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Review

A Review of the Techno-Economic Feasibility of Nanoparticle Application for Wastewater Treatment

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Abstract: The increase in heavy metal contamination has led to an increase in studies investigating alternative sustainable ways to treat heavy metals. Nanotechnology has been shown to be an environmentally friendly technology for treating heavy metals and other contaminants from contaminated water. However, this technology is not widely used in wastewater treatment plants (WWTPs) due to high operational costs. The increasing interest in reducing costs by applying nanotechnology in wastewater treatment has resulted in an increase in studies investigating sustainable ways of producing nanoparticles. Certain researchers have suggested that sustainable and cheap raw materials must be used for the production of cheaper nanoparticles. This has led to an increase in studies investigating the production of nanoparticles from plant materials. Additionally, production of nanoparticles through biological methods has also been recognized as a promising, cost-effective method of producing nanoparticles. Some studies have shown that the recycling of nanoparticles can potentially reduce the costs of using freshly produced nanoparticles. This review evaluates the economic impact of these new developments on nanotechnology in wastewater treatment. An in-depth market assessment of nanoparticle application and the economic feasibility of nanoparticle applications in WWTPs is presented. Moreover, the challenges and opportunities of using nanoparticles for heavy metal removal are also discussed.

Keywords: adsorption; heavy metal; nanoparticle; techno economic

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1. Introduction

Environmental contamination has become a public concern, particularly heavy metal contamination, since it can result in health implications for humans [1]. Heavy metal contamination is increasing due to rapid industrialization [2]. Over 0.03 million tons of Cr and 0.8 million tons of Pb were disposed of in the natural environment in the past decade [3]. Due to the threat these heavy metals pose to the health of mankind, governments in different countries have set stringent discharge limits for heavy metals and demanded that industries comply with these limits [4]. Silver (Ag), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), calcium (Ca), antimony (Sb), and cobalt (Co) are some of the heavy metals found in wastewater treatment plants (WWTPs).

The severity of the environmental harm caused by these metals has led to many researchers investigating efficient removal methods of these metals [5]. A number of treatment technologies such as chemical precipitation, solvent extraction, ion exchange, and membrane separation have proven to be efficient in heavy metal removal [6,7]. However, these methods have drawbacks, such as the requirement of post treatment due to the production of hazardous byproducts and the requirement of high capital investments [8,9]. The application of nanotechnology has drawn attention due to the interesting adsorption capabilities of nanoparticles. Nanotechnology is used in four different applications in wastewater treatment (Figure 1). Adsorption is one of the highly studied fields in nanotechnology.

Activated carbon is one of the adsorbents that have been intensively investigated. It comes in two forms: granular activated carbons (GACs) and powdered activated carbons (PACs). The powdered activated carbons are preferred over granular activated carbons owing to benefits such as high adsorption capacity, which results in high specific surface areas. However, granular activated carbons have slower settling and removal tendencies, thus making it difficult to separate from an aqueous solution. It is for this reason that PACs are currently applied only in batch mode systems in WWTPs, while GACs are employed more in continuous systems since they are easily separable. Nevertheless, GACs have a lower adsorption capacity for contaminants in aqueous solutions; the low adsorption capacity of GACs has been linked with low mass transfer of the targeted contaminant and the fouling effect [10].

Nanomembranes are also an interesting nanotechnology option. They are generally used for oil–water separation. Like other technologies, nanomembranes have their drawbacks, such as fouling of the membrane. Nonetheless, their benefits have made them a great candidate for wastewater treatment. The wettability of the membrane is an interesting property of nanomembranes. To date, there have been a number of membranes produced from materials with high wettability; such membranes include metallic mesh membranes, carbon nanotube membranes, and polymeric membranes. However, the fabrication of these membranes is not ideal, since it involves dangerous operation processes and toxic chemicals. This has led to increased interest in the electrospinning method, which is used to produce polymer based membranes that have a large surface-to-volume ratio, controllable sizes of pores, good flexibility, and great structural flexibility [11,12].

Nanotechnology can also be used in disinfection of pathogens. Silver and zinc oxide nanoparticles are some of the common nanoparticles used for disinfection. Using nanoparticles for disinfection has raised the interest of many researchers, since the traditional methods of disinfecting wastewater, such as chlorination, ozonation, and ultraviolet treatment, have been shown to be ineffective for total disinfection of wastewater, due to the acquired resistance to these methods by waterborne pathogens. This highlights the need for sustainable methods; hence, the application of nanoparticles has been gaining popularity [13].

To date, numerous nanoparticles have been studied and have proven to have excellent capability to absorb heavy metals from wastewater [14,15]. Although nanotechnology has been shown to be a promising technology for wastewater treatment, particularly for heavy metal removal, its application in WWTPs is still limited. The main factor hindering the application of nanotechnology in WWTPs is the high production cost of nanoparticles, which results in high operational costs of nanotechnology in WWTPs. Thus, scientists have invested time in trying to find cheaper and improved methods of producing nanoparticles [16,17]. Although a lot has been done to improve nanotechnology application for wastewater treatment, there are still limited studies reporting on the techno economic feasibility of nanotechnology, particularly in the context of wastewater treatment. Hence, this study aims to review the techno economic feasibility of using nanotechnology in WWTPs. This study will also evaluate the economical sustainability of nanotechnology in WWTPs.

