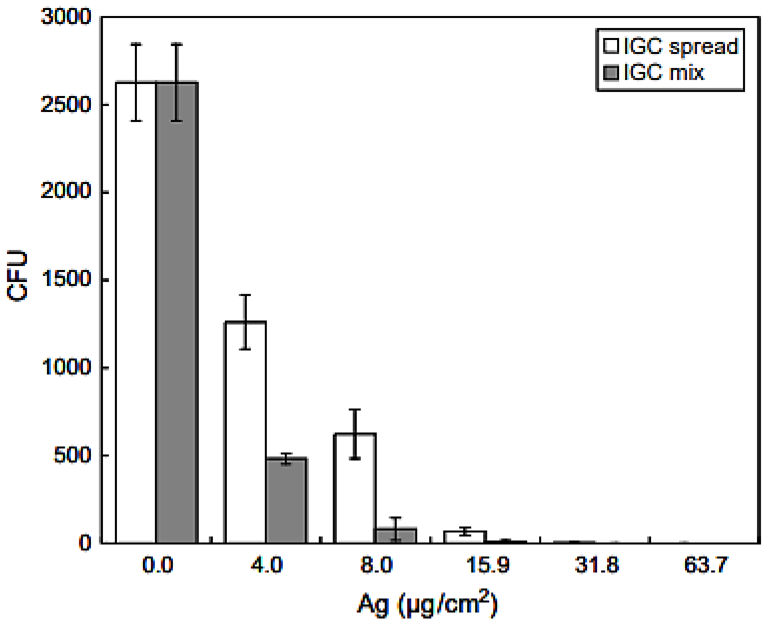

Figure 5. Antimicrobial effect of silver nanoparticles on bacteria spread on plates containing silver nanoparticles and on bacteria mixed with silver nanoparticles and then spread on a plate. The IGC method was used to produce these nanoparticles [101].

Silver nanoparticles have been demonstrated to be effective in eliminating over 700 microorganisms found in WWTPs. Silver nanoparticles target microorganisms through more than three mechanisms. This implies a reduced possibility of mutation resulting in resistance. Even at very low concentrations, silver nanoparticles are very effective. The silver ions bind to the DNA of the microorganisms, preventing them from taking up salt and phosphorous, which are necessary transport mechanisms for the bacteria [105]. This also prevents the necessary respiratory mechanisms required for the cell's survival. Silver nanoparticles have also been used as an effective larvicidal agent. They are also used as antifouling membranes in UF processes. Silver nanoparticles have been shown to be effective against drug-resistant bacteria and biofilm-forming bacteria, as they prevent the biofilm from forming [106]. Madeła [107] examined the influence of 2 mg/L AgNPs on the biological wastewater treatment process in an SBR reactor. The AgNPs showed enhancing effects on the efficiency of the treatment process, as determined by the TOC removal (Figure 6). A similar study [108] by the same author using CuNPs, as subsequently presented, showed the opposite effect. Recently, silver-loaded magnetic nanoparticles were utilised for the removal of coliform bacteria and heterotrophic bacteria, as well as the reduction in the COD of wastewater treatment plants [109,110]. The smaller size of these nanoparticles provided an increased surface area for the effective adsorption of organic matter in the water sample. Another key and recent advancement in the application of AgNPs is the hybrid application of nano-silver and other polymers, which has been demonstrated to be an effective method for removing heavy metals from wastewater [110]. For, example, the combination of AgNP and polyvinyl alcohol/aminopropyltriethoxysilane is an effective route for the removal of Mn^{2+} ions, as well an effective antifungal agent [111]. In addition, AgNP complexed with the Schiff base N-(4-hydroxy-3-methoxybenzylidine)-biphenyl-4-amine is effective for the removal of Cu^{2+} ions [112].

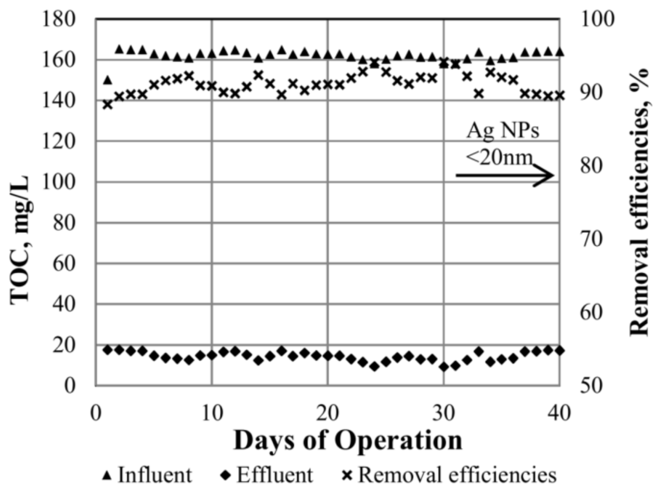

Figure 6. The impact of AgNPs on TOC removal in an SBR [107].

4.5. Copper Nanoparticles

Copper nanoparticles also possess exceptional antimicrobial qualities against Gram-positive and Gram-negative bacteria. The antimicrobial impacts of silver and copper particles on *E. coli*, *S. aureus* and *Bacillus subtilis* were examined in the work of Ruparelia et al. [113]. Copper showed a higher antibacterial activity in the inactivation of *B. subtilis*, whereas the silver nanoparticles outperformed copper in ensuring the inaction of *E. coli* and *S. aureus*. Thus, copper nanoparticles have a great affinity towards *B. subtilis* and are a good choice of nanomaterials for the purpose of inactivation. A study by Suleiman et al. [114] investigated water decontamination by synthesised copper oxide (CuO) nanoparticles alone and CuO nanoparticles stabilised with a surfactant. The nanoparticles were formed using a precipitation method (which is environmentally friendly, safe and simple). The average size of the rod-shaped nanoparticles was between 7 and 12 nm. Parameters such as the nanoparticle size, the concentration of nanoparticles, pH, temperature of wastewater and contact were considered. The antimicrobial effects of CuO were observed when the concentration reached 100 µg/mL. However, the antimicrobial effects of the CuO nanoparticles stabilised with a surfactant were observed when the concentration was only 10 µg/mL. Of the three different sizes (9.1, 11.4 and 12.4 nm) of nanoparticles produced, the largest 12.4 nm particles had the least significant antibacterial activity, whereas the 11.4 nm particles showed the best antibacterial effects. The bacteria considered were total coliforms (TC), faecal coliforms (FC) and *E. faecalis*. Figure 7 also illustrates the impact of the contact times applied on the observed antibacterial activity.

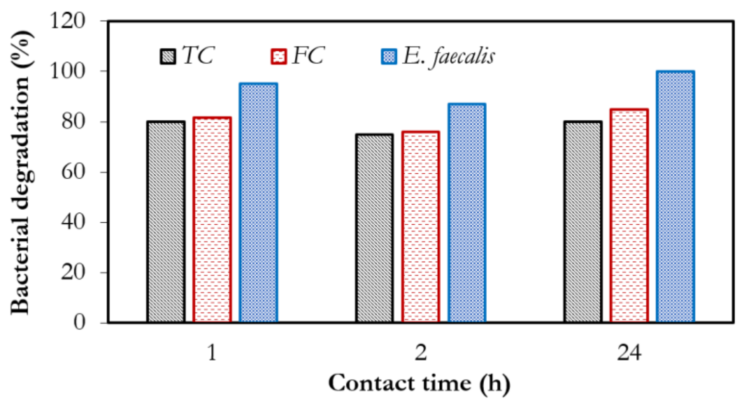

Figure 7. Contact times of 1, 2 and 24 h of CuO and their effects on TC, FC and *E. faecalis* degradation [114].

It was also realised that a lower temperature (25 °C) was required for inactivation when the surfactant stabilised CuO nanoparticles were used, compared to the 30 °C requirement of the ordinary CuO nanoparticles. The typical average temperature of wastewater is between 10 and 20 °C but can be higher because of warm effluents originating from households and businesses. The pH also has an impact on the antibacterial effect of CuO nanoparticles with and without the surfactant. Table 4 shows the results of the antibacterial effects on TC, FC and *E. faecalis* using CuO nanoparticles alone and those modified with the surfactant tetra-octylammonium bromide (TOAB(3)).

Table 4. The antibacterial effects of pH 6, 7 and 8 using CuO nanoparticles alone and modified with a surfactant (TOAB(3)) [114].

Bacteria/pH	6		7		8	
	CuO (4)	CuO-TOAB (3)	CuO (4)	CuO-TOAB (3)	CuO (4)	CuO-TOAB (3)
TC	88%	97%	87%	96%	86%	94%
FC	89%	95%	88%	92%	86%	90%
E. faecalis	92%	98.5%	91%	98%	89%	97%

Cu nanoparticles can also be synthesized via one-pot synthesis using underwater plasma [115]. The one-pot synthesis method has the advantages of an improved reaction time and high throughput. A schematic of the one-pot method is presented in Figure 8.

