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Review Article

Plant-Derived Iron Nanoparticles for Removal of Heavy Metals

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Nanoparticle synthesis has seen exponential development recently as its characteristics of high surface area, high rate of adsorption, and easy, cost-effective synthesis have been exploited for the purpose of ground water purification via the removal of organic and inorganic compounds, along with the removal of heavy metals and microbes. The synthesis of Zero-Valent Iron Nanoparticles (ZVI NPs) by green methods has proved to be environmentally friendly in many ways as it employs the use of naturally occurring plant extracts. These nanoparticles have large surface areas and efficiently remove heavy metals. The reducing potential of these ZVI NPs is mostly −0.44 V, thus allowing them to reduce heavy metal compounds such as cadmium, lead, zinc, copper, and arsenic present in wastewater. Irradiated nanoparticles have also exhibited antimicrobial resistance and adsorption. It is also observed that nanoparticles show a higher rate of efficacy at a lower pH. The adsorbent, which is ZVI NPs in this case, when present in large doses reduces heavy metal compounds rapidly and effectively.

1. Introduction

Considering their bioaccumulation, toxicity, and persistence, heavy metals have become an increasingly serious environmental concern. Heavy metals wastewaters are progressively being dumped into the environment, either directly or indirectly, as industry develops rapidly, particularly in developing countries. Contrary to organic pollutants, heavy metals are non-eco-friendly; thus, they tend to build up in living beings. Many heavy metals in their ionic form are lethal or carcinogenic [1]. Heavy metals can be found in the industrial wastes produced by the leather processing, quarrying, electroplating, and paper manufacturing industries [2].

Cr(VI) is a highly noxious, soluble, and mobile metalloid [3]. Chronic exposure to chromium(VI) causes diarrhea, liver damage, and tumor. Its adverse effects include damage of DNA, itchy skin, and deterioration of the immune system. Exposure to chromium(VI) by inhalation causes acute poisoning and damage to the respiratory passageways. In addition, prolonged contact with the skin may cause allergies, rashes, skin inflammation, and so on [4]. It is also evident that humans are also very susceptible to acute mucosal inflammation, hepatic and renal damage, extensive injury to the capillaries, and central nervous system injuries upon excessive consumption of Cu(II) [5]. Furthermore, Cd(II) is toxic to animals and humans and can have a lot of

long-term and short-term effects on human health. Cd(II) can enter into the body by breathing, ingestion, or absorption by skin. A brief cadmium exposure can cause vomiting, diarrhea, spasms, peripheral neuropathy, liver injury, seizures, shock, alteration of the kidney function, and effects on the lungs, circulatory system, liver, and nervous system. Moreover, cadmium can affect the lungs, kidneys, bones, growth and can cause cancer in the long run [6]. Lastly, Pb(II) is a very lethal and cumulative poison that builds up mostly in the kidneys, bones, muscles, and brain. Chronic lead poisoning damages the kidneys, neurological and reproductive system, brain, and liver [7]. Hence the extraction of Cr(VI), Cu(II), Cd(II), and Pb(II) from any water source as well as wastewater is highly essential.

ZVI NPs and its composites have recently attracted much attention as potential multifunctional applicants for a broad array of functions. Treatment of water and wastewater [8], soil remediation [9], membrane antifouling agents [10], and antibacterial and anticancer compounds [11] are some of the applications. Removal of mercury [12], cadmium [6], arsenic, chromium [13], lead [14], dyes [15, 16], and many other pollutants have been reported to be effective with nano-adsorbents, ZVI NPs. In addition to their high specific surface area, nZVIs are highly reactive, allowing them to eliminate a broad variety of pollutants from water [17]. The chemical synthesis of these substances, however, presents numerous constraints and questions, involving the harmfulness of the compounds used and hazardous by-products, which can often harm the environment [14]. Consequently, green solvents, such as extracts from plants with great antioxidant power, are being widely utilized [18]. Various extracts from different plants have been found to be risk free for living creatures, a reusable resource, and ecologically acceptable resources that contain polyphenols that work as stabilizing and reducing agents for the synthesis of nZVI in a "green" manner and extend its reactivity [19].

Nanoparticles synthesized from plant extracts have varied sizes and shapes and therefore vary in their capacity to remove contaminants from soils and aqueous solutions [20]. The main objective of the review is to illustrate the green synthesis of nZVI NPs from different plant parts and sources and removal of heavy metals like Cu(II), Cr(VI), Cd(II), and Pb(II) from wastewater.

2. Role of Phytonanotechnology

Phytonanotechnology is a novel and developing area of study in the modern medical science era. It allows the transformation of metals into nanoparticles by the use of plant extracts. Phytonanotechnology does not require any use of detrimental chemicals. Nanoparticles like iron, silver, gold, copper, and zinc are characterized by UV spectroscopy, X-ray diffraction, SEM, and so on. They have agronomic application as the plant extract constituents help in stabilization. This synthesis is cost-effective, eco-friendly and has very few side effects.