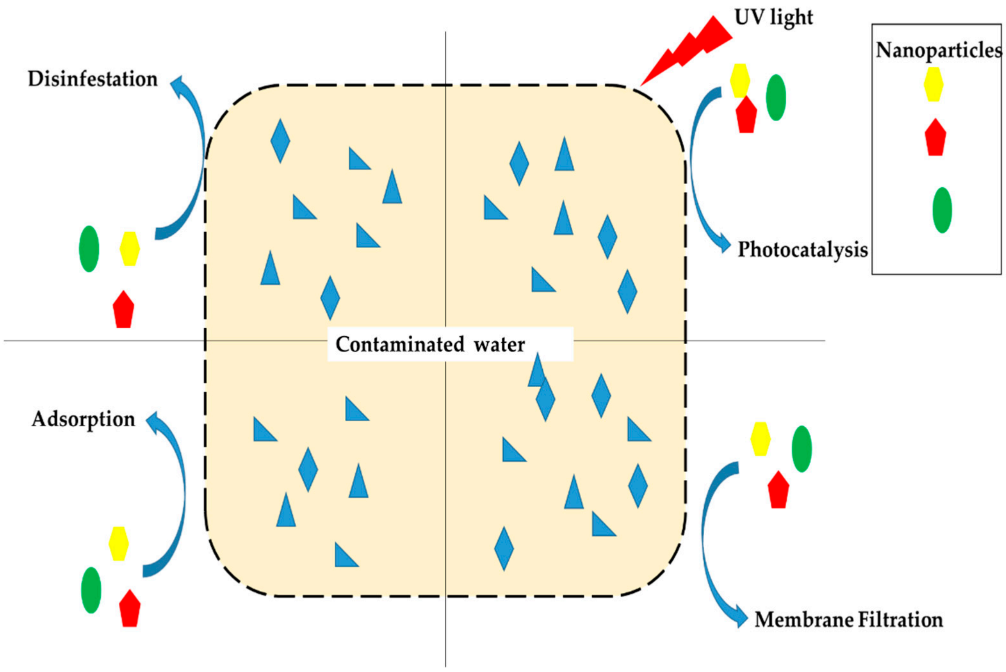

Figure 1. Different applications of nanoparticles in wastewater treatment, modified from [18].

2. Overview of Nanotechnology Application in Wastewater Treatment

Nanotechnology involves the use of particles that have a nano-size, known as nanoparticles. Nanoparticles are known for having large surface area and unique physiochemical properties. They have gained attention in the wastewater treatment sector as they possess adsorption properties that can be used for water purification. Additionally, nanoparticles can also be used in different applications in WWTPs, e.g., membrane filtration, heterogeneous photocatalysis, heterogeneous photo-Fenton, disinfection, and microbial control. Nanoparticles use an adsorption mechanism for heavy metal removal; they are capable of binding to contaminants such as heavy metals.

This is caused by surface energy and the affinity of surface atoms to be occupied by surrounding atoms in their outer surface when an absorbent is positively charged. In some cases, spontaneous adsorption cannot occur, especially when interacting with uncharged heavy metals. Thus, sometimes, the metal oxidation state may require modification. This can be done by using adsorbents that can act as either an oxidizing or reducing intermediate, which are capable of exchanging electrons with aqueous species [19]. Nanoparticles have been shown to be effective in the removal of bacteria and toxic chemicals such as arsenic, mercury, etc. However, concerns have been raised regarding the risks that may arise as a result of the high reactivity of nanoparticles caused by large surface area to volume ratios. Nevertheless, it has been shown that water purification through nanoparticles does not cause any problems to human health or the environment [20]. The application of nanotechnology in WWTPs is discussed in the following paragraphs.

2.1. Photocatalysis Technology

Photocatalysis technology has been investigated for treatment of water contaminated with hazardous aromatic compounds. Titanium dioxide (TiO_2) and Zinc oxide (ZnO) are among the highly used semiconductor photocatalysts. TiO_2 is particularly preferred since it is inexpensive. ZnO has also gained popularity, despite the fact that it is likely to cause photocorrosion under irradiation as a result of its wide energy band gap. Photocatalysis generally uses semiconductor materials with electrons (e^-) that can jump to a conduction band when irradiated by light; this results in positively charged holes (h^+) in the valence band. This occurs when the energy of the photon in the incident light is higher or equal to the band gap energy. The pair of e^- and h^+ therefore move to the surface, where they undergo reduction and oxidation reactions. These reactions aid in the conversion of valence states in the treatment of various heavy metals. The drawback of photocatalysis is that high energy is required due to the wide band energy gap. Hence, research on developing photocatalysts that have suitable and efficient band gaps has gained popularity. Catalysts such as bio-based catalysts, C_3N_4, and ZnO have been shown to have efficient band energy gaps [19–21]. Another limitation of photocatalysts is that they work well when they are exposed to ultraviolet light (UV) irradiation. Their activity under visible and solar light is restricted; this is due to the fact that UV light only constitutes 4–6% of solar light, while visible light constitutes 45%. These drawbacks limit the application of photocatalysis in large-scale wastewater treatment systems [22].

Magnetic nanoparticles are also popular, since they have been shown to have greater photocatalytic abilities. Furthermore, magnetic nanoparticles have other interesting properties, such as a modifiable surface, compact size, elevated surface zones and volume ratios, and strong bio-compatibilities. Magnetic nanoparticles have been investigated, and their performance has been shown to depend on three aspects: material, composition, and dimensions of 1–100 nm. Different materials such as Fe_2O_3/Fe_3O_4, pure metals Fe and Co, and spinel-type ferromagnets $MgFe_2O_4$, $MnFe_2O_4$, and $CoFe_2O_4$ can be used for the synthesis of magnetic nanoparticles [23].

However, the application of magnetic nanoparticles for water purification may cause eugenol allergy, toxicity, genotoxicity, phytotoxicity, skin irritation, and several other health problems, including the risk of kidney disease. Additionally, some magnetic nanoparticles are carcinogenic as a result of precursor salts in the nanoparticles. Therefore, further investigations are still required to reduce the health hazards posed by the application of magnetic nanoparticles for water purification [24].