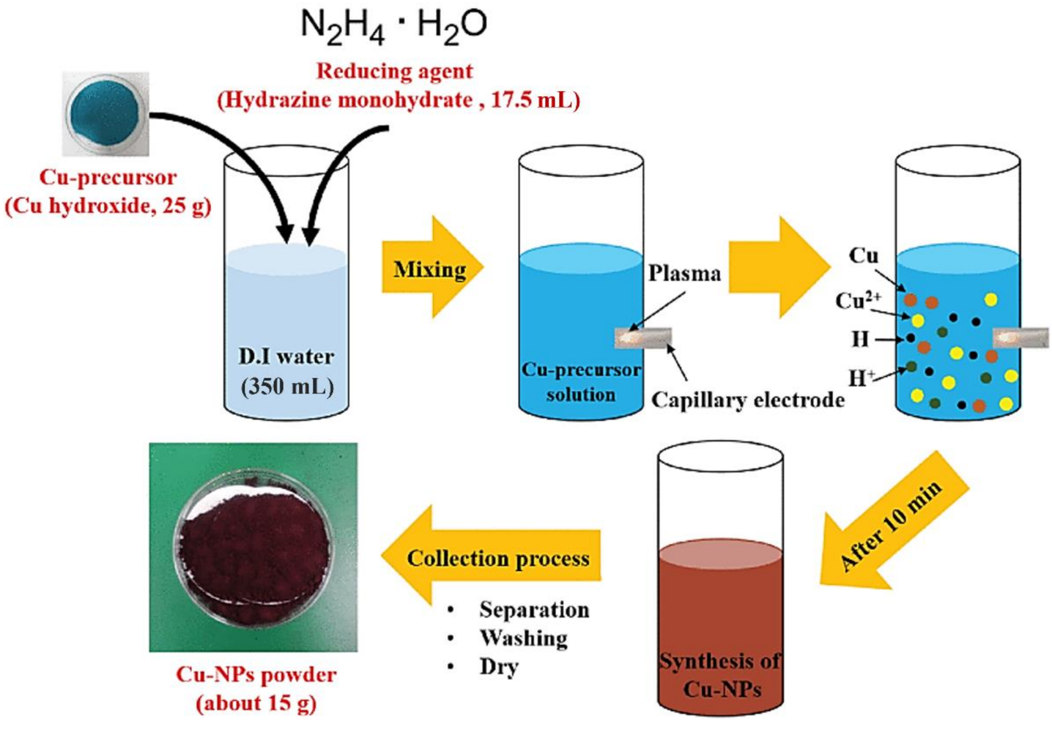

Figure 8. Schematic of the one-pot synthesis of Cu nanoparticles. Adapted from Hu et al. [115].

In addition to the antimicrobial properties of Cu (although it is not as effective as Ag), Cu nanoparticles also act as surface area and pore volume enhancers of polymeric beads (the commonly applied substrate for nanoparticle utilisation during large-scale applications) [116]. Thus, they can provide the Ag nanoparticles (in the beads) with better access to different bacteria when Cu and Ag nanoparticles are simultaneously applied for wastewater treatment. As in the case of Silver, the combination of Cu nanoparticles with the –SH groups of key microbial enzymes is the probable inactivation mechanism [117]. However, further studies are required to validate this mechanism. It has been found that Cu nanoparticles (CuNP), particularly at high concentrations, can alter the physicochemical properties of activated sludge. Chen et al. observed a decrease in the flocculation capacity of activated sludge at a CuNP concentration between 30 and 50 mg/L [118]. However, at a lower concentration of 0.1–10 mg/L, there was no observable impact on the activated sludge (Figure 9) and the consequent removal of nitrogen from the wastewater, as nearly all the CuNPs were absorbed by the activated sludge [119]. Conversely, Madeła [108] showed that a CuNP concentration of 3 mg/L resulted in the decreased effectiveness of wastewater treatment from 92.17% to 71.9% (based on the TOC values). Similar observations were also reported by Chen et al. [120], where phosphorus removal was studied. Thus, CuNPs may negatively impact the activity of activated sludge in sequencing batch reactors. This was attributed to the changes in the microorganism concentration in the activated sludge. These observations demonstrate the impact of the CuNP concentration on the activated sludge, and it can thus be argued that CuNPs may be better utilised for the subsequent disinfection stages of the treatment process. Other copper-containing nanoparticles, such as $CuFe_2SO_4$ NPs, have also found numerous applications for water treatment, particularly when they are combined with other materials (as a surface coating) to enhance their adsorption capacities, as well as for photodegradation [121].

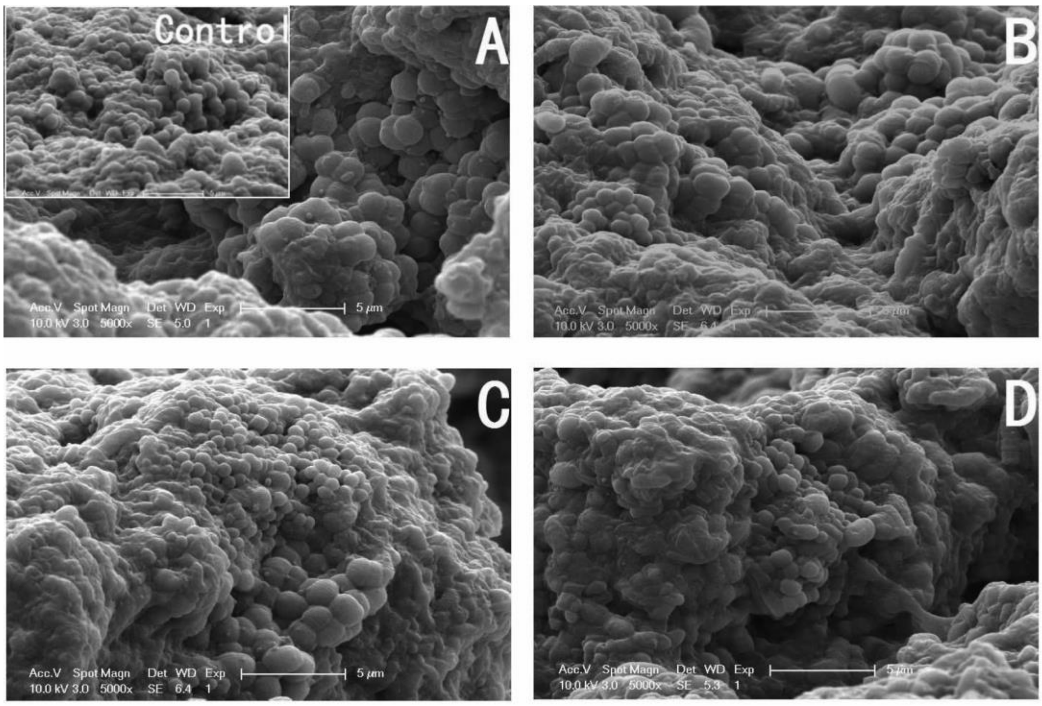

Figure 9. SEM images showing activated sludge exposed to different concentrations (0.1 mg/L (**A**), 1 mg/L (**B**), 5 mg/L (**C**) and 10 (**D**) mg/L) of CuNPs [119]. The surfaces of the cells did not seem to be damaged by the concentrations investigated. However, the toxic effects of CuNPs (at higher concentrations) are illustrated in another study by the authors [118].

4.6. Iron Nanoparticles

The study by Daniel et al. [106] illustrated the antibacterial properties of iron nanoparticles, particularly zero-valent iron nanoparticles. These particles were shown to inactivate Gram-negative *E. coli.*, as well as *Pseudomonas fluorescents* and *B. subtilis.* Iron oxide nanoparticles are also promising candidates for contaminant removal in WWTPs due to their easy separation, low cost, magnetic properties, robust adsorption capacity and improved stability. Iron oxide nanomaterials have also successfully been used as an adsorbent of heavy metals (Pb, Zn, Hg, Ni, Cd, Cr), which are increasingly problematic, even at low levels, due to their toxicity to humans, animals and plants [122,123]. Iron oxide nanoparticles were also shown to eliminate mercuric ions, cadmium ions and copper ions in the work of Xu et al. [37]. Zero-valent iron particles were also used to remove methyl blue from water and from a water-ethanol mixture (50:50) in a study by Sawafta and Shahwan [124].

They realised that water solutions achieved the best removal of methyl blue compared to the water-ethanol solution. Table 5 presents some of the bacteria that can be removed by silver, copper and iron oxide nanoparticles. Recent advances in the application of these nanomaterials have featured the development of spinel ferrite nanoparticles (SFNPs) and their derivative composites (SFNCs) (Figure 10), which are sometimes used as photocatalysts [121]. Some of the commonly applied spinel ferrites include Fe_3O_4, $CuFe_2O_4$, $MnFe_2O_4$, $ZnFe_2O_4$, $NiFe_2O_4$ and $CoFe_2O_4$ [125]. Recently, SFNPs were utilised for the degradation of dyes in textile effluents under visible light [126]. A 99% degradation of methylene blue was observed using Fe_3O_4@TiO_2 with H_2O_2 [127]. The removal of phenols and chlorophenols (one of the largest groups of environmental pollutants) was also effectively demonstrated using SFNPs [128,129]. Graphitic carbon sand composite and bentonite-supported $MnFe_2SO_4$ were applied for the degradation of ampicillin (AMP) and oxytetracycline (OCT) antibiotics under visible light; 96% and 99% degradations of AMP and OTC were observed after the treatment [130]. It is important to mention that the use of these NPs has been complemented by several oxidation-based treatment techniques, such as ozone, hydrogen peroxide and UV-based treatment methods. Catalytic ozonation, which involves the hybrid application of ozone and NPs, has been effectively utilised for the degradation of phenacetin (PNT) [131]. This process results in the generation of critical intermediates, such as H_2O_2 and $OH^{\bullet}$ radicals, which further accelerate the decontamination process.

Table 5. Silver, copper and iron oxide nanoparticles and some of the pathogens they are effective against (adapted from [35,106,113]).

