

# Purification process and reduction of heavy metals from industrial wastewater via synthesized nanoparticle for water supply in swimming/water sport

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**Abstract.** Heavy metals, widely present in the environment, have become significant pollutants due to their excessive use in industries and technology. Their non-degradable nature poses a persistent environmental problem, leading to potential acute or chronic poisoning from prolonged exposure. Recent research has focused on separating heavy metals, particularly from industrial and mining sources. Industries such as metal plating, mining operations, tanning, wood and chipboard production, industrial paint and textile manufacturing, as well as oil refining, are major contributors of heavy metals in water sources. Therefore, removing heavy metals from water is crucial, especially for safe water supply in swimming and water sports. Iron oxide nanoparticles have proven to be highly effective adsorbents for water contaminants, and efforts have been made to enhance their efficiency and absorption capabilities through surface modifications. Nanoparticles synthesized using plant extracts can effectively bind with heavy metal ions by modifying the nanoparticle surface with plant components, thereby increasing the efficiency of heavy metal removal. This study focuses on removing lead from industrial wastewater using environmentally friendly, cost-effective iron nanoparticles synthesized with Genovese basil extract. The synthesis of nanoparticles is confirmed through analysis using Transmission Electron Microscope (TEM) and X-ray diffraction, validating their spherical shape and nanometer-scale dimensions. The method used in this study has a low detection limit of 0.031 ppm for measuring lead concentration, making it suitable for ensuring water safety in swimming and water sports.

**Keywords:** heavy metals; industrial wastewater; nanoparticles; swimming/water sports; water supply

## 1. Introduction

The aspiration is to create and utilize materials that possess nanometer-scale dimensions. Nanostructured materials are characterized by their solid structure, where atomic arrangement, constituent crystals, and chemical composition are dispersed throughout the material at a scale of a few nanometers. Within these materials, crystals or nanometer-sized grains exist, which can exhibit variations in terms of atomic structure, crystallographic orientations, or chemical composition compared to the rest of the material (Hasan 2015).

The interesting industrial properties of these materials are increasing day by day. Nanomaterials compared to coarse grain materials. They have unique properties (Cui and Wu 2023, Ding *et al.* 2023, Hou *et al.* 2023, Huang 2023, Shi and Teng 2023, Wang 2023, Wang *et al.* 2023, Zhang 2023). When the size of the material is reduced below 100 nm, it shows unusual properties based on quantum mechanisms, which can have properties such as conductivity, heat transfer, melting temperature, optical properties, and magnetization (Xu *et al.* 2022). Nanotechnology is considered the second industrial revolution

due to its unique features in the production of products (Chen *et al.* 2020, 2023, Bai *et al.* 2021, Dong *et al.* 2022, Geng *et al.* 2022). Reducing the size of nanoparticles leads to an increase in the surface volume fraction of atoms and creates unique properties that make it necessary to study their surface chemistry (Falyouna *et al.* 2022).

Nanoparticle synthesis can be achieved through chemical and physical means. When exploring the production of nanomaterials, two broad perspectives can be considered: chemical methods and physical methods. These approaches involve distinct processes and techniques for creating nanoparticles, each offering its own advantages and considerations (Chen *et al.* 2021, Esparham *et al.* 2021, Raj *et al.* 2021, Faramoushjan *et al.* 2021, Cai *et al.* 2021, Maheswaran *et al.* 2022, Shariq *et al.* 2022). By examining these two perspectives, a comprehensive understanding of nanoparticle synthesis can be obtained.

The first category includes the top-down method, which is the method of crushing a piece of material by cutting or breaking intermolecular bonds to reduce it to the desired size. It is possible to break down materials so that they reach nanometer dimensions (Mohammadi *et al.* 2020, Wang *et al.* 2020a, 2023, Ugurlu and Ozturk 2021, Dehghanbanadaki *et al.* 2022). In another class, group the methods from bottom to top. During this fabrication method, atoms and molecules are precisely placed together to form a nanostructure achieved through self-assembly.