2.2. Adsorption Technology

Adsorption is one of the popular processes for heavy metal removal. The process of adsorption involves the accumulation of liquid solute (adsorbate) into the surface of the solid (adsorbent), thereby forming an atomic or molecular film. Several absorbents have been studied for their ability to treat heavy metals from wastewater, with the more frequently used adsorbents being activated carbons, zeolites, and clay minerals [25]. Nanotechnology-based adsorption has gained popularity due to its efficiency in treating wastewater, operational flexibility, and large surface area. Moreover, the reversible nature of nanoparticles make them great candidates for wastewater treatment since they can be regenerated. Adsorption offers many benefits, such as easy maintenance, high efficiency, and easy operation. Nano-sized metal oxides are among the adsorbents that have been intensively studied. Nano-sized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides, and cerium oxides (CeO_2) have been shown to be promising for heavy metal removal in aqueous systems [26]. The synthesis of these adsorbents has evolved over the years, with more innovative and cost-effective synthesis methods emerging. The mechanism of heavy metal removal by adsorbents has been said to be similar to Lewis acids–bases. Moreover, nano-absorbents have been shown to a have high specific sorption capacity as a result of sorption sites at the surface [27].

2.3. Nano-Membrane Technology

Nano-membranes have also raised the interest of environmental researchers. Their low production costs compared to traditional membranes have made them a favorable alternative to traditional membranes. Carbon nanotubes (CNT) are a renowned alternative option for membrane technology, owing to their outstanding mechanical strength, flexible preparation, and high electron affinity [28]. Nano-membranes are produced from various materials, such as non-metal particles, nano-metal particles and nano-carbon tubes [29]. Nano-membranes are porous, thin-layered, and impermeable to salt, microorganisms, and heavy metals. Furthermore, they are ideal for wastewater treatment due to their selectivity. The treatment process with nano-membranes tends to be fast, and the fouling is lower in nano-membranes compared to traditional membranes. The combination of different nano-materials with polymer-based membranes has been shown to produce excellent nano-membranes for wastewater decontamination. Additionally, materials with antibacterial properties, such as carbon-based materials, have also been shown to efficiently reduce fouling while increasing the mechanical stability of nano-membranes. Another way of reducing fouling is doping with nano-materials such as alumina, TiO_2, and zeolite. Doping with silver-like metal is said to present great potential for the reduction of membrane fouling and the prevention of bacterial growth on membranes [30].

2.4. Nanotechnology Disinfection

The non-specific nature of nanoparticles makes them capable of removing a wide range of contaminants as well as bacterial cells; this property is now exploited for the removal of pathogenic bacteria in wastewater treatment. Nanoparticles have been shown to be a promising technology in disinfection of wastewater as compared to traditional disinfectants, which produce toxic by-products. Silver is one of the popular nanoparticles; it has high specific area and outstanding antimicrobial properties. These properties make silver a great disinfectant alternative for wastewater. Additionally, silver is commonly used as a biocide in various household products. However, the release of silver nanoparticles into the environment affects naturally occurring microbes [31]. The mechanism of antibacterial activity of silver nanoparticles is different to that of magnetic nanoparticles. The antibacterial activity of silver nanoparticles is said to result from reactive oxygen species (ROS) generation. Moreover, other mechanisms have been documented in the literature, e.g. the interaction between silver nanoparticles and the surface structure of material cells, as well as the reaction between sulfur and phosphorous of cell macromolecules and silver ions. Silver nanoparticles have been shown to be efficient for disinfection of both gram-positive and -negative bacteria. In recent studies, silver nanoparticles have been combined with magnetic nanoparticles to facilitate the recovery of silver; this combination has also been reported to be able to penetrate biofilm effortlessly compared to when silver nanoparticles are used alone. Nanoparticles with magnetic properties can also be used for microbial disinfection. Magnetite has been reported to be among the strongest magnetic species of transient mental oxides. The mechanism of disinfection by magnetic nanoparticles involves the release of reactive oxygen species, which destroy proteins and Deoxyribonucleic Acid (DNA) in the bacterial cells, thereby causing an antibacterial effect through chemical disinfection and the adsorption of ions. Additionally, their magnetic characteristics make them easily separable from aqueous solutions [32]. Table 1 shows nanoparticles with excellent heavy metal removal efficiency.

Table 1. Heavy metal adsorption efficiency of different nanoparticles.

Ref	Optimum pH	Nanoparticle Used	Contaminant	Initial Contaminant Dose	Adsorbent Dosage	Removal Efficiency	Removal Efficiency
Abdi et al. [33]	pH 5	NF membranes with different magnetic graphene-based hybrids	Copper dye retention	20 mg/L	-	-	Copper removal 92% Dye retention of 99%
Arshad et al. [34]	pH 7	Graphene oxide embedded calcium alginate	Pb(II)	-	5 mg/mL	602 mg/g for Pb(II)	99.6%
Sahraei and Ghaemy [35]	pH 6	Modified gum tragacanth/graphene oxide composite hydrogel	Pb(II), Cd(II), and Ag(I)	60 mg/L	20 mg	142.50 mg/g for Pb(II) 112.50 mg/g for Cd(II) 132.12 mg g^{-1} for Ag(I)	94% for Pb(II) 79.40% for Cd(II) 83.55% for Ag(I)
Kumar et al. [36]	pH 8	ZnO and SnO_2	Malachite Green Oxalate (MGO) hexavalent Chromium (Cr)	20 mg/L for MGO 3 mg/L for Cr	80 mg/L of SnO_2 and ZnO for MGO removal 300 mg/L SnO_2 and ZnO for hexavalent Chromium (Cr)	-	Malachite Green Oxalate: 95% by ZnO 92% by SnO_2 Adsorption of Cr: 95% by ZnO 87% by SnO_2
Fouda et al. [37]	pH 7.5	MgO	Co, Pb, Cd, and Ni	-	1.0 mg/mL	149.1 for Co 148.6, for Pb 135 for Cd 149.9 for Ni	94.2% ± 1.2% for Cr 63.4% ± 1.7% for Co 72.7% ± 1.3% for Pb 74.1% ± 1.8% for Cd 70.8% ± 1.5% for Ni
Gu et al. [7]	pH range of 3–7	ZnO	Cr^{3+}	-	1 g/L	88.547 mg/g for Cr^{3+}	99.5% for Cr^{3+}
Shi et al. [38]	pH of 8.0	Fe_3O_4	Cu^{2+}, Cd^{2+}, and Pb^{2+}		1 mg/mL	18.8 mg/g for Cu^{2+}, 20.9 mg/g for Cd^{2+} 21.5 mg/g for Pb^{2+}	96.2% for Cu^{2+}, 87.4% for Cd^{2+} 91.1% for Pb^{2+}
Khoso et al. [39]	Cr(VI) ions at pH 3 Pb(II) ions at pH 5 Cd(II) at pH 5	Nickel-Ferrite Nanoparticles (NFNs)	Cr(VI), Pb(II), and Cd(II)	30 mg for Cr(VI) ions 40 mg for Pb(II) 40 mg for Cd(II)	10 mg	-	85.8% for Cr(VI) ions 75.25% for Pb(II) ions 77.41% for Cd(II) ions