Nanoparticle	Pathogen
Silver	*Klebsiella pneumoniae, Bacillus anthracis, Bacillus subtilis, Staphylococcus aureus, Acinetobacter baylyi, E. coli, Candida albicans, Salmonella Typhimurium, Salmonella epidermidis, P. aeruginosa, P. vulgaris, methicillin sensitive S. aureus.*
Copper	*Micrococcus luteus, Staphylococcus aureus, Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa, Aspergillus flavus, Aspergillus niger and Candida albicans.*
Iron Oxide	*Staphylococcus aureus, Shigella flexneri, Bacillus licheniformis, Bacillus brevis, Vibrio cholerae, Pseudomonas aeruginosa, Streptococcus aureus, Staphylococcus epidermidis, Bacillus subtilis.*

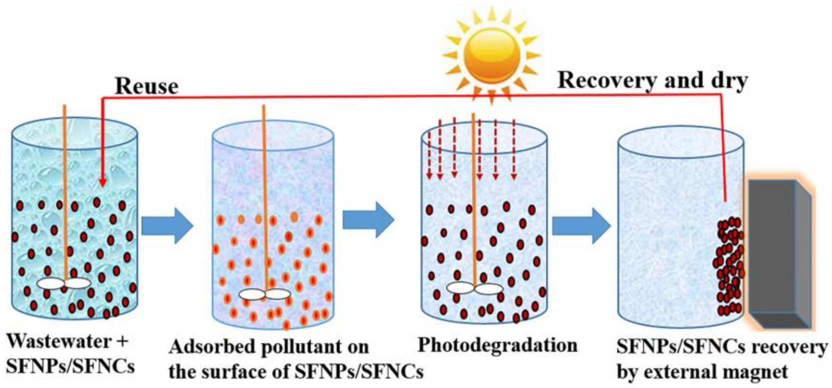

Figure 10. Schematic representation of wastewater treatment using SFNPs/SFNCs, showing their potential for recovery and reuse [125].

5. Challenges of Nanoparticle Application

In addition to surfactant stabilisers, more investigations are required to fully comprehend and improve the stability of nanoparticles, as well as the development of a new understanding of the mechanisms of surface energy reduction. There are also concerns that other compounds (apart from the target contaminant) may be adsorbed during the nanoparticle treatment of wastewater, leading to a reduction in the general efficiency of the decontamination process. A typical example of this is the adsorption of phosphates instead of heavy metals, which are usually the constituents of interest. To combat this limitation, chelating ligands have been grafted onto the surfaces of nanoparticles to aid in the uptake of heavy metals from the water. The environmental fate of engineered nanomaterials and their possible effects on human health are also a growing concern and have not been adequately investigated in the literature. Thus, further investigations are required regarding the toxicity and pathology of nanomaterials and their impacts on the environment. Upon entry into the environment, there are many mechanisms of exposure to humans, including dermal contact, the inhalation of water aerosols and ingestion of contaminated drinking water. Predictions of the possible physical and biological effects have proven difficult, but they are necessary [37]. Of particular difficulty is the generalization of the materials' toxicity, as different behaviours are often observed for the different nanomaterial types. The adsorption of nanoparticles has been observed in the gastrointestinal tract, enabling them to be further distributed around the body. The data collected on the health effects of nanoparticles is too generic to form a concrete conclusion.

There are various sources from which nanomaterials can leach into the environment, such as point sources including WWTPs and manufacturing plants or nonpoint sources such as runoffs. Thus, future studies must analyse both sources to ascertain the presence and concentrations of nanoparticles. Samples from WWTP effluents, surface waters and soil ought to be considered. Drinking water usually undergoes many treatment steps to ensure the removal of nanomaterials, such as flocculation, filtration coagulation and sedimentation. Alum coagulants have been proven to remove various amounts of nanoparticles from water, but the amount depends on the water chemistry and the amount of alum coagulant used [132,133]. Metal oxide nanoparticles have been removed from water using a 0.45 µm filter [132]. However, further research is required on the effectiveness of nanoparticle removal by filtration. Additionally, new developments on the techniques and methods used for nanoparticle detection and characterization are needed. These methods must be suitable for use in complex matrices such as surface waters, and they must be highly sensitive, robust and cost-effective [134]. The specific challenges affecting the nanomaterials of interest in this study (carbon nanotubes, graphene-based nanomaterials and silver, copper and iron nanoparticles) are presented below.

5.1. Carbon Nanotubes

Although CNTs are promising materials for wastewater purification, there are some limitations. The synthesis and application of these membranes are still at an early stage. Furthermore, the cost of synthesis, improving the scale of manufacturing, and the environmental impacts and commercial readiness are the current considerations limiting their extensive large-scale application. Their release into the environment is a source of concern, as they constitute an occupational inhalation exposure risk. They also have the potential to negatively affect aquatic life if leached from WWTPs into the environment. Studies on rats showed that they had pulmonary inflammation and lung cellular propagation after exposure to CNTs [135,136]. The toxicity of CNTs also depends on factors such as their physical state, the way they are manufactured and the presence of impurities [43]. Functionalisation with carboxyl groups has been identified as a viable route for mitigating the toxicity of CNTs (particularly MWCNTs). Allegri et al. [137] demonstrated that the nanoparticle size (a consequence of the production route) affects the toxicity levels.

5.2. Graphene-Based Nanomaterials

In a similar way to CNTs, GBNs can be released from WWTPs into the environment and can pose a potential risk. As graphene is a relatively new material, evidence of its positive or negative biological impacts on humans is scarce. A recent study performed on animals demonstrated that the inhalation of graphene and graphene oxide induced lung damage [61]. However, there are preventative measures which can be taken to avoid the release and transportation of GBNs into the environment. They can be fixed to 2D membranes, which allow for the selective separation of certain molecules. They can also be collected and added to 3D aerogels or hydrogels, which makes their handling much easier, and they can be recycled and reused, thus reducing waste [69].

5.3. Fullerenes

An in vitro cytotoxicity investigation of SWNT, MWNT and fullerene in alveolar macrophages revealed an order of cytotoxicity based on mass of SWNT > MWNT > C60. At low concentrations of C60 of up to 226.00 $\mu g/cm^2$, no significant cytotoxicity was observed. High concentrations of C60 induced cell injury [138]. Another study revealed the severe harmful effects of C60 materials (concentrations of 50 mg/kg) on mouse embryos in vivo and in vitro [93]. There is still no known toxicity to humans; however, more investigations are required, considering that these nanomaterials can leach into underground water or persist after the treatment of drinking water. The influences of C_{60}'s interactions with micro-contaminants on the toxicity of river biofilms were investigated. The studied micro-contaminants were triclosan, diuron and venlafaxine. The results showed no toxic effects on the river biofilms by the C60. Moreover, the exposure of the contaminants with C_{60} at low concentrations revealed antagonistic effects in the case of diuron (decreased toxicity) and a synergistic effect (toxicity effects increase) in the case of triclosan [139]. The molecular structure of the contaminants plays a vital role in the mechanism of interaction with C_{60}.

5.4. Silver Nanoparticles

One of the limitations of using silver nanoparticles for WWT is the potentially high large-scale implementation costs, despite their relatively cheap preparation methods on the lab scale. Thus, it is implied that the economic viability of the materials' large-scale production may constitute a source of concern, depending on the intended application [101]. Despite the widely claimed low toxicity of silver nanoparticles [140], there are new reports on the adverse effects of silver nanoparticles on the reproduction of some experimental animals. The lungs and liver may also be at risk, as well as potential neurotoxic effects when inhalation occurs above the maximum admissible concentration [141,142]. However, the grafting of AgNPs onto selected polymers is a potential solution that could be used to mitigate the eco-safety concerns, as well as the prevalent challenge of nanoparticle coalescence [143].

5.5. Iron Nanoparticles

Zero-valent iron nanoparticles are prone to oxidation, aggregation and difficulty in their separation from aqueous solutions. However, coating these nanoparticles with an inert material, prevents their aggregation and improves their diffusion. Favela-Camacho et al. demonstrated the potential of sodium citrate, sodium metasilicate and colloidal silica from tetraethyl orthosilicate to stabilise suspensions of magnetite nanoparticles [144]. Encapsulation in a matrix, conjugation with supports and emulsification have been proposed as viable methods for enhancing their performance in wastewater treatment [145,146].

5.6. Copper Nanoparticles

The possible toxic effects of copper nanoparticles are unknown and remain to be a subject of ongoing investigation. A study by Chen et al. [118] examined the impact of copper nanoparticles (20–40 nm; 99% purity) on the physical-chemical properties of sludge. Properties such as dewatering, the surface charge, hydrophobicity, settleability, flocculation and extracellular polymer substance content were assessed using different concentrations of copper nanoparticles. At a concentration of 5 ppm, no observable effect on the tested parameters was observed. However, at concentrations of 30 ppm and 50 ppm, the hydrophobicity, flocculation ability and phosphorus removal efficiency decreased, whereas the surface charge and extracellular polymer substance content increased. This led to the conclusion that high concentrations of copper nanoparticles can alter the physical and chemical properties of sludge, which in turn affect the efficiency of wastewater treatment.

This concentration threshold effect and the nonuniform impact on the key parameters of the water quality present optimisation challenges when working with these nanomaterials.

6. Discussion

As water scarcity is a current and ongoing global problem, the search for improved methods of treating wastewater more efficiently for the purpose of reuse is important and necessary, particularly with climate change and population growth being the two main drivers of water scarcity. Conventional treatment technologies (preliminary, primary, secondary and tertiary), which mainly remove the bulk of the contaminants in wastewater, are essential for water purification. Considering the pitfalls of each treatment step, nanotechnology has been discussed as a potential solution that addresses these limitations. Some of the advantages of NP deployment include the removal of pathogens, pharmaceuticals, CECs and organic and inorganic contaminants in the nanoscale range. Most nanotechnology-based processes are environmentally friendly and recyclable. Adsorption is the widely adopted nano-based separation process, although membrane filtration is also effective and considered to have similar performance. However, membrane filtration processes are often plagued by the possibility of fouling. In this review, the use of CNTs was also presented, emphasizing their main advantage of low running/operational costs, as no external energy is required to propel the wastewater through the CNT. The hydrophilic and hydrophobic elements of CNTs enable the continuous flow of water while the contaminants are caught and removed. CNTs are a good choice for the removal of organic and inorganic contaminants, as well as PAHs. Their strength and antifouling properties also make them desirable for WWTPs.

