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### Effect of Metal Nanoparticles on Phosphate Removal from Aqueous Solutions: A Review

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ABSTRACT
Phosphate (P) is a major pollutant that leads to deterioration and pollution of natural
water quality as well as the death of living organisms in those waters. With the rapid increase in the world population and incorrect disposal of wastewater, water pollution with P increases; therefore, reduction of it has received significant attention in the scientific community. This paper reviews the reported literature on traditional methods used to remove P from water and the advantages and disadvantages of each of them in addition to discussing the employed for modern advantages of each
of them, in addition to discussing the application of modern adsorption technology to remove P from water using metallic nanomaterials, and discusses their unique
properties and high adsorption capacity of P from water, then highlights the challenges and multiple gaps that may affect the efficiency of the removal process, in order to reach the best and fastest technology to remove P from water with the highest efficiency and the lowest possible cost.

#### 1. Introduction

Water is an essential source for all living creatures and for human societies with their various cultures and customs. Unfortunately, some of the biological, chemical, and physical characteristics of natural waters have been altered due to the improper disposal of human waste and pollutants. This includes the dumping of materials such as organic or inorganic materials, toxic substances, and pollutants from various sources, which are among the main causes of changes in water quality. These changes can lead to the proliferation of disease organisms and the death of living organisms, making the water unsafe for both the environment and drinking [1]. When effluent water containing pollutants is introduced into clean natural water, it can cause significant changes in water quality and alter the structure of the ecosystem [2]. Water pollution, defined as any physical, chemical, or biological change in water quality that negatively impacts living organisms in the environment or makes a water resource unsuitable for its beneficial uses, is a serious issue that must be addressed.

Water pollution has a devastating impact on humans and all other organisms on Earth, such as animals, plants, marine life, and birds. According to Mei et al. [3], water pollution caused by industrial pollutants has caused a scarcity of pure fresh water. It is worth noting that the impact of these pollutants on natural running water depends on the type of pollutant, its concentration in the water, and the length of time the community is exposed to it. Ensuring access to clean, affordable water for drinking is a crucial humanitarian goal and a major challenge. Therefore, the use of non-conventional water sources and the reuse and treatment of sewage water have become

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advanced forms of water supply to reduce this consumption of natural water and highlight its importance. Since traditional techniques for treating natural water and wastewater are limited, advanced technologies are needed to produce clean water efficiently and at a low cost without causing any harm to humans or the environment.

#### 2. Phosphate in Water

Phosphate (P) is a necessary nutrient in the natural water environment, but it is usually found in low concentrations. However, man-made sources such as detergents, fertilizers, pesticides, and additives, as well as the improper disposal of domestic, industrial, and agricultural wastewater, can increase the amount of P in the water [4]. This can lead to changes in the environment, nature, and quality of the water and harm the natural food chain of aquatic organisms through a decrease in dissolved oxygen levels, which are essential for the life and growth of living organisms and fish. Eutrophication, or the excessive growth of harmful aquatic algae and plants, can also occur, leading to the death of aquatic life. Since 1970, the increase in sewage water discharged into the water has played a significant role in the emergence of eutrophication, which has caused changes in the nature and quality of water as well as the death of living organisms [5].

Phosphate is also a major cause of efflorescence in natural waters, but stabilizing or controlling its concentration in water remains a difficult environmental problem [6]. According to the Environmental Protection Agency, the total amount of P in water should not exceed 0.05 mg/L [7, 8]. Taha et al. [9] found that the concentration of P in irrigation canals in Egypt ranges from 7 to 10 mg/L, while in drainage channels it ranges from 2 to 12 mg/L.

#### 3. Methods for Removing Phosphate from Water

There are several methods available for removing P from water, including physical-chemical methods and biological methods. Chemical methods, which involve the use of expensive reagents and coagulants that can create secondary pollution, are generally avoided. Physical-chemical methods are expensive due to the complexity of the processes. These approaches are broadly categorized as "treatment procedures" for eliminating P from wastewater. The most commonly used methods for removing P include adsorption, chemical precipitation [10], physicochemical processes [11], and improved biological removal of P [12]. In the last two decades, iron particles have received attention due to their reactive and absorbent properties [13]. P can also be removed from wastewater through biological absorption by microorganisms or chemical precipitation with metal cations. These methods can be applied in wastewater treatment plants to remove P from liquid waste. A biological process can be used to remove the majority of the P concentration, while a chemical process can be used to remove the remaining concentration in the effluent to be disposed of.