3. Market Assessment of Nanoparticles in the Wastewater Treatment Sector

The demand for water continues to rise. Water scarcity is a problem in many countries, especially developing countries that do not have proper treatment systems in place. As such, the United Nations (UN) warned that 1.8 million people will be living in countries that have a water scarcity problem and two-thirds of the world population will likely live under stress conditions due to water scarcity by 2025 [40]. Additionally, the World Health Organization also estimated that 1.1 billion people do not have proper access to clean drinking water, and there will be a 30% rise in the demand for fresh water by 2030. Moreover, it is projected that 80% of wastewater will be discharged to the environment without any treatment if the population grows as per current projections [41].

The speed at which the population is growing as well as the rate at which urbanization is expanding has forced cities to expand without proper plans in place for waste disposal facilities. As a result, the United Nations Environment Program (UNEP) Global Environment Outlook (GEO) has expressed concerns with regards to the risks that the African continent is facing as a result of the dumping of hazardous waste due to poor monitoring and improper strategies for waste disposal. The result of the rapid growth of industrialization has also led to widespread heavy metal pollution. This is due to the fact that most resources in African counties are directed towards economic growth and industrialization, thus neglecting environmental management. A study conducted by the WHO indicated that a quarter of the disease burden in humans results from environmental pollution [42].

The treatment of contaminated water has been said to be the core aspect of meeting the global water demand. Furthermore, it has been noted that 70–80% of all problems arising in developing countries are associated with water pollution. Thus, resources have been invested in developing wastewater treatment systems. The common method for the removal of contaminants is the sludge method; however, as a result of the increase in demand for fresh water, there has been a push to treat water to meet the standards appropriate for reuse in other recreational activities [43,44]. This has resulted in an increase in the sludge production in an attempt to increase the effectiveness of biological wastewater treatment processes to accommodate the rising population demand. It is reported that the total national sludge discharge was 68.5 billion tons in China in 2012. This is a 3.7% increase from the discharge of 2013, which was 2.5 and 23.5 million tons of ammonia nitrogen and chemical oxygen demand (COD), respectively [45].

Such a drastic increase is an indicator of the urgency to establish a sustainable approach for the treatment of wastewater. Several treatment methods have been investigated for their efficiency for wastewater treatment. Biological methods have been found to be promising; although they have been shown to be efficient for nutrient removal [46], they are not effective for heavy metal removal. Other methods have also been investigated; however, they have downsides, such as the use of toxic chemicals and the production of toxic byproducts. The use of nano-absorbents has been shown to be a sustainable alternative that could solve the problem of environmental pollution resulting from heavy metal discharge. Table 2 shows the overall global production of different nanoparticles.

Table 2. Global production of nanoparticles [47].

Type of Production	Type of Nanoparticles	Minimum Global Production (Tons)	Maximum Global Production (Tons)
Nanoparticles produced in Large volume	TIO_2	60,000	15,000
	ZnO	32,000	36,000
	Silicon dioxide (SiO_2)	185,000	1,400,000
	Aluminium oxide (AL_2O_3)	5000	10,100
	CNT	1550	1950
	Nanoclays	25,000	51,000
	CeO_2	880	1400

Table 2. *Cont.*

Type of Production	Type of Nanoparticles	Minimum Global Production (Tons)	Maximum Global Production (Tons)
Nanoparticles produced in Large volume Low volume	Quantum dots	4.5	9
	Antimony tin oxide (ATO)	120	225
	Copper oxide (CuO)	290	570
	Ag	135	420
	cellulose nanofibers (CNF)	400	1350
	Bismuth oxide (Bi_2O_3)	35	55
	cobaltic oxide	5	<10
	Dendrimers	0.3	1.25
	Fullerenes and POSS	40	100
	Graphene	60	80
	Gold (Au)	1	3
	Iron oxide (FE_2O_3)	9	45
	Magnesium oxide (MgO)	15	30
	Manganese oxide (MnO_2)	2	3.5
	Nickel (Ni)	5	20
	Zirconium oxide (ZrO_2)	80	300

4. Contributing Factors to the Production Cost of Nanoparticles

The application of nanoparticles in the treatment of heavy metals has drawn attention mainly because of the benefits. Although the nanoparticle application in wastewater can potentially address the drawbacks of using chemical and physical treatment methods, the challenges associated with the application of nanoparticles outweigh the benefits. Thus, its application is still restricted. In this section, some of the factors that contribute to the cost of nanoparticle production are discussed. Many methods of nanoparticle synthesis have been reported. Some of the methods include physical and chemical methodologies such as chemical reduction and photochemical processes [48].