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The bottom-up production method is only used to make materials in nanometer dimensions, but the top-down production method is also used to produce nano and micro materials. In another category of nanoparticle production, different methods are used to obtain optimal unique properties of materials (Cao *et al.* 2022, Zhang *et al.* 2022a, Cheng *et al.* 2023, Huang *et al.* 2023). These properties are not limited to a size such as diameter, length and volume, particle size distribution, symmetry of surface properties, surface coatings, purity, and ease of use and are often for mass production (Zhang *et al.* 2022b, Wu *et al.* 2023, Zhao *et al.* 2023).

Currently, chemical methods are commonly employed for the production of nanoparticles. However, these methods are associated with certain drawbacks, primarily due to the use of hazardous and toxic substances. The environmental harm caused by such substances, the residual presence of toxic reagents, the limitations in their applicability for biological and medical research, as well as the substantial costs involved in their preparation and maintenance, have fueled the motivation to explore alternative synthesis approaches for these materials. This has spurred the development of various physical methods for nanoparticle synthesis, offering potential solutions to the aforementioned challenges (Huang *et al.* 2021a, Hu *et al.* 2022, Li *et al.* 2022, Guo *et al.* 2023). Physical methods provide alternatives that minimize or eliminate the use of harmful chemicals, reducing environmental impacts and ensuring compatibility with biological and medical applications. Moreover, these methods offer opportunities for improved control over nanoparticle properties, such as size, shape, and surface characteristics. Examples of physical methods include laser ablation, arc discharge, thermal decomposition, and solvothermal techniques, among others. These approaches rely on physical phenomena, such as high-energy laser pulses, electric discharges, or controlled heating and cooling processes, to generate nanoparticles. By harnessing the principles of physics, these methods provide pathways to produce nanoparticles with enhanced purity, tunable properties, and reduced environmental footprint. The exploration of physical methods for nanoparticle synthesis is driven by the desire to overcome the limitations and drawbacks associated with chemical methods. Through continuous research and development, the scientific community aims to expand the repertoire of efficient, environmentally friendly, and cost-effective approaches for obtaining nanoparticles. This progress not only supports advancements in various fields, including materials science, electronics, energy, and healthcare, but also contributes to sustainable and responsible nanotechnology practices (Duan *et al.* 2015, Hasan 2015).

In recent times, there has been a significant focus on advancing green chemistry methodologies and environmentally friendly approaches in the synthesis of nanomaterials. These endeavors involve the utilization of plant or fruit extracts as stabilizers and capping agents to effectively control the growth of nanocrystals. Green nanotechnology endeavors to minimize the environmental impacts associated with the manufacturing and utilization of nano-based

materials and products. The use of plants as a readily available and sustainable source for the preparation of biocompatible nanoparticles has garnered considerable attention. This approach offers several notable advantages, including cost-effectiveness, non-toxicity, and the production of highly pure nanoparticles (Alsultan Abdulmajeed 2021, Dai *et al.* 2021, Alimoradlu and Zamani 2022, Behdinin and Moradi-Dastjerdi 2022, Thakur *et al.* 2022, Zhao *et al.* 2022). Moreover, nanoparticles synthesized through this method exhibit greater uniformity in terms of particle size distribution and enhanced stability compared to alternative techniques. By harnessing the potential of plant extracts, green nanotechnology provides a viable solution for addressing environmental concerns and sustainability considerations in nanomaterial synthesis. The use of natural sources as stabilizers and capping agents reduces the reliance on hazardous chemicals and promotes the development of eco-friendly nanomaterials (Hou *et al.* 2021, Huang *et al.* 2021b, Xu *et al.* 2021, Wang *et al.* 2022a). This not only aligns with the principles of green chemistry but also opens up new possibilities for the production of nanoparticles with desired properties for various applications. The exploration of green nanotechnology not only contributes to the development of environmentally friendly nanomaterials but also has implications for diverse fields such as medicine, electronics, and energy. The ability to obtain highly pure nanoparticles with controlled size and improved stability is crucial for their successful implementation in various technological advancements (Liu *et al.* 2018, Wang *et al.* 2020b, Lin *et al.* 2021, Tian *et al.* 2022, Sun *et al.* 2023). As research in green nanotechnology progresses, the understanding of plant extract-mediated synthesis methods continues to expand. Efforts are being made to optimize the extraction techniques, investigate the mechanisms underlying the stabilization and growth control of nanoparticles, and explore the wide range of plant sources that can be utilized. These advancements in green nanotechnology not only contribute to sustainable material synthesis but also pave the way for the development of innovative and eco-friendly solutions in nanoscience and nanotechnology (Karthik *et al.* 2022).