# 3.1. Physical-chemical treatment method for removing phosphate compounds

The removal of phosphate compounds from wastewater can be achieved using physical-chemical methods such as chemical precipitation, adsorption, magnetic field treatment, electric coagulation and floatation, and crystallization, as noted by Ruzhitskaya & Gogina [14]. There are many other physicalchemical methods that have been developed for removing P from aqueous solutions, including electrolysis, reverse osmosis, and ion exchange, but they have not been widely adopted due to their high costs and relative complexity, as noted by Chen et al. [15] and Mahdavi & Akhzari [16].

# 3.1.1. The chemical precipitation treatment method for removing phosphate compounds

The chemical precipitation method is a commonly employed technique for removing P from water, especially in small to medium-sized treatment plants. This method entails the use of coagulants, such as polyvalent metal ions like calcium (Ca<sup>2+</sup>), aluminum (Al<sup>3+</sup>), and ferric ions (Fe<sup>3+</sup>), which are mixed with water to remove inorganic particles of P ions [17]. Upon the addition of reagent ions, soluble phosphoric acid salts react with them, forming highly dispersed colloidal P precipitates. Additionally, the chemical reacts with water-borne bases to produce deposits. These coagulated and suspended colloidal phosphate precipitates also adsorb some organic phosphorusbearing compounds, which are then removed from the system. The conversion of P species (e.g., H<sub>n</sub>PO<sub>4</sub><sup>1-</sup>,  $HPO_4^{2-}$ ) to  $PO_4^{(3-)}$  occurs during this process [13], as depicted in the following reaction:

$$H_n PO_4^{(3-n)-} + n OH^- \to PO_4^{(3-)} + nH_2O$$
 (1)

The most commonly used coagulant for removing P from water is calcium ions, which are usually added in the form of lime (Ca  $(OH)_2$ ). Lime reacts with the natural alkalinity of bicarbonate and precipitates as calcium carbonate (CaCO<sub>3</sub>), thereby raising the pH of the water. The excess calcium then reacts with P, further increasing the pH to above 10 (Eqs. 2 and 3).

 $10Ca^{2+} + 6PO_4^{3-} + 2OH^{-} \leftrightarrow Ca_{10} (PO_4)_6 (OH)_2 \qquad (2)$ 

$$Ca (OH)_2 + HCO_3 \rightarrow CaCO_3 \downarrow + H_2O + OH^-$$
 (3)

In addition to raising the pH, lime also reacts with phosphate to form calcium oxalate apatite (Eq. 4), which is less soluble and can be removed from the water.

$$5Ca + 4OH^{-} + 3HPO_{4}^{2-} \rightarrow Ca_{5} OH(PO_{4}) \downarrow + 3H_{2}O \qquad (4)$$

The solubility of calcium oxalate apatite decreases with increasing pH, and phosphorus removal is more efficient at pH values above 9.5, where almost all of the phosphorus is precipitated [14].

The precipitation of P using aluminum ions  $(Al^{3+})$ and ferric ions  $(Fe^{3+})$  differs from the precipitation using calcium ions  $(Ca^{2+})$ , where the trivalent ions interact with orthophosphate to form a metal precipitate-phosphate, as shown in Eqs. 5 and 6.

$$Al^{3+} + H_n PO_4^{(3-n)} \leftrightarrow AlPO_4 \downarrow + nH^+$$
(5)

$$Fe^{3+} + H_n PO_4^{(3-n)} \leftrightarrow FePO_4 \downarrow + nH^+$$
 (6)

Sources of  $(Al^{3+})$  and  $(Fe^{3+})$ , such as alum (aluminum sulphate) and ferric chloride  $(FeCl_3)$ , are used for this purpose [18]. When aluminum sulphate is added to water in the presence of alkali, a reaction (Eq. 7) occurs. In the presence of P, a reaction (Eq. 8) takes place, resulting in the formation of aluminum phosphate and other compounds. The aluminum hydroxide sludge flakes have the ability to adsorb both aluminum phosphate and colloidal particles of solid impurities, facilitating the removal of phosphorus from wastewater.