The chemical reduction method is reported to be cost effective [49]; however, the heat needed for precursor mixing may result in an escalation of production costs. Moreover, an unexpected increase in production costs may occur, since catalysts may sometimes be needed to speed up the reaction. Furthermore, solvents may also occasionally be required to make the media soluble for the interaction of chemicals [50]. To address these issues, several studies have suggested the use of organic solvents and chemical reagents that are soluble in water, cheap, and environmentally friendly. In addition, reactions that occur at room temperature must be adopted in the production of nanoparticles to avoid the costs associated with dealing with the treatment of hazardous by-product waste and other unexpected expenses [51].

Table 3 shows the cost of producing different nanoparticles using different methods. Nandatamadini et al. [52] reported estimations of cobalt nanoparticle synthesis through chemical reduction. According to Nandatamadini et al. [52], 543 g of Co nanoparticles is produced by 570.24 g of cobalt (II) chloride hexahydrate, 218.88 g of CTAB, and 908.16 g of sodium borohydride, ethanol, and water. Moreover, using a stoichiometric calculation, Nandatamadini et al. [52] estimated the production cost of Co nanoparticles; the estimated cost of raw materials was 1.5247 USD/gram for cobalt (II) chloride hexahydrate, 2.4526 USD/gram for CTAB, and 1.3297 USD/gram for sodium borohydride. Moreover, the energy and labor costs were also estimated to be 24.9375 USD/day and 8 USD/day, respectively. Nanoparticles are not stable, and therefore a surface modification of nanoparticles may be necessary. Furthermore, the modification of each nanoparticle depends on the targeted contaminant. Traditionally, the modification involves adsorption or conjunction of polymers and polymerization of the surface [53].

This demands the customization of nanoparticles in accordance with water characteristics. Thus, the cost of nanoparticles can vary depending on the characteristics of the influent in the WWTP. This may result in potential unexpected changes in operational costs of WWTPs. In attempts to reduce production costs of nanoparticle production, biosynthesis has been proposed as a cost-effective alternative [54]. Some studies have suggested that a cost-effective method of nanoparticle production should occur under ambient temperatures and neutral pH and must be environmentally friendly [55]. Additionally, the biological production of nanoparticles has gained traction over the years due to its benefits, such as environmental friendliness, being inexpensive, and being simple to scale up for large-scale production. It has been reported that the biological production of nanoparticles has slower kinetics and offers better manipulation and control over crystal growth and stabilization. Moreover, plant extracts have also been reported as cost-effective and sustainable raw materials for nanoparticle production [54]. The operating time for nanoparticle production is generally estimated using Equation (1):

$$TCI = FCE + WCC \quad (1)$$

where TCI is total capital investment, FCE is proposed plant and fixed capital estimation, and WCC is working capital cost.

Table 3. Cost of producing different nanoparticles.

Name of Nanoparticle	Production Technology	Total Production Cost	Ref
Cu/Zn	biosynthesized	USD/year 131,387.20	Noman et al. [56]
chitosan microbeads	topologies CM process	USD/year 37,838,536.68	Meramo-Hurtado et al. [57]
chitosan microbeads modified with TiO_2 nanoparticles	topologies $CMTiO_2$ process	USD/year 64,792,191.25	Meramo-Hurtado et al. [57]
ZnO	-	USD/year 57,124.32	Yashni et al. [58]
rare earth elements	-	USD/year 1,006,002.00	Liu et al. [59]
copper oxide	green synthesis	USD/year 2,219,500	Mahmoud et al. [60]

The annual operation cost is generally estimated using Equation (2):

$$AOC = CRM + CWG + CU + CE \quad (2)$$

where AOC refers to the annual operating cost, CRM refers to the raw material costs, CWG refers to the waste generation from the production process, CU refers to the cost of utilities, and CE refers to the extra costs.

5. Challenges of Nanoparticle Application for Heavy Metal Removal in Wastewater Treatment

Adsorption has been known to be a more sustainable treatment method for heavy metal pollution than physico-chemical methods, which have disadvantages such as high sludge production, technical restrictions, etc. [36]. However, the application of adsorption in WWTPs is still limited. It is therefore important to review the issues prohibiting its application in WWTPs, the work that has been done to address some of these issues, and the gaps in the existing research.

5.1. Using Graphene Oxide Nano-Sheets in WWTPs

Graphene oxide nano-sheets are among the nanomaterials that have been reported to be efficient for heavy metal removal. However, many issues, such as instability, lack of ease in separation from the treated water, and agglomeration during adsorption, which results in a high surface energy, prohibit its application in WWTPs. The difficulties in separation of nanoparticles using traditional methods were not only reported in graphene oxide nano-sheets; bio-char has also been reported to be difficult to separate from treated water [61].

This may result in the disposal of water containing nanoparticles, thereby causing a negative impact on the receiving environment. Many scientists have proposed solutions to overcome these problems. The use of magnetic separation methods has been highlighted as a possible solution to the separation problem [62,63]. Another problem of using graphene oxide is that graphene oxide nano-sheets have a negative effect on membranes, especially when used directly. They can damage the membranes, therefore affecting the membrane's reusability. This is due to the aggregation of graphene sheets on the samples passing through the membrane [33]. The constant replacement of the membranes may escalate the cost of using graphene oxide nano-sheets; hence, numerous studies have tried to engineer graphene oxide surfaces to overcome these shortfalls [64–66].

5.2. Using Magnetic Nanoparticles in WWTPs

Magnetic nanoparticles have drawn attention due to their remarkable properties, which can influence the magnetic field to allow for manipulation. However, magnetic nanoparticles such as magnetic iron oxide can oxidize in air due to high chemical activity. The oxidation may result in magnetic nanoparticles losing their magnetism as well as their dispersing and adsorbing properties; this is normally avoided by surface modification. Although the modification of magnetic nanoparticles has many benefits, separation of magnetized nanoparticles has been said to be difficult in wastewater owing to leaching of the surfactant materials. Scholars have investigated ways of overcoming the challenges associated with modified magnetic nanoparticles. Mixing magnetic nanoparticles with other nanoparticles has been shown to be a great way of preventing the need to modify the surface of the magnetic nanoparticles [14].