Many structural properties of GBNs make them an attractive technology for contaminant removal. The chips and defined edges increase the surface area of GO and rGO, providing many binding sites on their surfaces and thus enhancing pollutant removal. The final structural properties of the produced graphene depend on the production method adopted. Liquid exfoliation can produce graphene on a large scale but yields a less pure form compared to production by chemical exfoliation. The chemical stability of GBNs in WWTPs is desirable, as they can withstand the extreme acidic and alkaline conditions that are commonly found in WWTPs. For the removal of PAHs, dyes and antibiotics, GO and rGO are more effective. The hydrophobic and hydrophilic properties of GOs also make them an attractive choice for water purification. It is crucial to emphasize that pH plays a key role in the adsorption capacity, as decreasing the pH of an aqueous solution increases the adsorption capacity of GOs.

Overall, silver nanoparticles are a fitting choice for pathogen removal, as they remove more than 700 different microorganisms and have excellent antifouling qualities. In WWTPs, biofilms cause problems by building up in pipes and inducing blockages. The use of silver nanoparticles for treating wastewater can ease this problem. As they possess a very low toxicity to animal cells, their exposure to the environment poses low risks. The applied temperature during their synthesis is a key factor affecting the size of the produced nanoparticles. Furthermore, iron oxide nanoparticles are particularly effective in removing lead contamination. The stability and adsorption capacity of iron nanoparticles make them extremely attractive. The development of spinel ferrite nanoparticles represents a key advancement in the application of iron-based nanoparticles for WWT. Furthermore, lower concentrations of CuO nanoparticles can be used if they are stabilised with a surfactant. This is crucial for determining their effective concentration levels for WWT applications and the corresponding synthesis costs. The smaller the size of the CuO nanoparticles, the better the antibacterial properties. Copper nanoparticles would be a good choice for the removal of *Bacillus subtilis*, as they have a strong affinity toward this microorganism. Temperatures between 25 °C and 30 °C would be optimal when applying CuO nanoparticles for WWT. Overall, modifying these nanoparticles with a surfactant provides additional benefits compared to the independent application of the nanoparticles. However, CuNPs (at certain thresholds) may have negative effect on activated sludge; thus posing a threat to the wastewater treatment process.

Membrane fabrication costs, their purification and the large-scale production of these nanomaterials are the key challenges affecting their translation to industrial settings/commercial implementation [147]. In addition to the potential toxicity of the nanomaterials, unknown by-products that form (via interactions between chemicals and pollutants) during wastewater treatment also pose an environmental concern. Furthermore, toxicity information on several of these nanomaterials is limited, despite the increasing research attention they have received (particularly in the case of carbon nanotubes). Thus, further investigations are required in this regard. The progressive reduction in the efficiency of nanoparticles over repeated treatment cycles also requires further investigation. This may be attributable to factors such as nanoparticle erosion and the accumulation of decomposition products on the active sites. In addition, the application of nanoparticles and ozone nanobubbles has tremendous potential for micropollutant removal, and is deserving of further investigation for the improvement of wastewater treatment efficiencies [148].

7. Conclusions

It is evident that the current large-scale WWT technologies have efficiency limitations, which result in the discharge of harmful compounds into the environment. The main risk is the ingestion of pathogen-laden water, which causes diverse illnesses, particularly in developing countries. Nanotechnology was discussed as a potential solution that can be used to address these limitations and a viable means of meeting the United Nations' sustainable development goals for clean water and sanitisation. The efficient removal of contaminants in the nanoscale range relies on the combination of current WWT technologies and nanotechnologies. The use of nanoparticles is promising, as some of them can be cost-effective, environmentally friendly and recyclable, particularly on a small scale. The ease of adaptability to existing treatment plants is also noteworthy, as major infrastructure may not be required. For the removal of organic and inorganic pollutants and PAHs, CNTs appear to be commonly used. GBNs are a popular choice for the decontamination of PAHs, dyes and antibiotics, whereas for pathogen removal, silver, copper and iron nanoparticles are most desirable. Silver/copper/iron nanoparticles can be coated onto CNTs or GBNs to enhance the removal of organic and inorganic pollutants, PAHs, dyes, antibiotics and pathogens. Surfactant modification, particularly for CuO nanoparticles, increases the contaminant removal efficiency in wastewater and should be further investigated using other classes of nanomaterials. The use of nanoparticles for WWT is still in its early stage, and more lab-scale and pilot-scale research and testing must be performed before their full-scale implementation in WWTPs. Further investigations are also required to determine the environmental effects of these nanomaterials, as well as their viability, via techno-economic assessments.

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Abbreviations

BSA	Bovine serum albumin
CEC	Contaminants of emerging concern
CFU	Colony forming unit

CNT	Carbon nanotube
CuO	Copper oxide
EDC	Endocrine disrupting chemicals
FC	Faecal coliforms
FO	Forward osmosis
FOG	Fats, oils and grease
GBN	Graphene-based nanosheets
GO	Graphene oxide
ICG	Inert gas condensation
MF	Microfiltration
MWCNT	Multi-walled carbon nanotube
NF	Nanofiltration
OCG	Oxygen-containing groups
PAH	Polycyclic aromatic hydrocarbons
rGO	Reduced graphene oxide
RO	Reverse osmosis
SBR	Sequencing batch reactor
SWCNT	Single-walled carbon nanotube
TAOB	Tetra-octyl ammonium bromide
TC	Total coliforms
TDS	Total dissolved solids
UF	Ultrafiltration
UV	Ultraviolet
WWT	Wastewater treatment
WWTP	Wastewater treatment plant

References

1. Diallo, M.; Duncan, J.; Savage, N. *Nanotechnology Applications for Clean Water: Solutions for Improving Water Quality*; William Andrew: Norwich, NY, USA, 2009; ISBN 0815519737.
2. Cheriyamundath, S.; Vavilala, S.L. Nanotechnology-based wastewater treatment. *Water Environ. J.* **2021**, *35*, 123–132. [CrossRef]
3. Nations, U. Sustainable Development Goals. Available online: https://sdgs.un.org/goals (accessed on 14 September 2022).
4. Cooley, H.; Ajami, N.; Ha, M.-L.; Srinivasan, V.; Morrison, J.; Donnelly, K.; Christian-Smith, J. Global water governance in the twenty-first century. In *The World's Water*; Springer: Berlin/Heidelberg, Germany, 2014; pp. 1–18.
5. WHO; UNICEF. *Progress on Drinking Water and Sanitation: 2012 Update*; WHO: Geneva, Switzerland; UNICEF: New York, NY, USA, 2012.
6. Madhura, L.; Singh, S.; Kanchi, S.; Sabela, M.; Bisetty, K. Inamuddin Nanotechnology-based water quality management for wastewater treatment. *Environ. Chem. Lett.* **2019**, *17*, 65–121. [CrossRef]
7. Bodzek, M.; Konieczny, K.; Kwiecińska-Mydlak, A. Nanotechnology in water and wastewater treatment. Graphene–the nanomaterial for next generation of semipermeable membranes. *Crit. Rev. Environ. Sci. Technol.* **2020**, *50*, 1515–1579. [CrossRef]
8. Tlili, I.; Alkanhal, T.A. Nanotechnology for water purification: Electrospun nanofibrous membrane in water and wastewater treatment. *J. Water Reuse Desalin.* **2019**, *9*, 232–248. [CrossRef]
9. Jain, K.; Patel, A.S.; Pardhi, V.P.; Flora, S.J.S. Nanotechnology in wastewater management: A new paradigm towards wastewater treatment. *Molecules* **2021**, *26*, 1797. [CrossRef]
10. Taran, M.; Safaei, M.; Karimi, N.; Almasi, A. Benefits and application of nanotechnology in environmental science: An overview. *Biointerface Res. Appl. Chem.* **2021**, *11*, 7860–7870. [CrossRef]
11. Tang, Z.; Ma, D.; Chen, Q.; Wang, Y.; Sun, M.; Lian, Q.; Shang, J.; Wong, P.K.; He, C.; Xia, D. Nanomaterial-enabled photothermal-based solar water disinfection processes: Fundamentals, recent advances, and mechanisms. *J. Hazard. Mater.* **2022**, *437*, 129373. [CrossRef]
12. Petronella, F.; De Biase, D.; Zaccagnini, F.; Verrina, V.; Lim, S.-I.; Jeong, K.-U.; Miglietta, S.; Petrozza, V.; Scognamiglio, V.; Godman, N.P. Label-free and reusable antibody-functionalized gold nanorod arrays for the rapid detection of *Escherichia coli* cells in a water dispersion. *Environ. Sci. Nano* **2022**, *9*, 3343–3360. [CrossRef]
13. Shiraishi, Y.; Yasumoto, N.; Imai, J.; Sakamoto, H.; Tanaka, S.; Ichikawa, S.; Ohtani, B.; Hirai, T. Quantum tunneling injection of hot electrons in Au/TiO_2 plasmonic photocatalysts. *Nanoscale* **2017**, *9*, 8349–8361. [CrossRef]
14. Riffat, R. *Fundamentals of Wastewater Treatment and Engineering*; CRC Press: Boca Raton, FL, USA, 2012.
15. Crini, G.; Lichtfouse, E.; Wilson, L.D.; Morin-Crini, N. Conventional and non-conventional adsorbents for wastewater treatment. *Environ. Chem. Lett.* **2019**, *17*, 195–213. [CrossRef]
16. Gautam, S.; Saini, G. Use of natural coagulants for industrial wastewater treatment. *Glob. J. Environ. Sci. Manag.* **2020**, *6*, 553–578.
17. Amin, M.T.; Alazba, A.A.; Manzoor, U. A review of removal of pollutants from water/wastewater using different types of nanomaterials. *Adv. Mater. Sci. Eng.* **2014**, *2014*, 825910. [CrossRef]