$$Al_{2}(SO_{4})_{3} + 6HCO_{3^{-}} \rightarrow 2Al (OH)_{3} + 3SO_{4}^{2^{-}} + 6CO_{2}$$

$$Al_{2}(SO_{4})_{3}14H_{2}O + 2PO_{4}^{3^{-}} \rightarrow 2AlPO_{4} \downarrow + 3SO_{4}^{2^{-}} + 3SO_{4}^{2^{-$$

(8)

When salts of trivalent iron  $(Fe^{3+})$  are used as coagulants, the following reaction occurs, as shown in (Eq. 9):

 $14H_2O$ 

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \downarrow$$
 (9)

Where three valence irons  $(Fe^{3+})$  are formed when divalent iron is combined with green vitriol, it is oxidized to three valence irons, as in (Eq. 10):

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} \tag{10}$$

To remove FePO<sub>4</sub> particles and other solid particles in wastewater, excess ferric ions must be added to generate iron hydroxide sediment, which has colloidal sizes. The sediment also acts as an adsorbent for other phosphorus-containing compounds. Precipitating flaky iron hydroxide sediment can be challenging, and

organic polymers are often necessary to obtain clear supernatant water.

Chemical precipitation is often used for treating high concentrations of P in industrial wastewater, but due to its limitations, the development of adsorbents for bulk P removal has been studied [19]. It has been observed that chemical methods provide a higher removal rate for P than the biological treatment method, but chemical methods have several disadvantages, including severe environmental impacts and negative effects on human health, which can lead to cancer infection and death. Moreover, the use of chemical compounds requires water to undergo reprocessing to prevent the risks associated with their use, and the costs involved can be high. In addition, chemical methods can produce secondary contamination, which further limits their effectiveness [14].

### 3.1.2. The adsorption method for removing phosphate compounds

In the adsorption method, sorbents with high adsorption capacities up to 95%, such as granulated aluminum oxide, activated aluminum oxide, and aluminum sulphate, are commonly used. However, low adsorption capacities are the problem with sorbents like iron oxides and natural ores such as calcite, goethite, activated red clay, and activated carbon, as reported by Chitrakar et al. [20] and Hussain et al. [21]. Recent studies have evaluated various adsorbents for removing P from water, including slag [22, 23], red clay [24], thermally treated natural playworker [25], iron-based components [26], zirconium [27], coal fly ash [28], crab shells [28], lithium intercalated gibbsite [29], and Mg-Mn doublelayered hydroxides [30]. Despite the potential of sorbents for P removal, their implementation requires strict pre-treatment of the liquid discharge, leading to increased complexity and cost of purification processes, as pointed out by Bunce et al. [31].

Previous studies have tested sorbents for removing P from water, such as Mezenner & Bensmaili 's [32] study, which used waste iron hydroxide-eggshell as an adsorbent under multiple experimental conditions, including solute concentration, contact time, adsorbent dose, and solution temperature. The results showed that waste iron hydroxide-eggshell particles could be an excellent agent for removing P from wastewater.

Iron oxides and natural ores like calcite have been proven to remove P from water, but they have low adsorption capacities, as reported by several studies. The absorption capacity of iron oxide is 11.2 mg PO<sub>4</sub><sup>3-</sup>/g [33] and 19.02 mg PO<sub>4</sub><sup>3-</sup>/g [34], while natural ores such as calcite have an absorption capacity of 3.1 mg PO<sub>4</sub><sup>3-</sup>/g [35]. FeOOH has an absorption capacity of 17.3 mg PO<sub>4</sub><sup>3-</sup>/g [20], activated red clay has an absorption capacity of 9.8 mg PO<sub>4</sub><sup>3-</sup>/g [33], and activated carbon has an absorption capacity of 3.02 mg PO<sub>4</sub><sup>3-</sup>/g [21].

# 3.1.3. The magnetic field method for removing phosphate compounds

The process of magnetic field treatment for removing P from wastewater involves binding P to insoluble compounds using a reagent, followed by the addition of magnetic material to create a magnetic field that isolates the phosphate-containing sediment [14].

### 3.1.4. The crystallization method for removing phosphate compounds

Crystallization is another physical-chemical method that involves the formation of P crystals in wastewater at crystallization centers, which are then removed from the system either on filters or in suspended sludge [14]. These methods have demonstrated high efficiency in P removal, with some achieving complete removal in certain cases.