Moreover, functionalization of the core of magnetic nanoparticles with chelating ligands to enhance adsorption has also been investigated by many scholars [67–69]. Although there have been significant improvements in magnetic nanoparticles, there remain gaps that need to be addressed, especially for wastewater applications. One example is the issue of controlling the size, cost, and environmental impact by producing magnetic nanoparticles with an appropriate shape and composition. Moreover, the application of biodegradable adsorbents has also been suggested [70–72]. Some studies have reported interesting nanoparticle shapes, such as spheres, tubes, rods, and prisms [73]. Figure 2 shows the biosynthesis of nanoparticles from plant materials.

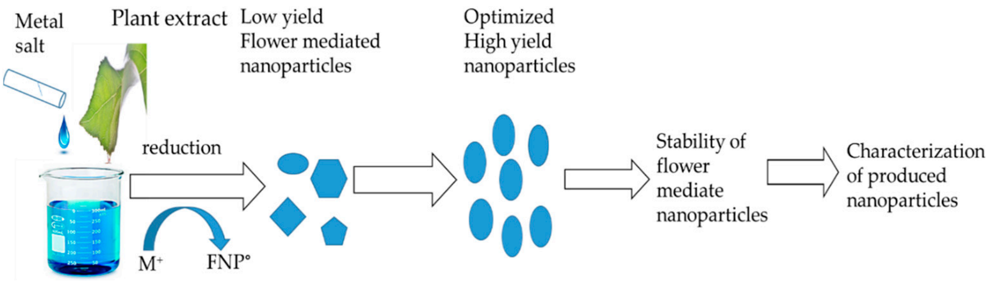

Figure 2. Mechanism of producing nanoparticles from plant extracts, modified from [41].

5.3. Using Polymeric Hydrogels in WWTPs

Polymeric hydrogels are among the biodegradable adsorbents that have been studied. Polymeric hydrogels are popular owing to benefits such as biodegradability, low cost, bio-compatibility, high efficiency, and appropriate water absorbency. However, polymeric hydrogels also require modification. Grafting with vinyl monomers have been shown to be an appropriate approach to introduce functional groups to enhance the adsorption capacity of polymeric hydrogels [35]. nO-nanoparticles have also been shown to be effective for heavy metal removal; their biocompatibility and low production costs have earned them popularity in the nanotechnology field.

Arshad et al. [34] investigated the adsorption capacity of modified gum tragacanth/graphene oxide composite, which is a bio-polymer–based absorbent. The study examined the adsorption capability on Pb(II), Cd(II), and Ag(I). The results obtained from this study indicated that the adsorption capacity of gum tragacanth/graphene oxide composite was 142.50, 112.50, and 132.12 mg/g for Pb(II), Cd(II), and Ag(I), respectively. The author further recommended gum tragacanth/graphene oxide composite as a potential low-cost absorbent, as it is a reusable bio-sorbent and easily available. Meramo-Hurtado and González-Delgado [57] conducted a techno-economic assessment of chitosan, a bio adsorbent made from renewable sources; the results indicated that the production of bio-based chitosan was less expensive, thus making it a competitive adsorbent for wastewater treatment (Table 3).

5.4. Using Activated Carbon in WWTPs

Activated carbon is another absorbent that has been reported as a promising adsorbent for heavy metal removal, although several studies show that this adsorbent is highly efficient for heavy metal removal [74,75].

Its application in wastewater treatment is still restricted due to limitations such as low selectivity, high cost and regeneration problems. While activated carbon can be regenerated successfully, the regeneration method, which is normally through thermal adsorption, is not considered to be environmentally friendly. Another hindrance in the application of activated carbon is the difficulty in separation. It has been suggested that regeneration and reactivation be considered as a viable option to reduce its production costs, which have been reported to be 0.70–1.50 USD/kg in Europe, and regeneration costs, which have been estimated to be 0.70–0.85 USD/kg [76]. Carbons from agricultural sources have been also recommended as a sustainable solution for cost-effective carbon-based adsorbents [77].

Wang et al. [78] reported a removal rate of 54.6% of heavy metal by blue-green fluorescent carbon nanoparticles synthesized by chitosan. This nanoparticle was synthesized through a cost-effective and environmentally friendly method known as the hydrothermal method. While there are many other limitations to the adsorption technology, cost has been highlighted as the main hindrance. Hence, there has been a rise in studies investigating biological methods of producing nanoparticles. There are several nanoparticles that have been successfully produced from biological methods, e.g., ZnO, Cu, CuO, Au, Se, Fe_2O_3, etc. These biological nanoparticles are normally produced by different species of bacteria, fungi, actinomycetes, and yeasts [37].

6. Emerging Research in Nanotechnology for Heavy Metal Removal

Several researchers have done outstanding work in developing innovative solutions to address some of the drawbacks of nanotechnology in WWTPs. Recent interesting work has been done to address issues such as low removal capacity, low surface area, and regeneration problems [79], including the development of fast and continuous microfluidic systems for the production of 5 nm TiO_2 nanoparticles by Deng et al. [80]. The TiO_2 nanoparticles produced from this method were said to display great adsorption and photocatalytic performance. Xu et al. [81] also successfully produced magnetic nickel ferrite through an innovative alcohol solution combustion-calcination method. The resultant nano-absorbent was shown to address the various drawbacks associated with the process of preparing magnetic nano-ferrite. This method of producing magnetic nickel ferrite had several benefits, such as short preparation time, homogeneous products, no necessity of dispersant, and straightforward control of magnetism. Moreover, the nanoparticle produced from this method displayed interesting properties, such as improved adoption area, exceptional stability, low production cost, great saturation, and simple separation by external magnets. However, it is still a challenge to separate small-sized magnetic nanoparticles from aqueous solutions; thus, their separation generally requires the application of a stronger external magnetic field. This may result in high energy consumption and high operating costs of magnetic nanoparticles, thereby increasing post-treatment costs of nanoparticles. Furthermore, this makes it difficult to separate magnetic nanoparticles for recycling proposes. Hence, some researchers have been exploring innovative and low-energy-consuming magnetic separators that have high magnetic field strength. Li et al. [82] successfully designed a high-magnetic-field-strength and low-energy-consuming magnetic separator, using chromium separation by Nd-Fe-B magnetic bars.