18. Britannica Wastewater Treatment. Available online: https://www.britannica.com/technology/wastewater-treatment/Primary-treatment#/media/1/666611/19281 (accessed on 14 September 2022).
19. Pei, M.; Zhang, B.; He, Y.; Su, J.; Gin, K.; Lev, O.; Shen, G.; Hu, S. State of the art of tertiary treatment technologies for controlling antibiotic resistance in wastewater treatment plants. *Environ. Int.* **2019**, *131*, 105026. [CrossRef]
20. Dutta, A.; Sarkar, S. Sequencing batch reactor for wastewater treatment: Recent advances. *Curr. Pollut. Rep.* **2015**, *1*, 177–190. [CrossRef]
21. Ge, H.; Batstone, D.J.; Keller, J. Operating aerobic wastewater treatment at very short sludge ages enables treatment and energy recovery through anaerobic sludge digestion. *Water Res.* **2013**, *47*, 6546–6557. [CrossRef] [PubMed]
22. Taheran, M.; Naghdi, M.; Brar, S.K.; Verma, M.; Surampalli, R.Y. Emerging contaminants: Here today, there tomorrow! *Environ. Nanotechnol. Monit. Manag.* **2018**, *10*, 122–126. [CrossRef]
23. Bassin, J.P.; Castro, F.D.; Valério, R.R.; Santiago, E.P.; Lemos, F.R.; Bassin, I.D. The impact of wastewater treatment plants on global climate change. In *Water Conservation in the Era of Global Climate Change*; Elsevier: Amsterdam, The Netherlands, 2021; pp. 367–410.
24. Gerba, C.P.; Pepper, I.L. Municipal wastewater treatment. In *Environmental and Pollution Science*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 393–418.
25. Achokhavatia Tertiary Wastewater Treatment in India. Available online: https://chokhavatia.com/skills/treatment-processes/tertiary-treatment/ (accessed on 14 September 2022).
26. Liu, Z.-Q.; Huang, C.; Li, J.-Y.; Yang, J.; Qu, B.; Yang, S.-Q.; Cui, Y.-H.; Yan, Y.; Sun, S.; Wu, X. Activated carbon catalytic ozonation of reverse osmosis concentrate after coagulation pretreatment from coal gasification wastewater reclamation for zero liquid discharge. *J. Clean. Prod.* **2021**, *286*, 124951. [CrossRef]
27. Joo, S.H.; Tansel, B. Novel technologies for reverse osmosis concentrate treatment: A review. *J. Environ. Manag.* **2015**, *150*, 322–335. [CrossRef]
28. de Almeida Lopes, T.S.; Hessler, R.; Bohner, C.; Junior, G.B.A.; de Sena, R.F. Pesticides removal from industrial wastewater by a membrane bioreactor and post-treatment with either activated carbon, reverse osmosis or ozonation. *J. Environ. Chem. Eng.* **2020**, *8*, 104538. [CrossRef]
29. Epelle, E.I.; Macfarlane, A.; Cusack, M.; Burns, A.; Amaeze, N.; Richardson, K.; Mackay, W.; Rateb, M.E.; Yaseen, M. Stabilisation of Ozone in Water for Microbial Disinfection. *Environments* **2022**, *9*, 45. [CrossRef]
30. Epelle, E.I.; Emmerson, A.; Nekrasova, M.; Macfarlane, A.; Cusack, M.; Burns, A.; Mackay, W.; Yaseen, M. Microbial Inactivation: Gaseous or Aqueous Ozonation? *Ind. Eng. Chem. Res.* **2022**, *61*, 9600–9610. [CrossRef] [PubMed]
31. Bora, T.; Dutta, J. Applications of nanotechnology in wastewater treatment—A review. *J. Nanosci. Nanotechnol.* **2014**, *14*, 613–626. [CrossRef] [PubMed]
32. Carpenter, A.W.; de Lannoy, C.-F.; Wiesner, M.R. Cellulose nanomaterials in water treatment technologies. *Environ. Sci. Technol.* **2015**, *49*, 5277–5287. [CrossRef] [PubMed]
33. Jiang, M.; Qi, Y.; Liu, H.; Chen, Y. The Role of Nanomaterials and Nanotechnologies in Wastewater Treatment: A Bibliometric Analysis. *Nanoscale Res. Lett.* **2018**, *13*, 233. [CrossRef]
34. Yin, Z.; Cui, C.; Chen, H.; Duoni; Yu, X.; Qian, W. The Application of Carbon Nanotube/Graphene-Based Nanomaterials in Wastewater Treatment. *Small* **2020**, *16*, 1902301. [CrossRef]
35. Hsueh, Y.H.; Lin, K.S.; Ke, W.J.; Hsieh, C.T.; Chiang, C.L.; Tzou, D.Y.; Liu, S.T. The antimicrobial properties of silver nanoparticles in bacillus subtilis are mediated by released Ag+ ions. *PLoS ONE* **2015**, *10*, e0144306. [CrossRef]
36. Hadei, M.; Mesdaghinia, A.; Nabizadeh, R.; Mahvi, A.H.; Rabbani, S.; Naddafi, K. A comprehensive systematic review of photocatalytic degradation of pesticides using nano TiO_2. *Environ. Sci. Pollut. Res.* **2021**, *28*, 13055–13071. [CrossRef]
37. 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.; et al. Use of iron oxide nanomaterials in wastewater treatment: A review. *Sci. Total Environ.* **2012**, *424*, 1–10. [CrossRef]
38. Nag, A.; Mukhopadhyay, S.C. Fabrication and implementation of carbon nanotubes for piezoresistive-sensing applications: A review. *J. Sci. Adv. Mater. Devices* **2021**, *7*, 100416. [CrossRef]
39. Moaseri, E.; Karimi, M.; Maghrebi, M.; Baniadam, M. Fabrication of multi-walled carbon nanotube–carbon fiber hybrid material via electrophoretic deposition followed by pyrolysis process. *Compos. Part A Appl. Sci. Manuf.* **2014**, *60*, 8–14. [CrossRef]
40. Parveen, S.; Rana, S.; Fangueiro, R. A review on nanomaterial dispersion, microstructure, and mechanical properties of carbon nanotube and nanofiber reinforced cementitious composites. *J. Nanomater.* **2013**, *2013*, 80. [CrossRef]
41. Öner, D.; Ghosh, M.; Bové, H.; Moisse, M.; Boeckx, B.; Duca, R.C.; Poels, K.; Luyts, K.; Putzeys, E.; Van Landuydt, K.; et al. Differences in MWCNT- and SWCNT-induced DNA methylation alterations in association with the nuclear deposition. *Part. Fibre Toxicol.* **2018**, *15*, 11. [CrossRef] [PubMed]
42. Donaldson, K.; Aitken, R.; Tran, L.; Stone, V.; Duffin, R.; Forrest, G.; Alexander, A. Carbon nanotubes: A review of their properties in relation to pulmonary toxicology and workplace safety. *Toxicol. Sci.* **2006**, *92*, 5–22. [CrossRef] [PubMed]
43. Ihsanullah. Carbon nanotube membranes for water purification: Developments, challenges, and prospects for the future. *Sep. Purif. Technol.* **2019**, *209*, 307–337. [CrossRef]
44. Endo, M.; Iijima, S.; Dresselhaus, M.S. *Carbon Nanotubes*; Elsevier: Amsterdam, The Netherlands, 1996; ISBN 0080426824.
45. Das, R. Carbon nanotube in water treatment. In *Nanohybrid Catalyst Based on Carbon Nanotube*; Springer: Berlin/Heidelberg, Germany, 2017; pp. 23–54.