Iron and its alloys are the most common ferromagnetic metals and materials in everyday applications. Iron is the fourth most abundant element in the earth's crust, and reactions related to iron play an essential role in the cycle of a wide range of environmental pollutants (Wang *et al.* 2021, 2022b, Yang *et al.* 2021, Zhang *et al.* 2022c). In 1990, iron nanoparticles were used as purifiers of polluted water. Among the magnetic nanoparticles, iron oxide nanoparticles have provided a suitable path for the technology of magnetic separation of pollutants due to the ease of manufacturing, the possibility of functionalizing and coating these nanoparticles, and having super magnetic properties compared to the bulk state. Iron oxide nanoparticles are of great importance (Rashtbari *et al.* 2022). Because it is easy to dissolve in the magnetic field, it is separated and reused, which helps reduce costs (Babel and Kurniawan 2003). The results have shown that iron oxide nanoparticles are very absorbent and suitable for removing heavy metals (Miklos *et al.* 2018). One of the most

important goals of environmentalists and supporters is to remove toxic and dangerous substances from the cycle of nature. Toxic substances are usually made up of atoms that are not harmful in themselves, but the way these atoms are joined together produces toxic substances. Lead is a chemical element with the symbol Pb and atomic number 82. It is a heavy metal that is denser than most typical materials. Lead is soft and malleable and too has a reasonably lower melting point. When freshly cut, lead is silvery with a touch of blue, it degrades to a dull gray color when disclosed to air. Lead has the most increased atomic number of any stable element, and three of its isotopes are endpoints of major nuclear decay chains of heavier elements. Lead toxicity became widely acknowledged in the late 19th century. Lead is a neurotoxin that gets into soft tissues and bones, it hurts the nervous system and intrudes with the function of biological enzymes, causing neurological illnesses from behavioral issues to brain damage and also affecting general health, cardiovascular, and renal systems. Lead is an entirely toxic metal concerning nearly every organ and system in the human body. Most consumed lead is absorbed into the bloodstream (Zhang *et al.* 2011). The primary cause of its toxicity is its predilection for meddling with the correct functioning of enzymes. It does so by attaching to the sulfhydryl levels seen on many enzymes or mocking and replacing other metals, which serve as cofactors in many enzymatic reactions. The essential metals that lead interacts with have calcium, iron, and zinc. High levels of calcium and iron tend to deliver some safety from lead poisoning, lower classes yield increased exposure (Rabinowitz 1995, Rieuwerts 2017).

In recent years, the increase in water consumption has reduced water resources. The discharge of all types of domestic sewage, animal waste, industrial effluents, and agricultural drains has a significant contribution to the pollution of water sources. Limitation of water resources, lack of rainfall, and increased contamination of surface and underground water with heavy metals and other pollutants make it necessary to find environmental solutions to remove these substances from water sources. Among the sources of water pollution is heavy metals, which have attracted the attention of investigators due to their toxicity of these elements (Ricou *et al.* 1999, Raungsomboon *et al.* 2008).