# 3.1.5. The electric coagulation and floatation method for removing phosphate compounds

The electrocoagulation and floatation methods can ensure complete removal of P. In a study conducted by Dura & Breslin [36], P was removed to levels below the limit of detection over a time period of 30 to 60 minutes, depending on the initial concentration of P, using an Al-Mg anode in the coagulant. The Al-Mg alloy exhibited good performance, and complete removal of P was achieved from two real water samples after 15 minutes. However, excessive energy and electricity consumption were observed with this method, leading to reduced efficiency due to local corrosion of the cell elements caused by chloride ion attack. Ultimately, the efficiency of P removal in this method is significantly influenced by cell capacities [36].

Physical-chemical processes have long been utilized for controlling P through their reliable and efficient removal. However, they are not without drawbacks, such as the high operating energy and periodic maintenance requirements, which lead to increased operational costs, as highlighted by Crini & Lichtfouse [37]. Furthermore, extraneous solids produced during physical-chemical treatments often necessitate additional treatment steps, making the method unsuitable for large-flow water treatment operations [37]. 3.2. Biological treatment method for removing phosphate compounds

Recent research has focused on the use of the biological treatment method to remove phosphorus, with biological methods being considered a costeffective and environmentally friendly alternative to chemical treatment, according to Acevedo et al. [39] and Nguyen et al. [40]. However, Seviour et al. [41] have cautioned that this method's reliability is often inconsistent and can be challenging to control effectively due to fluctuating performance and a high reliance on skilled operators for phosphorus removal.

According to Mulkerrins et al. [42], the biological removal of phosphorus involves using phosphateaccumulating organisms (PAOs) to remove phosphorus from water. This process occurs in two stages, starting with anaerobic conditions where microorganisms release accumulated phosphate (PO43-) by breaking down polyphosphates, which are the forms in which phosphorus is stored in biomass, while consuming degradable organic compounds such as volatile fatty acids (VFAs). In aerobic conditions, these microbes absorb P through a process called super sorption, resulting in a decreased P concentration in water due to accumulation in microbial biomass. Almeelbi [13] has noted that maintaining a sufficient ratio of VFAs or rbCOD (fraction of total COD) to orthophosphoric is crucial to ensuring healthy bacterial intake in the aerobic phase. However, Panswad et al. [43] have highlighted the impact of temperature on the generation of VFAs, where PAOs are affected by high temperatures above 30 °C, leading to decreased P uptake.

Several studies have highlighted the multiple drawbacks of using the biological treatment method for removing P from water. Crini & Lichtfouse [37] noted that this method is inefficient in removing small particles of pollutants and non-biodegradable compounds. Also, this method is a slow process that needs large areas to expand the stages of the removal process. Additionally, the biological treatment method mainly relies on microorganisms, which makes it vulnerable to climate change. Prior treatment, such as physical-chemical treatment, may also be necessary. Due to the lack of good control, the proliferation and generation of biological sludge may occur, leading to product deterioration, which necessitates periodic management and maintenance of microorganisms and a good understanding of the enzymatic processes that govern the decomposition of materials. According to O. Ruzhitskaya & Gogina [14], conventional biofiltration can only remove 20%-40% of P, and using more sludge can increase P removal to 50%, but this is still insufficient.

#### 4. Nano-Metal Technology

#### 4.1. Uses of nanoparticles in the environment

The use of nanoparticles (NPs) in water treatment processes has become a reality, and a large list of materials based on nanostructures is now available on the market or under final research steps [44]. Reducing the permissible level of pollution in drinking water is a major challenge now, according to Jia et al. [45]. Nanotechnology has been proven to be effective in various fields, such as the detection of pollutants, the treatment and removal of environmental pollutants, pesticide and soil pollution control, and air and water pollution control. Nanoparticles are used as polymer catalysts to enhance the ultrafiltration process and purify drinking water without the need for chlorination. The use of nanotechnology is expected to grow by 30% annually over the past decade, providing a tremendous opportunity for the development of water supply systems and the application of nanomaterials in the field of wastewater treatment [46, 47]. NPs of metal oxides such as titanium dioxide  $(TiO_2)$ , zinc oxide (ZnO), and tungsten oxide (WO<sub>3</sub>) are ideally used in water treatment technologies due to their superior ability to improve water properties and remove pollutants better than traditional chemical, biological, and physical treatment methods [48, 49].