Another interesting nanotechnology field is nano-membranes. Nano-membrane separation has been shown to be a highly effective technology. However, several issues that limit application of nano-membrane filtration, especially in complex wastewater, have been documented. Fouling is one of the major problems hindering membrane application in wastewater treatment. Fouling is caused by blockage of pores, attachment of microbial cells in the membrane, accumulation of absorbed organic compounds, formation of filter cake, and inorganic precipitation [83]. Several researchers have investigated sustainable ways of improving nano-membranes. Cao et al. [84] developed a visible light inducible self-cleaning superhydrophilic nanofibrous membrane with antifouling properties; the membrane was produced through a combination of electrospun silver/β-cyclodextrin/polyacrylonitrile (Ag/β-CD/PAN) and the growing of the zinc oxide (ZnO) layer in situ. The developed membrane displayed an impressive separation of oil and dye from wastewater while presenting a high flux recovery of over 90%. These results are comparable with the results obtained by Lu et al. [85], who reported a separation capacity with a maximum flux of 6779.66 L m^{-2} h^{-1} and a visible light photocatalytic degradation efficiency of 96.5% over 90 min by a novel Zeolitic Imidazolate Framework-8/Graphene oxide/Polyacrylonitrile (ZIF-8/GO/PAN). Moreover, Shakiba et al. [86] successfully modified polyacrylonitrile (PAN) electrospun nanofibers with polyaniline (PANI) for separation of oil/water. The resultant membrane had a good oil rejection of 98.8% for PAN/40%PANI@40 °C membrane.

Metal-organic frameworks (MOFs) are adsorbent materials that have been gaining popularity recently. They are organic–inorganic hybrid materials formed by the self-assembling of metal ions and organic ligands with the aid of coordination bonds. The metal-organic frameworks (MOFs) have been shown to have high adsorption capacity. They have exceptional characteristics, which include large specific surface area, open metal sites, and porosity. These properties make them an ideal candidate for heavy metal removal. Moreover, water-stable MOFs (WMOFs) have been shown to be photo responsive and thus can absorb light via organic linkers or metal centers. The synergistic and coupling effect between the photocatalytic and adsorption systems during heavy metal removal by WMOFs results in outstanding pollutant removal. The stability and removal capacity of MOFs can be enhanced by the introduction of suitable functional groups for the targeted contaminant [87]. Yu et al. [88] developed a highly stable iron-based metal-organic framework (Fe-MOF) with low metal leaching and improved the catalytic ozonation performance. This was done by tuning the Lewis acidity of Fe-MOFs. Additionally, Hu et al. [89] successfully fabricated stable and durable MOF-based melamine foams (MFs), which were able to destroy up to 100% of organic pollutants within 10 min.

7. Economic Evaluation of Nanoparticle Application for Heavy Metal Treatment

The rapid growth in population has resulted in an increase from 30% to 55% between 1950 and 2018. It has been estimated that by 2050, 68% of the world's population will be residing in cities. The speedy increase in urbanization has been noted to contribute to global warming. Thus, the UN has agreed to the agenda 2030 for sustainable development [90]. Water is a critical factor in the survival of humans; hence, some studies have evaluated the role of WWTPs to support sustainable development goals (SDGs) by reviewing SDG6, which aims to ensure that everyone has access to clean water and sanitation. Wastewater treatment is the sector that will enable the world to meet the safe water demand. However, 90% of the countries in developing regions still do not treat their wastewater before it is released into the environment [91].

This may be a barrier to the realization of the targeted goals by many countries. These problems are as a result of financial constraints, particularly in developing countries. It has been noted that the investments in place are not sufficient to build or improve infrastructure to achieve SDG6. Thus, it has been noted that the world will not meet the SDG6 target by 2030 due to the high investments needed to achieve this goal. The estimated investment required to build the infrastructure needed to achieve the 2030 agenda has been estimated to be around USD 90 billion, with investment needed per year to meet water- and wastewater-related goals between years 2016 and 2030 estimated to be USD 46 billion for urban areas and USD 25 billion for rural areas. Hence, cost-effective sustainable wastewater infrastructure systems must be developed urgently [90].

The urgency for developing sustainable technologies for the treatment of wastewater has led to researchers investing time and resources in efficient, environmentally friendly, and cost-effective technologies. This has led to many countries basing their selection of technologies to use for wastewater treatment mainly on economic and environmental considerations. Malik et al. [91] and Bhaduri et al. [92] reviewed the indicators that can be used to evaluate the progress of the UN in achieving SDG6. Both these studies noted that low-income regions will struggle to meet SDG6 due to financial restrictions [93]. Nanotechnology has been reported to be a promising technology in terms of sustainability. However, the application of this technology is still partial, owing to the high investment required to implement it. Several studies have assessed the techno-economic feasibility of implementing this technology in WWTPs [94,95].

Mahmoud et al. [60] investigated using coagulation and adsorption by Fe/Cu nanoparticles in textile WWTPs. The study estimated the annual capital expenditure for coagulation and adsorption plants to be 0.0208 USD/m^3, the energy costs to be 0.00054 USD/m^3, and the material cost for coagulant and adsorbent materials to be 0.15 USD/m^3 and 6.1 USD/m^3, respectively. Moreover, the authors also estimated the labor costs and maintenance costs for the system as 0.1 USD/m^3 and 0.0037 USD/m^3, respectively. Therefore, the total operational expenses were estimated to be 6.35 USD/m^3. This operational cost is greater than the estimation of operational costs for the combination of electrocoagulation and ozonation processes for the treatment of textile water reported by Yin et al. [96], which was found to be 5.8 USD/m^3.