Genovese basil, also known as “baxaicò” or “baxeicò” in the Ligurian language, belongs to the *Ocimum basilicum* cultivar. It represents a distinct category of Italian basil, primarily cultivated in the Pera region of the hills west of Genoa. Genovese basil is characterized by its small size, featuring delicate, oval-shaped, light green leaves that gently curve downward. The plant emits a subtle fragrance that becomes more pronounced as it flowers, carrying a unique blend of sea salt and essential oils. Notably, it lacks the minty aroma commonly found in other basil species. Modern cultivation practices for Genovese basil involve growing it in controlled environments with diffuse lighting, often beneath glass structures. The plants are carefully hand-harvested when the leaves are still young, contributing to their mild flavor and light color. This particular cultivation approach is adopted due to the basil’s sensitivity

to temperatures below 60°F (15°C). Optimal germination occurs within a temperature range of 70 to 78°F (21 to 26°C). In the context of the discussed research, a novel and cost-effective method for removing lead from industrial wastewater is proposed. This method involves the use of iron nanoparticles coated with a layer measuring approximately 12 atoms thick, with the amount of lead present determined through atomic absorption spectrometry. Notably, this approach utilizing coated nanoparticles has not been previously explored. Through the experimentation conducted in this study, the efficacy of these coated nanoparticles in removing lead from wastewater is evaluated and discussed. The utilization of Genovese basil extract in the synthesis of the iron nanoparticles adds further value to this research. The unique properties of the basil extract play a role in modifying the surface of the nanoparticles, enhancing their ability to bind with heavy metal ions and facilitating efficient lead removal (Sharafzadeh and Alizadeh 2011, Trettel *et al.* 2018, Ciriello *et al.* 2021).

The central objective of this study is to investigate the purification process and reduction of heavy metals, particularly lead, in industrial wastewater, specifically for water supply in swimming/water sports. The research focuses on utilizing synthesized nanoparticles, specifically iron nanoparticles coated with a thin layer, to effectively remove lead contaminants from the water. By exploring the potential benefits and applications of these coated nanoparticles, the study aims to contribute to the field of industrial wastewater treatment for the specific purpose of ensuring water quality in swimming and water sport activities. Additionally, the incorporation of Genovese basil extract in the synthesis process enhances the method’s environmental friendliness, simplicity, and cost-effectiveness, further emphasizing its relevance to water supply in swimming and water sports.

## 2. Materials and techniques

### 2.1 Chemicals and reagents

The objective of this research is to develop a method for effectively extracting lead metal from industrial waste by employing environmentally friendly iron nanoparticles, which are synthesized using green techniques. The measurement of lead concentration is conducted using an Atomic Absorption Spectrometer, ensuring accurate and precise results. To achieve this goal, the study employs the following materials and equipment:

Ammonia (NH<sub>3</sub>) FeCl<sub>3</sub>, FeCl<sub>2</sub>·4H<sub>2</sub>O, Hydrochloric acid, ethanol, and deionized distilled water. All of them were purchased from Merck company with high purity. Genovese basil, scale, ultrasonic bath, centrifuge, and atomic absorption spectrometer equipped with background correction with a deuterium lamp and a lead hollow cathode lamp with a present intensity of 0.5 mA and a measurement wavelength of 217 nm.

All chemicals used existed of analytical reagent quality and worked without additional purification. All solutions

used during the investigations were freshly formulated using ultrapure water obtained from a water distillation system.

## 2.2 Sample preparation

In preparing the process, after entering the laboratory, the sample is first dried in such a way that wet and moist samples are dried using a laboratory oven at a maximum temperature of 120 degrees Celsius. Then the dried sample is ground, and its powder is used.

To obtain extracts, samples of this plant are ground into powder because they may contain lumps stuck together. These extracts are obtained through the evaporation of extracts that are obtained at low pressure and less than 60 meters and are 3 to 6 times stronger. They are rawer than raw materials. The reason for extract evaporation at low temperature and pressure is that they are sensitive to heat and decompose. With this method, it is protected against heat.