46. Kalra, A.; Garde, S.; Hummer, G. Osmotic water transport through carbon nanotube membranes. *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 10175–10180. [CrossRef] [PubMed]
47. Balarak, D.; Zafariyan, M.; Igwegbe, C.A.; Onyechi, K.K.; Ighalo, J.O. Adsorption of acid blue 92 dye from aqueous solutions by single-walled carbon nanotubes: Isothermal, kinetic, and thermodynamic studies. *Environ. Process.* **2021**, *8*, 869–888. [CrossRef]
48. Dutta, A.K.; Ghorai, U.K.; Chattopadhyay, K.K.; Banerjee, D. Removal of textile dyes by carbon nanotubes: A comparison between adsorption and UV assisted photocatalysis. *Phys. E Low-Dimens. Syst. Nanostruct.* **2018**, *99*, 6–15. [CrossRef]
49. Zhang, Y.; Li, Y.; Wang, M.; Chen, B.; Sun, Y.; Chen, K.; Du, Q.; Pi, X.; Wang, Y. Adsorption of Methylene Blue from Aqueous Solution Using Gelatin-Based Carboxylic Acid-Functionalized Carbon Nanotubes@ Metal–Organic Framework Composite Beads. *Nanomaterials* **2022**, *12*, 2533. [CrossRef]
50. Essa, W.K.; Yasin, S.A.; Abdullah, A.H.; Thalji, M.R.; Saeed, I.A.; Assiri, M.A.; Chong, K.F.; Ali, G.A.M. Taguchi L25 (54) Approach for Methylene Blue Removal by Polyethylene Terephthalate Nanofiber-Multi-Walled Carbon Nanotube Composite. *Water* **2022**, *14*, 1242. [CrossRef]
51. Akha, N.Z.; Salehi, S.; Anbia, M. Removal of arsenic by metal organic framework/chitosan/carbon nanocomposites: Modeling, optimization, and adsorption studies. *Int. J. Biol. Macromol.* **2022**, *208*, 794–808. [CrossRef]
52. Mazumder, M.A.J.; Chowdhury, I.R.; Chowdhury, S.; Al-Ahmed, A. Removal of Pb2+ from water using the carbon nanotube-g-poly [(sodium methacrylate)-co-2-(methacryloyloxy) ethyl acetoacetate]: Experimental investigation and modeling. *Environ. Sci. Pollut. Res.* **2022**, *29*, 54432–54447. [CrossRef] [PubMed]
53. Jamshidian, M.; Sadeghalvad, B.; Ghasemi, I.; Ebrahimi, H.; Rezaeian, I. Fabrication of polyethersulfone/functionalized MWCNTs nanocomposite and investigation its efficiency as an adsorbent of Pb (II) ions. *Arab. J. Sci. Eng.* **2021**, *46*, 6259–6273. [CrossRef]
54. Wang, H.; Shang, H.; Sun, X.; Hou, L.; Wen, M.; Qiao, Y. Preparation of thermo-sensitive surface ion-imprinted polymers based on multi-walled carbon nanotube composites for selective adsorption of lead (II) ion. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *585*, 124139. [CrossRef]
55. Zhang, B.; Jin, Y.; Huang, X.; Tang, S.; Chen, H.; Su, Y.; Yu, X.; Chen, S.; Chen, G. Biological self-assembled hyphae/starch porous carbon composites for removal of organic pollutants from water. *Chem. Eng. J.* **2022**, *450*, 138264. [CrossRef]
56. Salam, M.A. Preparation and characterization of chitin/magnetite/multiwalled carbon nanotubes magnetic nanocomposite for toxic hexavalent chromium removal from solution. *J. Mol. Liq.* **2017**, *233*, 197–202. [CrossRef]
57. Alijani, H.; Shariatinia, Z. Effective aqueous arsenic removal using zero valent iron doped MWCNT synthesized by in situ CVD method using natural α-Fe_2O_3 as a precursor. *Chemosphere* **2017**, *171*, 502–511. [CrossRef]
58. Sun, W.; Jiang, B.; Wang, F.; Xu, N. Effect of carbon nanotubes on Cd (II) adsorption by sediments. *Chem. Eng. J.* **2015**, *264*, 645–653. [CrossRef]
59. Li, Y.-H.; Ding, J.; Luan, Z.; Di, Z.; Zhu, Y.; Xu, C.; Wu, D.; Wei, B. Competitive adsorption of Pb2+, Cu2+ and Cd2+ ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon N. Y.* **2003**, *41*, 2787–2792. [CrossRef]
60. Rodríguez, C.; Leiva, E. Enhanced heavy metal removal from acid mine drainage wastewater using double-oxidized multiwalled carbon nanotubes. *Molecules* **2019**, *25*, 111. [CrossRef]
61. DaNa Graphene. Available online: https://nanopartikel.info/en/knowledge/materials/graphene/ (accessed on 14 September 2022).
62. Jayakaran, P.; Nirmala, G.S.; Govindarajan, L. Qualitative and Quantitative Analysis of Graphene-Based Adsorbents in Wastewater Treatment. *Int. J. Chem. Eng.* **2019**, *2019*, 9872502. [CrossRef]
63. Jayakaran, P.; Nirmala, G.; Lakshmanarao, G. Synthesis and Analysis of Graphene Nano Composite. *Compos. Mater.* **2019**, *2*, 43.
64. Lee, C.; Chang, H.; Jang, H.D. Synthesis of Porous Graphene Balls by the Activation and Aerosol Process for Supercapacitors Application. *Part. Aerosol Res.* **2019**, *15*, 183–190.
65. Huang, T.; Yan, M.; He, K.; Huang, Z.; Zeng, G.; Chen, A.; Peng, M.; Li, H.; Yuan, L.; Chen, G. Efficient removal of methylene blue from aqueous solutions using magnetic graphene oxide modified zeolite. *J. Colloid Interface Sci.* **2019**, *543*, 43–51. [CrossRef] [PubMed]
66. Makhado, E.; Pandey, S.; Ramontja, J. Microwave assisted synthesis of xanthan gum-cl-poly (acrylic acid) based-reduced graphene oxide hydrogel composite for adsorption of methylene blue and methyl violet from aqueous solution. *Int. J. Biol. Macromol.* **2018**, *119*, 255–269. [CrossRef] [PubMed]
67. Peng, W.; Li, H.; Liu, Y.; Song, S. A review on heavy metal ions adsorption from water by graphene oxide and its composites. *J. Mol. Liq.* **2017**, *230*, 496–504. [CrossRef]
68. Hossain, M.D.F.; Akther, N.; Zhou, Y. Recent advancements in graphene adsorbents for wastewater treatment: Current status and challenges. *Chin. Chem. Lett.* **2020**, *31*, 2525–2538. [CrossRef]
69. Yang, K.; Wang, J.; Chen, X.; Zhao, Q.; Ghaffar, A.; Chen, B. Application of graphene-based materials in water purification: From the nanoscale to specific devices. *Environ. Sci. Nano* **2018**, *5*, 1264–1297. [CrossRef]
70. Abd-Elhamid, A.I.; Elgoud, E.M.; Emam, S.; Aly, H.F. Superior adsorption performance of citrate modified graphene oxide as nano material for removal organic and inorganic pollutants from aqueous solution. *Sci. Rep.* **2022**, *12*, 9204. [CrossRef]
71. Farooq, N.; Shanableh, A.; Qureshi, A.M.; Jabeen, S.; ur Rehman, A. Synthesis and characterization of clay graphene oxide iron oxide (clay/GO/Fe_2O_3)-nanocomposite for adsorptive removal of methylene blue dye from wastewater. *Inorg. Chem. Commun.* **2022**, *145*, 109956. [CrossRef]