Thus, Mahmoud et al. [60] suggested that the operational expenses can be reduced by using green synthesized nanoparticles rather than using chemical synthesized nanoparticles. Proanthocyanidins, which are complex flavonoid polymers from cereals, legume seeds, and fruits, have also been investigated for green synthesis of proanthocyanidin-functionalized Fe_3O_4 nanoparticles for heavy metal removal [38]. Moreover, entrapping nanoparticles for reuse can also be another option to reduce cost. Several studies have successfully proven that nanoparticles can be recycled [97–99]. However, the literature on the recycling of nanoparticles for heavy metal removal in large-scale treatment as well as techno-economic analyses of how the recycling of nanoparticles can impact the cost of nanotechnology in wastewater is still limited.

Additionally, Noman et al. [56] investigated using Cu/Zn nanoparticles as a bacterial disinfectant for the treatment of wastewater. The results obtained from this study indicated that the fixed capital estimation for the design of an appropriate treatment plant with 1000 m^3 capacity would cost USD 950,000, while the operational costs and working capital costs of the treatment plant were estimated to be USD 475,000 and USD 61,750, respectively. This results in a total investment cost of USD 1,425,000.

Table 4 shows a comparison of costs of operating different technologies for the treatment of wastewater. Although it has been argued that using green nanoparticles could potentially reduce operational costs, from the data shown in Table 4, it is clear that adsorption is still costly, even though green synthesized nanoparticles are used. Much work has been done in developing cost-effective and environmentally friendly nanoparticles. However much still needs to be done to reduce the cost, such that its application fits into the average operating budget of WWTPs.

Table 4. Cost of operating different technologies for heavy metal and pathogen removal in wastewater.

Technology	Catalyst	Targeted Contaminant	Removal Efficiency	Cost USD/Year	Ref
adsorption	honeydew peel activated carbon	Cr^{3+} Zn^{2+}	83.49% Cr^{3+} and 88.88% Zn^{2+}	97,050.00	Yunus et al. [100]
coagulant	cassava peel	Alum CPS mixture of CPS	83.44% alum, 76.83% CPS, 32.87% mixture of CPS	21,370.00	Kumar et al. [5]
reduction–precipitation–settling process	-	Cr(VI)	85% Cr(VI)	43,875.98	Rodríguez et al. [94]
ionic exchange and photocatalytic process	-	Cr(VI)	85% Cr(VI)	53,767.78	Rodríguez et al. [94]
pathogen disinfection biosynthesized by *Aspergillus iizukae*	Cu/Zn	pathogen disinfection *E. coli* *S. aureus*	inactivation (6 $\log_{10}$) of *E. coli* (5.21 $\log_{10}$) of *S. aureus*	131,387.20	Noman et al. [56]

The prices of nanoparticle raw materials for nanoparticle production is noted to vary depending on the country where the study is conducted. A techno-economic study of magnesium oxide production conducted by Febriani et al. [57] in Indonesia indicated that raw materials for the production of 375,000 kg of magnesium oxide cost 483,750 USD; magnesium nitrate, sodium bicarbonate, and sodium hydroxide market prices were 2.00 USD/kg, 0.25 USD/kg, and 0.90 USD/kg, respectively. The equipment cost for magnesium oxide production was estimated to be 44,943 USD. The author further indicated that the annual utility for this production was 41,271 USD/kWh, and salary cost was estimated to be 10 USD/day. These estimations were slightly lower than the estimation made by Yashni et al. [101], who reported a production cost of ZnO NPs in Malaysia. The author indicated that the total cost for raw materials (orange peels) and Zinc Acetate Dehydrate to be 00.00 and 259.00 USD/kg, respectively. The utilities, which include electricity and water, were 0.04 USD/kWh and 0.01 USD/m^3, respectively. Labor costs were estimated to be 10,000 USD/employee. Therefore, the total production was estimated to be 57,124.32 USD/year. Additionally, the market price of nanoparticles was reported to be 5 USD/L, 4 USD/L, 1 USD/kg, and 16 USD/kg for titanyl isopropoxide, nitric acid, glycine, and TiO_2 nanoparticles, respectively [102], and 2 USD/pack (1 kg) of magnesium oxide nanoparticles [101]. Due to the high cost of nanoparticles, coupling nanotechnology with traditional heavy metal removal methods has been said to reduce the cost of producing/purchasing nanoparticles. Mahmoud et al. [60] reported the annual capital expenditure of coupling coagulation and adsorption by Fe/Cu nanoparticles in textile wastewater. The use of agricultural waste as an absorbent for heavy metals was shown to be a cheaper alternative. Abd et al. [103] conducted a techno-economic study using rice husk for Cu(II) adsorption in Egypt. The market price of rice husk raw materials was estimated to be 42 €/t for a 1200 t/y production with operational, energy, and labor (five workers) costs of 50,400 €/y, 32,040 €/y, and 46,900 €/y respectively. It is important to note that these estimations may vary owing to the current economic standing in different parts of the world.

8. Conclusions

The use of nanotechnology for the treatment of contaminated water is receiving a lot of attention due to its interesting benefits. Although there are numerous studies reporting the high efficiency of different nanoparticles, the application of nanotechnology in wastewater treatment is still limited, owing to the high operating costs associated with this technology. Thus, there is a growing interest in investigating the low-cost methodologies of producing nanoparticles. Although there have been numerous attempts to reduce the costs incurred by application of nanotechnology in wastewater, from the comparison with other technologies, it was shown here that nanotechnology remains costly for wastewater treatment, even with recent developments. Therefore, more advances are needed to further reduce costs, such that this technology can be applied even in developing countries.

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