## 2.3 Synthesis of iron nanoparticles

There are various methods to produce nanoparticles, but the use of plants has been given much attention in synthesizing nanoparticles due to their low cost and compatibility with the environment. In this research, the green synthesis of iron nanoparticles using Genovese basil extract has been carried out to remove lead in industrial wastewater.

In this research, iron chloride (II) and iron chloride (III) with different concentrations were brought to volume by hydrochloric acid (2M), and the prepared solution was mixed with different volume ratios and stirred using a magnetic stirrer for 20 minutes. Ammonia with different concentrations was added drop by drop to change the pH of the mixture from acidic to alkaline. Then Genovese basil extract was added to the solution to cover the magnetic nanoparticles for 40 minutes. A black solution was obtained, which was placed at 70°C for 90 minutes. A solid precipitate was obtained, separated by a magnet and washed twice with distilled water and once with a double volume of ethanol, and dried at 50°C.

In this synthesis, 0.5 M FeCl<sub>2</sub> solution by weighing 0.3 g of it and dissolving it in distilled water and 1 M FeCl<sub>3</sub> solution by weighing 0.86 g of it and dissolving it in distilled water have been used.

## 2.4 Examining the amount of Pb absorption

After preparing iron magnetic nanoparticles, they were used to remove the Pb metal in industrial wastewater. First, the standard solution of 70 ppm Pb was prepared in a balloon, then 30 ml of the Pb standard was added to 0.3 g of magnetic nanoparticles coated with an Added Genovese basil. Adjust the pH of the solution to 6 and then put it on a stirrer for 10 minutes at room temperature so that the Pb metal can be absorbed in the iron magnetic nanoparticles. Then, the solution was centrifuged for 15 minutes at a speed of 1000 rpm to separate the nanoparticles, and just Pb metal

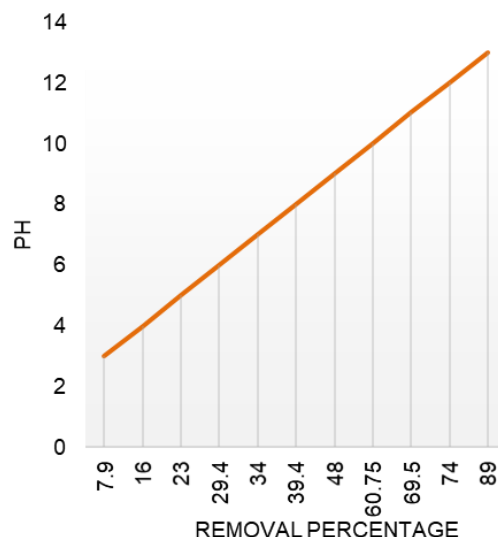


Fig. 1 The impact of pH on the removal percentage

remained in the solution. Furthermore finally, the amount of Pb was measured using atomic absorption spectroscopy.

## 3. Results

### 3.1 Optimizing factors affecting the test

To conduct experiments, it is necessary to conduct them in optimal conditions. The factors that affect the results should be identified and optimized. Here are the factors that need to be optimized:

pH, absorption time, the effect of initial concentration on the absorption rate, and the weight of coated magnetic nanoparticles were investigated. Each of these items is optimized in order, and their effects on the results can be seen.

### 3.2 The impact of pH

To select the impact of pH on lead absorption, the pH of the environment was varied in the field of 3-13. The outcomes indicate that the amount of Pb absorption increases with the increase in pH. The explanation for this increase can be related to the point that at high pH, the surface hydroxyl functional groups have a negative charge, which causes the absorption of cations. This result can be seen in Fig. 1.

### 3.3 The impact of absorption time

To investigate the effect of absorption time, a lead solution with a particular concentration was prepared at an optimized pH and stirred at various time intervals. The considered times are in the range of 0-10 minutes. After each time, the solution was centrifuged for 10 minutes at 1000 rpm, and then the amount of Pb metal was measured by an atomic absorption device. In Fig. 2, the effect of time on the amount of Pb absorption can be seen, and 8 minutes was chosen as the optimal time.