#### 4.2. Description of metal nanoparticles

The application of magnetic separation has broadened with recent advances in nanotechnology, including the treatment of water with magnetic nanoparticles for environmental remediation [50], bioanalysis [51], and therapeutic applications [52, 53]. Magnetic separation is a process that utilizes magnetic force to separate magnetically sensitive materials from a mixture. As stated by Li et al. [54], magnetic nanoparticles are a subset of nanoparticles that can be controlled by a magnetic field and frequently contain magnetic elements such as iron, nickel, and cobalt. These particles often exhibit superparamagnetic properties with a size between 1 and 100 nm. Superparamagnetic is seen in micro-magnetic or ferromagnetic NPs that exhibit paramagnetic activity below the Curie temperature. Micro-magnetic or ferromagnetic NPs exhibit paramagnetic activity below the Curie temperature. The magnetization of the NPs appears to be zero on average in the absence of an external magnetic field, but they can be magnetized like a paramagnet when an external magnetic field is applied. However, compared to paramagnets, their magnetic susceptibility is substantially greater.

#### 4.3. Advantages of using metal nanoparticles

The cost criterion has become increasingly important in selecting techniques to absorb pollutants like P, leading to a recent emphasis on the use of cheap sorbents, whether natural or artificial. Mishra et al. [11] indicated that most of the traditional techniques or treatments, such as extraction, absorption, and chemical oxidation, are generally effective, but they are often expensive and sometimes do not reach the required efficiency. Therefore, there is a need for effective, efficient, and affordable methods to reduce toxicants to safe handling levels. Nanotechnologies can provide a solution due to the unique properties of nanomaterials, which include high adsorption capacity. NPs like iron, silver, and titanium oxides have numerous potential applications, such as catalysts, nanotubes, bioactive NPs, and more. Thus, they are increasingly being utilized to purify and treat polluted water, with significant research focusing on the removal of specific pollutants from water.

Magnetic NPs are effective in treating and removing pollutants from wastewater, particularly organic pollutants. In addition to being highly efficient, renewable absorbent nanomaterials are costeffective, as noted by Corredor et al. [55] and Suhas et al. [56], which promotes further commercialization and development of nanomaterial applications, as indicated by Adeli et al. [58] and Saravanan et al. [57]. Metal oxides, such as Fe<sub>3</sub>O<sub>4</sub>, ZrO<sub>2</sub>, and CuO, have been extensively studied for P removal, as they have a strong adsorption capacity for it, as noted by L. Chen et al. [15].

Compared to conventional materials, the primary advantage of using NPs is their high surface area, which allows for the development of chemical reactions, physical exchanges, and other processes [59]. While traditional techniques like extraction, absorption, and chemical oxidation are generally effective, they can be expensive and sometimes fail to achieve the desired level of efficiency. Therefore, the ability to reduce the amount of toxic substances to safe levels with high effectiveness and an appropriate cost is crucial. In this regard, nanotechnologies can play a distinct and significant role. NPs have a high adsorption capacity, making them widely used in water purification and pollutant treatment. Metallic NPs are also crucial in wastewater treatment, particularly in the removal of organic pollutants. As a result, renewable nano-absorbent materials are highly cost-effective and encourage further commercialization, numerous leading to developments and applications, as indicated by Adeleye et al. [60].

Adeleye et al. [60] highlighted that the advancement of nanotechnology presents a new

opportunity to develop technologies that can contribute to solving technical challenges and addressing water problems by improving water quality. Nanotechnology involves manipulating materials at very small scales, resulting in nanomaterials that offer unique and surprising properties due to their high strength, conductivity, and large reaction rate. The discovery of these properties has led to numerous applications in different areas that can enhance human life, including water. Using nanotechnology in natural water and wastewater treatment not only overcomes challenges associated with traditional technology but also offers a modern, distinct approach for wastewater treatment and reuse that takes into account economic aspects and international water quality standards, achieving the highest efficiency at the lowest cost.

#### 4.4. Pollutants removal using metal nanoparticles

Metal oxides, particularly goethite, have demonstrated an effective approach to removing P from aqueous solutions, as indicated by Chitrakar et al. [20], Nowack & Stone [61], and Antelo et al. [62]. In addition, various nanomaterials, including nanozero iron (FeO), F<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, have been utilized in water treatment. Antelo et al. [62] have highlighted the significance of TiO<sub>2</sub> and its properties in chemical reactions, while Rahmani et al. [63] have underscored the importance of  $Al_2O_3$ material. Out of these NPs, Fe<sub>3</sub>O<sub>4</sub> is the most widely used, most efficient, and most effective classical nanoparticle in water and wastewater treatment, as confirmed by Hu et al. [65] and Panneerselvam et al. [64].