72. Kim, N.; Cha, B.; Yea, Y.; Njaramba, L.K.; Vigneshwaran, S.; Elanchezhiyan, S.S.D.; Park, C.M. Effective sequestration of tetracycline and ciprofloxacin from aqueous solutions by Al-based metal organic framework and reduced graphene oxide immobilized alginate biosorbents. *Chem. Eng. J.* **2022**, *450*, 138068. [CrossRef]
73. Mahmoud, M.E.; Fekry, N.A.; Abdelfattah, A.M. Engineering nanocomposite of graphene quantum dots/carbon foam/alginate/zinc oxide beads for efficacious removal of lead and methylene. *J. Ind. Eng. Chem.* **2022**, *115*, 365–377. [CrossRef]
74. Basha, I.K.; El-Monaem, A.; Eman, M.; Khalifa, R.E.; Omer, A.M.; Eltaweil, A.S. Sulfonated graphene oxide impregnated cellulose acetate floated beads for adsorption of methylene blue dye: Optimization using response surface methodology. *Sci. Rep.* **2022**, *12*, 9339. [CrossRef] [PubMed]
75. Omidi, M.H.; Azqhandi, M.H.A.; Ghalami-Choobar, B. Synthesis, characterization, and application of graphene oxide/layered double hydroxide/poly acrylic acid nanocomposite (LDH-rGO-PAA NC) for tetracycline removal: A comprehensive chemometric study. *Chemosphere* **2022**, *308*, 136007. [CrossRef] [PubMed]
76. Ebratkhahan, M.; Zarei, M.; Arsalani, N. Facile synthesis and preparation of graphite/chitosan/graphene quantum dots nanocomposite cathode for electrochemical removal of tetracycline from aqueous solution. *Sep. Purif. Technol.* **2022**, *299*, 121663. [CrossRef]
77. Tishbi, P.; Mosayebi, M.; Salehi, Z.; Fatemi, S.; Faegh, E. Synthesizing magnetic graphene oxide nanomaterial (GO-Fe_3O_4) and kinetic modelling of methylene blue adsorption from water. *Can. J. Chem. Eng.* **2022**, *100*, 3321–3334. [CrossRef]
78. Politaeva, N.; Yakovlev, A.; Yakovleva, E.; Chelysheva, V.; Tarantseva, K.; Efremova, S.; Mukhametova, L.; Ilyashenko, S. Graphene Oxide-Chitosan Composites for Water Treatment from Copper Cations. *Water* **2022**, *14*, 1430. [CrossRef]
79. Khah, M.H.; Jamshidi, P.; Shemirani, F. Applicability of an eco-friendly deep eutectic solvent loaded onto magnetic graphene oxide to preconcentrate trace amount of indigotin blue dye. *J. Mol. Liq.* **2021**, *342*, 117346. [CrossRef]
80. Nundy, S.; Ghosh, A.; Nath, R.; Paul, A.; Tahir, A.A.; Mallick, T.K. Reduced graphene oxide (rGO) aerogel: Efficient adsorbent for the elimination of antimony (III) and (V) from wastewater. *J. Hazard. Mater.* **2021**, *420*, 126554. [CrossRef]
81. Lobato-Peralta, D.R.; Duque-Brito, E.; Villafán-Vidales, H.I.; Longoria, A.; Sebastian, P.J.; Cuentas-Gallegos, A.K.; Arancibia-Bulnes, C.A.; Okoye, P.U. A review on trends in lignin extraction and valorization of lignocellulosic biomass for energy applications. *J. Clean. Prod.* **2021**, *293*, 126123. [CrossRef]
82. Kroto, H.W.; Heath, J.R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E. C60: Buckminsterfullerene. *Nature* **1985**, *318*, 162–163. [CrossRef]
83. Mohan, M.; Sharma, V.K.; Kumar, E.A.; Gayathri, V. Hydrogen storage in carbon materials. *Energy Storage-Wiley* **2019**, *159*, 781–801. [CrossRef]
84. Jani, M.; Arcos-Pareja, J.A.; Ni, M. Engineered Zero-Dimensional Fullerene/Carbon Dots-Polymer Based Nanocomposite Membranes for Wastewater Treatment. *Molecules* **2020**, *25*, 4934. [CrossRef] [PubMed]
85. Mojica, M.; Alonso, J.A.; Méndez, F. Synthesis of fullerenes. *J. Phys. Org. Chem.* **2013**, *26*, 526–539. [CrossRef]
86. Ruoff, R.S.; Tse, D.S.; Malhotra, R.; Lorents, D.C. Solubility of C60 in a variety of solvents. *J. Phys. Chem.* **1993**, *97*, 3379–3383. [CrossRef]
87. Sayes, C.M.; Fortner, J.D.; Guo, W.; Lyon, D.; Boyd, A.M.; Ausman, K.D.; Tao, Y.J.; Sitharaman, B.; Wilson, L.J.; Hughes, J.B.; et al. The Differential Cytotoxicity of Water-Soluble Fullerenes. *Nano Lett.* **2004**, *4*, 1881–1887. [CrossRef]
88. Scrivens, W.A.; Tour, J.M.; Creek, K.E.; Pirisi, L. Synthesis of 14C-Labeled C60, Its Suspension in Water, and Its Uptake by Human Keratinocytes. *J. Am. Chem. Soc.* **1994**, *116*, 4517–4518. [CrossRef]
89. Moussa, F.; Trivin, F.; Céolin, R.; Hadchouel, M. Fullerene Science and Technology Early effects of C 60 Administration in Swiss Mice: A Preliminary Account for in vivo C60 Toxicity. *Fuller. Sci. Technol.* **1996**, *4*, 21–29. [CrossRef]
90. Lyon, D.Y.; Fortner, J.D.; Sayes, C.M.; Colvin, V.L.; Hughes, J.B. Bacterial cell association and antimicrobial activity of a C60 water suspension. *Environ. Toxicol. Chem.* **2005**, *24*, 2757–2762. [CrossRef]
91. Bai, W.; Krishna, V.; Wang, J.; Moudgil, B.; Koopman, B. Enhancement of nano titanium dioxide photocatalysis in transparent coatings by polyhydroxy fullerene. *Appl. Catal. B Environ.* **2012**, *125*, 128–135. [CrossRef]
92. Nyberg, L.; Turco, R.F.; Nies, L. Assessing the impact of nanomaterials on anaerobic microbial communities. *Environ. Sci. Technol.* **2008**, *42*, 1938–1943. [CrossRef]
93. Tsuchiya, T.; Oguri, I.; Yamakoshi, Y.N.; Miyata, N. Novel harmful effects of [60] fullerene on mouse embryos in vitro and in vivo. *FEBS Lett.* **1996**, *393*, 139–145. [CrossRef]
94. Lima, J.D.M.; Gomes, D.S.; Frazão, N.F.; Soares, D.J.B.; Sarmento, R.G. Glyphosate adsorption on C6 0 fullerene in aqueous medium for water reservoir depollution. *J. Mol. Model.* **2020**, *26*, 110. [CrossRef] [PubMed]
95. Adam, A.M.; Saad, H.A.; Atta, A.A.; Alsawat, M.; Hegab, M.S.; Altalhi, T.A.; Refat, M.S. An environmentally friendly method for removing Hg(II), Pb(II), Cd(II) and Sn(II) heavy metals from wastewater using novel metal–carbon-based composites. *Crystals* **2021**, *11*, 882. [CrossRef]
96. Qi, K.; Selvaraj, R.; Al Fahdi, T.; Al-Kindy, S.; Kim, Y.; Wang, G.-C.; Tai, C.-W.; Sillanpää, M. Enhanced photocatalytic activity of anatase-TiO2 nanoparticles by fullerene modification: A theoretical and experimental study. *Appl. Surf. Sci.* **2016**, *387*, 750–758. [CrossRef]
97. Park, Y.; Singh, N.J.; Kim, K.S.; Tachikawa, T.; Majima, T.; Choi, W. Fullerol–titania charge-transfer-mediated photocatalysis working under visible light. *Chem. Eur. J.* **2009**, *15*, 10843–10850. [CrossRef]
98. WHO. Antibiotic Resistance. Available online: https://www.who.int/news-room/fact-sheets/detail/antibiotic-resistance (accessed on 14 September 2022).

99. Raffi, M.; Rumaiz, A.K.; Hasan, M.M.; Shah, S.I. Studies of the growth parameters for silver nanoparticle synthesis by inert gas condensation. *J. Mater. Res.* **2007**, *22*, 3378–3384. [CrossRef]
100. Bordoni, A.V.; Zalduendo, M.M.; Escobar, A.; Amenitsch, H.; Moya, S.E.; Angelomé, P.C. Phosphonate mesoporous hybrid thin films: Synthesis of organophosphosilane by thiol-ene click chemistry and applications in formation and stabilization of silver nanoparticles. *Microporous Mesoporous Mater.* **2020**, *295*, 109958. [CrossRef]
101. Baker, C.; Pradhan, A.; Pakstis, L.; Pochan, D.J.; Shah, S.I. Synthesis and antibacterial properties of silver nanoparticles. *J. Nanosci. Nanotechnol.* **2005**, *5*, 244–249. [CrossRef]
102. Iravani, S.; Korbekandi, H.; Mirmohammadi, S.V.; Zolfaghari, B. Synthesis of silver nanoparticles: Chemical, physical and biological methods. *Res. Pharm. Sci.* **2014**, *9*, 385.
103. Pietrzak, K.; Gutarowska, B.; Machnowski, W.; Mikołajczyk, U. Antimicrobial properties of silver nanoparticles misting on cotton fabrics. *Text. Res. J.* **2016**, *86*, 812–822. [CrossRef]
104. Morsi, R.E.; Alsabagh, A.M.; Nasr, S.A.; Zaki, M.M. Multifunctional nanocomposites of chitosan, silver nanoparticles, copper nanoparticles and carbon nanotubes for water treatment: Antimicrobial characteristics. *Int. J. Biol. Macromol.* **2017**, *97*, 264–269. [CrossRef] [PubMed]
105. Kumar, V.S.; Nagaraja, B.M.; Shashikala, V.; Padmasri, A.H.; Madhavendra, S.S.; Raju, B.D.; Rao, K.S.R. Highly efficient Ag/C catalyst prepared by electro-chemical deposition method in controlling microorganisms in water. *J. Mol. Catal. A Chem.* **2004**, *223*, 313–319. [CrossRef]
106. Daniel, S.; Malathi, S.; Balasubramanian, S.; Sivakumar, M.; Sironmani, T.A. Multifunctional silver, copper and zero valent iron metallic nanoparticles for wastewater treatment. In *Application of Nanotechnology in Water*; Wiley: New York, NY, USA, 2014; pp. 435–457.
107. Madeła, M. Impact of silver nanoparticles on wastewater treatment in the SBR. In *E3S Web of Conferences*; EDP Sciences: Les Ulis, France, 2019; Volume 86, p. 27.
108. Madeła, M. Effect of copper nanoparticles on biological wastewater treatment. *Desalin. Water Treat.* **2020**, *199*, 493–498. [CrossRef]
109. Najafpoor, A.; Norouzian-Ostad, R.; Alidadi, H.; Rohani-Bastami, T.; Davoudi, M.; Barjasteh-Askari, F.; Zanganeh, J. Effect of magnetic nanoparticles and silver-loaded magnetic nanoparticles on advanced wastewater treatment and disinfection. *J. Mol. Liq.* **2020**, *303*, 112640. [CrossRef]
110. Ganguly, K.; Dutta, S.D.; Patel, D.K.; Lim, K.-T. Silver nanoparticles for wastewater treatment. In *Aquananotechnology*; Elsevier: Amsterdam, The Netherlands, 2021; pp. 385–401.
111. Bryaskova, R.; Georgieva, N.; Pencheva, D.; Todorova, Z.; Lazarova, N.; Kantardjiev, T. Synthesis and characterization of hybrid materials with embedded silver nanoparticles and their application as antimicrobial matrices for waste water purification. *Colloids Surf. A Physicochem. Eng. Asp.* **2014**, *444*, 114–119. [CrossRef]
112. Bhargava, S.; Uma, V. Rapid extraction of Cu (II) heavy metal from industrial waste water by using silver nanoparticles anchored with novel Schiff base. *Sep. Sci. Technol.* **2019**, *54*, 1182–1193. [CrossRef]
113. Ruparelia, J.P.; Chatterjee, A.K.; Duttagupta, S.P.; Mukherji, S. Strain specificity in antimicrobial activity of silver and copper nanoparticles. *Acta Biomater.* **2008**, *4*, 707–716. [CrossRef]
114. Sivaranjani, S.; Prasath, V.A.; Pandiselvam, R.; Kothakota, A.; Mousavi Khaneghah, A. Recent advances in applications of ozone in the cereal industry. *LWT* **2021**, *146*, 111412. [CrossRef]
115. Huh, J.Y.; Kim, K.; Ma, S.H.; Choi, E.H.; Hong, Y.C. One-Pot Synthesis of Copper Nanoparticles Using Underwater Plasma. *IEEE Trans. Plasma Sci.* **2019**, *47*, 1690–1694. [CrossRef]
116. Khare, P.; Sharma, A.; Verma, N. Synthesis of phenolic precursor-based porous carbon beads in situ dispersed with copper–silver bimetal nanoparticles for antibacterial applications. *J. Colloid Interface Sci.* **2014**, *418*, 216–224. [CrossRef]
117. Allaker, R.P.; Memarzadeh, K. Nanoparticles and the control of oral infections. *Int. J. Antimicrob. Agents* **2014**, *43*, 95–104. [CrossRef] [PubMed]
118. Chen, H.; Zheng, X.; Chen, Y.; Li, M.; Liu, K.; Li, X. Influence of copper nanoparticles on the physical-chemical properties of activated sludge. *PLoS ONE* **2014**, *9*, e0092871. [CrossRef]
119. Chen, Y.; Wang, D.; Zhu, X.; Zheng, X.; Feng, L. Long-term effects of copper nanoparticles on wastewater biological nutrient removal and N_2O generation in the activated sludge process. *Environ. Sci. Technol.* **2012**, *46*, 12452–12458. [CrossRef] [PubMed]
120. Chen, H.; Li, X.; Chen, Y.; Liu, Y.; Zhang, H.; Xue, G. Performance of wastewater biological phosphorus removal under long-term exposure to CuNPs: Adapting toxicity via microbial community structure adjustment. *RSC Adv.* **2015**, *5*, 61094–61102. [CrossRef]
121. Masunga, N.; Mmelesi, O.K.; Kefeni, K.K.; Mamba, B.B. Recent advances in copper ferrite nanoparticles and nanocomposites synthesis, magnetic properties and application in water treatment. *J. Environ. Chem. Eng.* **2019**, *7*, 103179. [CrossRef]
122. Cheng, Z.; Tan, A.L.K.; Tao, Y.; Shan, D.; Ting, K.E.; Yin, X.J. Synthesis and characterization of iron oxide nanoparticles and applications in the removal of heavy metals from industrial wastewater. *Int. J. Photoenergy* **2012**, *2012*, 608298. [CrossRef]
123. Yadav, V.K.; Ali, D.; Khan, S.H.; Gnanamoorthy, G.; Choudhary, N.; Yadav, K.K.; Thai, V.N.; Hussain, S.A.; Manhrdas, S. Synthesis and characterization of amorphous iron oxide nanoparticles by the sonochemical method and their application for the remediation of heavy metals from wastewater. *Nanomaterials* **2020**, *10*, 1551. [CrossRef]
124. Sawafta, R.; Shahwan, T. A comparative study of the removal of methylene blue by iron nanoparticles from water and water-ethanol solutions. *J. Mol. Liq.* **2019**, *273*, 274–281. [CrossRef]