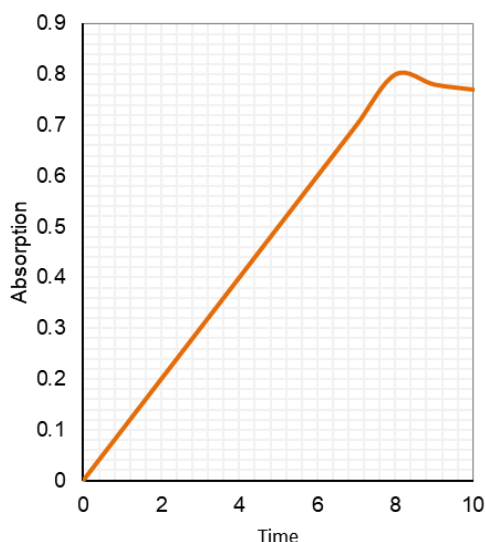


Fig. 2 The effect of absorption time

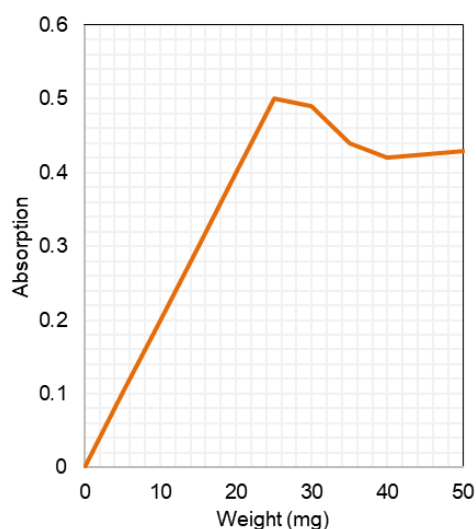


Fig. 3 The effect of the weight of coated magnetic nanoparticles on the absorption rate

### 3.4 The impact of absorption initial concentration on the absorption rate

One of the parameters affecting the absorption rate is the initial concentration of Pb. This effect was investigated by changing Pb concentration from 5 ppm to 100 ppm. It was found that with the increase in Pb concentration, the related absorption also increases (Fig. 2).

### 3.5 The effect of the weight of coated magnetic nanoparticles on the absorption rate

The effect of nanoparticles on absorption was investigated with 1 to 50 mg of nanoparticles. With the increase of nanoparticles, the amount of Pb absorption also increases, which is due to the increase of free sites on the surface of nanoparticles (Fig. 3). The highest amount of absorption was obtained when 20 mg of nanoparticles were used. This value as Optimum was selected.

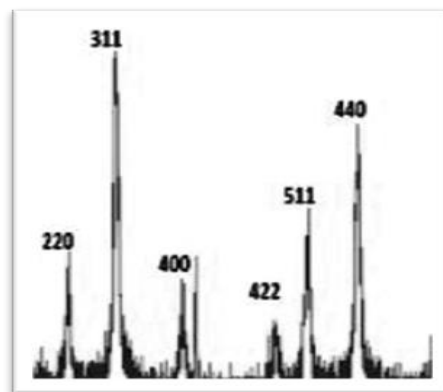


Fig. 4 The results of X-ray diffraction (XRD) analysis

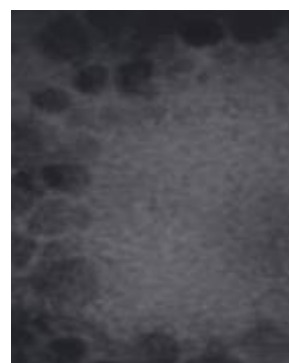


Fig. 5. TEM images of magnetic nanoparticles coated with plants

## 4. Detection limit (LOD):

Determine the ranges of concentration in which to extract the species. It can be done quantitatively, and the communication between signals is Measured, and there is a species concentration. It is mandatory.