#### 4.5. Toxicity of metal nanoparticles

The potential toxicity of nanomaterials is often associated with the very properties that make them useful, whereas, toxicity depends on both the size (which affects absorption) and the molecular structure of the nanomaterial elements (which generally determine toxicity endpoints) [66]. It has been shown that silver nanoparticles [67, 68], and CNTs [69, 70] have shape-dependent toxicity, although it is unclear whether these results are due to a high percentage formed on reactive surface sites exclusively at the nanoscale or are related to differences in shape-related bioavailability, absorption, and bioaccumulation potential [71]. The risks of many nanomaterials can be estimated and evaluated through the large toxicological database available for bulk analogues that have common components, however, the lack of bulk analogues for some allotropic nanomaterials such as fullerenes and CNTs precludes such comparisons and indicates the need for more high-resolution toxicity research. Therefore, in general, the life cycle of each stage of nanomaterials must be taken into account to assess risks and toxicities [72].

However, Mpongwana & Rathilal, [73] indicated that the application of magnetic nanoparticles for water purification may cause toxicity, genotoxicity, phytotoxicity, skin irritation, and some other health problems, including the possibility of kidney disease. In addition, some magnetic nanoparticles containing precursor salts may be carcinogenic. Therefore, it is necessary to conduct further investigations to reduce the health risks that may be caused by the application of magnetic nanoparticles for water purification [74].

Reducing risks to public health and the environment can be achieved by limiting potential exposure through the immobilization of nanoparticles on reactor surfaces or support media, this may also result in the added benefit of reduced nanoparticle aggregation and increased activity [75]. For nanoparticles that release toxic metals (for example, Ag nanoparticles and metallic QDs), controlling their dissolution is critical, this can be done by using a stabilization coating or by modifying the form and size of the nanoparticles. Barrier technologies (such as membranes and magnetic separation) can also be used to recover the nanoparticles and stop their release. Overall, to reduce risks, it must be taken into consideration when designing nanomaterials that all of its components are safe. There is no doubt that this strategy facing reducing toxicity without harming the performance of nanomaterials or restricting their activity represents a major and important scientific challenge [66].

#### 4.6. Sustainability of metal nanoparticles

Metal oxide nanomaterials, such as nano-iron oxide and nano-TiO<sub>2</sub>, are cost-effective and adsorptionefficient adsorbents, and their active adsorption sites can be increased by manipulating their surface structure, such as corners, edges, high-energy, and crystalline aspects [76, 77]. In addition, magnetite nanoparticles possess unique superparamagnetic properties that allow them to be easily separated from water in a weak magnetic field [78]. These magnetic properties provide a new class of core-structured nanoparticles, where the shell provides the required functionality while the magnetic core allows for easy separation of the particles [66].

Some previous studies have indicated the possibility of exploiting metallic nanoparticles after separating them and reusing them repeatedly in adsorption processes [5, 79, 80], which provides an

opportunity to increase the utilization of the metal nanoparticle adsorbent and thus obtain costeffectiveness while increasing removal efficiency. Therefore, metal nanoparticles can be judged as environmentally friendly materials.

In light of the above, Mpongwana & Rathilal [73] explained in their study that there is great scientific interest in sustainable and environmentally friendly methods of producing nanoparticles as a result of the growing desire to reduce the costs of applying nanotechnology for wastewater treatment. According to the suggestions of many researchers, it has been concluded that it is important to resort to using sustainable and cheap materials to produce cheaper nanoparticles, as some research has shown that recycling used nanoparticles can reduce the cost of using newly produced nanoparticles. As a result, nanotechnology has been reported as a promising technology in terms of sustainability, and several studies have successfully demonstrated the recycling potential of nanoparticles [81, 82, 83].

#### 4.7. Removing phosphate with metal nanoparticles

The utilization of metallic nanomaterials in adsorption offers several advantages, including their absorbable nature, regenerative properties, flexibility in design and operation, and economic recovery [55, 56]. Many different sorbent materials have been employed to improve water and wastewater quality standards by removing organic and mineral contaminants [48, 49]. Recently, the utilization of magnetic nanoparticles has expanded the scope of magnetic separation to include water treatment [50], bioanalysis [51], and therapeutic applications [52, 53].