125. Kefeni, K.K.; Mamba, B.B. Photocatalytic application of spinel ferrite nanoparticles and nanocomposites in wastewater treatment. *Sustain. Mater. Technol.* **2020**, *23*, e00140. [CrossRef]
126. Sun, M.; Han, X.; Chen, S. Synthesis and photocatalytic activity of nano-cobalt ferrite catalyst for the photo-degradation various dyes under simulated sunlight irradiation. *Mater. Sci. Semicond. Process.* **2019**, *91*, 367–376. [CrossRef]
127. Abbas, M.; Rao, B.P.; Reddy, V.; Kim, C. Fe_3O_4/TiO_2 core/shell nanocubes: Single-batch surfactantless synthesis, characterization and efficient catalysts for methylene blue degradation. *Ceram. Int.* **2014**, *40*, 11177–11186. [CrossRef]
128. Feng, X.; Guo, H.; Patel, K.; Zhou, H.; Lou, X. High performance, recoverable Fe_3O_4ZnO nanoparticles for enhanced photocatalytic degradation of phenol. *Chem. Eng. J.* **2014**, *244*, 327–334. [CrossRef]
129. Abou Taleb, M.F. Adsorption and photocatalytic degradation of 2-CP in wastewater onto CS/$CoFe_2O_4$ nanocomposite synthesized using gamma radiation. *Carbohydr. Polym.* **2014**, *114*, 65–72. [CrossRef]
130. Gautam, S.; Shandilya, P.; Priya, B.; Singh, V.P.; Raizada, P.; Rai, R.; Valente, M.A.; Singh, P. Superparamagnetic $MnFe_2O_4$ dispersed over graphitic carbon sand composite and bentonite as magnetically recoverable photocatalyst for antibiotic mineralization. *Sep. Purif. Technol.* **2017**, *172*, 498–511. [CrossRef]
131. Qi, F.; Xu, B.; Chu, W. Heterogeneous catalytic ozonation of phenacetin in water using magnetic spinel ferrite as catalyst: Comparison of surface property and efficiency. *J. Mol. Catal. A Chem.* **2015**, *396*, 164–173. [CrossRef]
132. Zhang, Y.; Chen, Y.; Westerhoff, P.; Hristovski, K.; Crittenden, J.C. Stability of commercial metal oxide nanoparticles in water. *Water Res.* **2008**, *42*, 2204–2212. [CrossRef]
133. Donovan, A.R.; Adams, C.D.; Ma, Y.; Stephan, C.; Eichholz, T.; Shi, H. Fate of nanoparticles during alum and ferric coagulation monitored using single particle ICP-MS. *Chemosphere* **2018**, *195*, 531–541. [CrossRef]
134. Tuccillo, M.E.; Boyd, G.R.; Sandvig, A.; Shatkin, J.A.; Dionysiou, D.D. Nanotechnology what are the Challenges and Emerging Benefits for Water Treatment? *Opflow* **2012**, *38*, 10–13. [CrossRef]
135. Dong, J. Signaling pathways implicated in carbon nanotube-induced lung inflammation. *Front. Immunol.* **2020**, *11*, 3250. [CrossRef]
136. Dong, J.; Ma, Q. Type 2 immune mechanisms in carbon nanotube-induced lung fibrosis. *Front. Immunol.* **2018**, *9*, 1120. [CrossRef]
137. Allegri, M.; Perivoliotis, D.K.; Bianchi, M.G.; Chiu, M.; Pagliaro, A.; Koklioti, M.A.; Trompeta, A.F.A.; Bergamaschi, E.; Bussolati, O.; Charitidis, C.A. Toxicity determinants of multi-walled carbon nanotubes: The relationship between functionalization and agglomeration. *Toxicol. Rep.* **2016**, *3*, 230–243. [CrossRef]
138. Jia, G.; Wang, H.; Yan, L.; Wang, X.; Pei, R.; Yan, T.; Zhao, Y.; Guo, X. Cytotoxicity of carbon nanomaterials: Single-wall nanotube, multi-wall nanotube, and fullerene. *Environ. Sci. Technol.* **2005**, *39*, 1378–1383. [CrossRef] [PubMed]
139. Freixa, A.; Acuña, V.; Gutierrez, M.; Sanchís, J.; Santos, L.H.M.L.M.; Rodriguez-Mozaz, S.; Farré, M.; Barceló, D.; Sabater, S. Fullerenes influence the toxicity of organic micro-contaminants to river biofilms. *Front. Microbiol.* **2018**, *9*, 1426. [CrossRef] [PubMed]
140. Lansdown, A.B.G. Silver in health care: Antimicrobial effects and safety in use. *Biofunctional Text. Ski.* **2006**, *33*, 17–34.
141. Ferdous, Z.; Nemmar, A. Health Impact of Silver Nanoparticles: A Review of the Biodistribution and Toxicity Following Various Routes of Exposure. *Int. J. Mol. Sci.* **2020**, *21*, 2375. [CrossRef]
142. Świdwińska-Gajewska, A.; Czerczak, S. Nanosrebro-szkodliwe skutki działania biologicznego [Nanosilver-harmful effects of biological activity]. *Med. Pracy* **2014**, *65*, 831–845.
143. Fiorati, A.; Bellingeri, A.; Punta, C.; Corsi, I.; Venditti, I. Silver nanoparticles for water pollution monitoring and treatments: Ecosafety challenge and cellulose-based hybrids solution. *Polymers* **2020**, *12*, 1635. [CrossRef] [PubMed]
144. Favela-Camacho, S.E.; Samaniego-Benítez, E.J.; Godínez-García, A.; Avilés-Arellano, L.M.; Pérez-Robles, J.F. How to decrease the agglomeration of magnetite nanoparticles and increase their stability using surface properties. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *574*, 29–35. [CrossRef]
145. Lu, H.; Wang, J.; Stoller, M.; Wang, T.; Bao, Y.; Hao, H. An overview of nanomaterials for water and wastewater treatment. *Adv. Mater. Sci. Eng.* **2016**, *2016*, 4964828. [CrossRef]
146. Stefaniuk, M.; Oleszczuk, P.; Ok, Y.S. Review on nano zerovalent iron (nZVI): From synthesis to environmental applications. *Chem. Eng. J.* **2016**, *287*, 618–632. [CrossRef]
147. Yaqoob, A.A.; Parveen, T.; Umar, K.; Mohamad Ibrahim, M.N. Role of nanomaterials in the treatment of wastewater: A review. *Water* **2020**, *12*, 495. [CrossRef]
148. Epelle, E.I.; Macfarlane, A.; Cusack, M.; Burns, A.; Okolie, J.A.; Mackay, W.; Rateb, M.; Yaseen, M. Ozone application in different industries: A review of recent developments. *Chem. Eng. J.* **2022**, *454*, 140188. [CrossRef]