To draw the grading curve, solutions with different concentrations of Pb are prepared and extracted under optimal conditions for these solutions. It was observed that the investigated range is a linear curve and has the equation of line  $Y = 0.0978x - 0.0069$ ,  $R^2 = 0.9922$ .

The detection limit of this measurement was obtained using the formula  $LOD = 3Sb/m$ , Sb is the blank standard deviation, m is The slope of the calibration curve, and the detection limit value for the lead was 0.031 ppm.

## 5. Investigating the properties of coated magnetic nanoparticles

X-ray diffraction and Transmission electron microscope analysis (TEM) were used to identify and determine the size of the resulting nanoparticles. Fig. 4 is related to XRD, by which the formation of iron nanoparticles. It was approved by Formula  $Fe_3O_4$ . The average dimensions of the crystals are about 14 nm was obtained.

Transmission electron microscope analysis can be seen in Fig. 5. The synthesized particles are spherical, and their size distribution is narrow and uniform.

## 6. Discussion

The vital need in nanotechnology is the development of bio-compatible processes with the environment. In this research, the production of iron nanoparticles by plant extract has been shown. In this study, using the principles of green synthesis and unlike chemical methods, iron nanoparticles by plant extract *Genovese basil* were synthesized.

The dry leaves of the plant were used to extract the antioxidant capacity of the dry leaves of the plants are higher than non-dry leaves. The mentioned plant has a high potential for regenerating and giving electrons to iron ions. In order to prove the presence of iron nanoparticles, Transmission electron microscope analysis and X-ray diffraction images have been used, which show that the particles are spherical and confirm their nanometer dimensions. In recent decades, environmental decay and the risk of human openness to heavy metals have risen dramatically due to the increasing use of industrial procedures. Due to the severe damage of these metals to health, their environmental removal, especially from water, has attracted much attention. Lead metal is a naturally occurring element found in small amounts in the earth's crust. While it has practical uses, it can harm humans and beasts and push harmful fitness effects. Pb metal can be found in any part of the environment - air, soil, and water.

Here, Synthesized nanoparticles were used to extract Pb heavy metal after optimizing the test conditions. Nanoparticle coating can be used to increase Pb absorption efficiency and be considered an effective method for lead removal. After washing and drying, the synthesized nanoparticles have a black color, which can be confirmed by taking photographs such as TEM.

## 7. Conclusions

This study focused on the development of bio-functionalized iron nanoparticles through the utilization of *Genovese basil* extract, allowing for enhanced bonding between heavy metals and iron. The application of these synthesized nanoparticles for water supply in swimming/water sports was considered. The isolation of water pollution through the absorption method was reviewed and optimized, considering its compatibility with the environment and the ease of reaction. The method of synthesizing nanoparticles using the mentioned plant extract for lead extraction from various water samples proved to be a novel approach with several advantages, including a short extraction time, cost-effectiveness, ease of use, accuracy, and high recovery rate.

It is important to note that lead metal poses significant risks to human health, as it can cause severe damage to the brain, kidneys, and even lead to death. Lead has the ability to mimic calcium, enabling it to cross the blood-brain barrier. This can result in the reduction of myelin sheaths, neuronal loss, disruption of neurotransmission pathways, and inhibited neuronal growth. Lead also interferes with key enzymes involved in heme synthesis, such as porphobilinogen synthase and ferrochelatase, leading to impaired heme synthesis and microcytic anemia.

Considering the growing emphasis on green chemistry and the use of environmentally friendly compounds, the utilization of nanoparticles synthesized through green methods is highly relevant. It is crucial to expand our understanding of the use of non-biodegradable nanoparticles and their compatibility with the environment, as well as their impact on biological systems and human health. These considerations should be fundamental aspects not only in the scientific applications of such materials but also in ensuring their safety and sustainability. By incorporating green and environmentally friendly approaches, the application of synthesized nanoparticles holds great promise for addressing water pollution and providing safe water supply for swimming and water sports activities.

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