The selection of a suitable adsorbent is crucial for an effective adsorption process [15, 84, 85]. Adsorption has been extensively employed in water purification and wastewater treatment for P removal. Active metal oxides, including Fe<sub>3</sub>O<sub>4</sub>, ZrO<sub>2</sub>, CuO, and others, have been investigated for their strong adsorption capabilities of both HPO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and are widely applied for dephosphorylation [15].

Due to their unique quantum-dependent properties, large surface area, and small particle size, nanomaterials differ significantly from bulk materials [57]. With the advancement of nanotechnology, nano sorbents have become widely employed for pollutant removal due to their high efficiency and dynamic ability, resulting in a large operating surface [57, 58]. Hence, nanomaterials are considered the best alternative for water purification due to their unusual reactivity, surface size, and size-dependent optical, chemical, and physical characteristics [46, 47]. The adsorption of P from water by metal oxide NPs has proven to be an effective and efficient technique for P removal [20, 61, 62].

In recent years, various nano-systems, including graphene nanotubes, carbon nanotubes (CNTs), zero iron (FeO), Fe<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, CuO, ZrO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, CO<sub>3</sub>O<sub>4</sub>, WO<sub>3</sub>, SnO<sub>2</sub>, and MgO NPs, have been extensively employed [5, 16, 46, 86]. Among these metal oxide NPs, Fe<sub>3</sub>O<sub>4</sub> NPs and WO<sub>3</sub> NPs have unique and highly efficient properties, high stability, continuous availability, low cost, high P removal efficiency, non-toxicity, and excellent insulation properties [64, 87, 88]. Therefore, they have been extensively used recently in wastewater treatment and the removal of phosphorus, organic pollutants, and other pollutants affecting water quality and nature.

### 4.8. The cost effectiveness of metal nanoparticles for wastewater treatment

The cost of employing nanoparticles to treat wastewater can differ based on a variety of variables, including the type of nanoparticles, the production process, the size of the wastewater treatment plant, and labor and energy costs in the area. The viability of implementing this technique in wastewater treatment plants from a technical and financial standpoint has been assessed in some research [89, 90].

The ability of some metallic nanoparticles, such as iron and copper nanoparticles, to coagulate and absorb in textile wastewater treatment plants has been studied by Mahmoud et al. [91], according to his study, the yearly capital expenses for coagulation and adsorption facilities are expected to be 0.0208 USD/m<sup>3</sup>, the cost of energy is 0.00054 USD/m<sup>3</sup>, and the costs of the materials used to make coagulant and adsorbent materials are 0.15 USD/m<sup>3</sup> and 6.1 USD/m<sup>3</sup>, respectively. Additionally, the authors calculated labor expenses and system maintenance costs as being 0.1 USD/m<sup>3</sup> and 0.0037 USD/m<sup>3</sup>, respectively, as a result, it was calculated that the total operational costs were 6.35 USD/m<sup>3</sup>.

The market price for some nanoparticles has been mentioned to be 2 USD/pack (1 kg) for magnesium oxide nanoparticles [92]. And 4 USD/L, 1 USD/kg, and 16 USD/kg, respectively, for nitric acid, glycine, and TiO<sub>2</sub> nanoparticles [93].

Moreover, it has been reported that recycling nanoparticles can reduce the cost of using newly produced nanoparticles, also, the option of capturing the nanoparticles for reuse can be another good costcutting proposal, this has led to an increase in studies looking at producing nanoparticles from plant materials, which is relatively cheaper, in addition, it has been recognized that the fabrication of nanoparticles through biological processes is a promising method with a relatively low price [73].

#### 5. Conclusion

In conclusion, metallic nanoparticle technology has been shown to be an effective alternative treatment method for removing P contaminants from water, with high adsorption capacity and fast removal rates. However, it is necessary to know and follow up on the obstacles that may affect the efficiency of P removal by metal nanomaterials, as they still need further investigations. It is also necessary to know the extent of the effect of other pollutants present in water or wastewater on the efficiency of the removal process and on the adsorption capacity of NPs. It is also important to know the extent to which these other pollutants are affected by the process of removing P from metal nanoparticles.

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