2.1. Plant-Mediated Iron Nanoparticles for Removal of Heavy Metals

2.1.1. Removal of Chromium. The synthesis of iron nanoparticles using date seed extract (*Phoenix dactylifera*) is a novel and green process involving the conversion of precursor salts of iron sulfate to iron sulfide nanoparticles in the presence of plant phytochemicals. This technique is very useful in the extraction of harmful heavy metal residues present in industrial wastewater, the heavy metal chromium, in particular, which is highly toxic and acts as a carcinogen. Locally acquired Khalsa date seed extracts were used and were ideal as they are composed of polyphenols, flavonoids, and various other phytochemicals that act as strong antioxidants, hence enabling the formation of iron nanoparticles. These ZVI NPs were analyzed thoroughly (using FTIR, XRD, and SEM) and were found to have a large surface area that was covered by iron and sulfide ions specifically; this in turn resulted in enhanced adsorption capacities. The nanoparticle size was found to be around 68 nm as observed via a scanning electron microscope. The aforementioned characterization techniques also indicated that the crystalline growth of ds-FeS NPs occurred along the *c*-axis (as observed in an XRD graph) and also that the various functional groups present in the extract of *Phoenix dactylifera* displayed differences in the broad peaks between the range of 1410–1625 cm^{-1} when compared to the FTIR graphs of the obtained ds-FeS NPs. Iron nanoparticles synthesized via this process were able to remove 97% of chromium present in a 13.4 mg/L concentration sample of wastewater. Additionally, it also had the capacity to remove ciprofloxacin, which is a pharmaceutical agent often found in industrial wastewater. The removal process, however, occurs at a pH of 7, which may be one of the only drawbacks [21].

In order to tackle the problem of heavy metal compounds which are ubiquitously present in industrial wastewater and sewage, a method was developed that enables the production of iron nanoparticles using extracts of the barberry plant. In this process, the leaves of the barberry plant are washed, dried, and powdered and then made into a solution. This extract was then mixed with ferric chloride solution in a 4 : 1 ratio and left to rest till darkening of the solution was seen, which indicated the synthesis of ZVI NPs. In accordance with the TEM analysis, it was confirmed that the iron nanoparticles synthesized had a spherical shape and had sizes that ranged between 20 and 40 nm. These ZVI NPs were homogeneous in nature and the shell-core structure observed was such that it prevented the oxidation of hexavalent chromium ions. Through FTIR analysis, various functional groups that take part in the photocatalytic reaction were identified; these functional groups act as "charge sinks" and enable the transportation of charges during the photocatalytic reaction. These functional groups are defined as covalent organic frameworks. The iron nanoparticles had a 100% reduction efficiency rate when the dosage taken was 0.675 g/L of wastewater at an ideal pH of 2. The photocatalytic reaction carried out is inversely proportional to the pH of the wastewater sample and follows pseudo-second-order kinetics [22].

The production of ZVI NPs and the mechanism of chromium adsorption from aqueous solutions was studied. This process employed the formation of iron nanoparticles from green tea extract and observed its use as a coating agent

as well as an adsorbent. A predetermined amount of extract of green tea was mixed with a pre-prepared amount of iron sulfate solution and oscillated at 150 rpm for 60 minutes to obtain solid iron nanoparticles. These iron nanoparticles were then analyzed using SEM and were found to have an irregular, spherical surface and sizes that ranged between 30 and 100 nm. The efficiency of these nanoparticles in reduction of hexavalent chromium ions was found to be 99.9% under optimal conditions. In this case, the reaction took place optimally at lower pH ranging between 3 and 5. It was observed that the efficacy of the adsorbents reduced at a higher pH. The dosage of the adsorbents should ideally be around 0.12 g/L in order to exhibit 100% efficacy. The reduction reaction was found to be endothermic and follows pseudo-second-order kinetics and kinetics of the adsorbents are best represented by the Langmuir model as it considers adsorption to occur in a monolayer-wise fashion. This method has an additional benefit, which is the increased reusability of the iron nanoparticles synthesized. The efficacy of the ZVI NPs remains around 90% for a fixed number of cycles (in this case, 3 cycles) [23].

An effective process involving green tea extract and montmorillonite was developed for the production of ZVI NPs, which could be used for the reduction and adsorption of Cr(VI) compounds present in industrial and domestic wastewater. This method involves mixing aliquots of green tea extract with montmorillonite and ferrous sulfate solution, which is then agitated and subsequently centrifuged in order to obtain dark, solid zero-valent iron nanoparticles. Through X-ray diffraction analysis, it was confirmed that the iron nanoparticles were encapsulated completely by a thick layer of tea polyphenols. SEM and TEM analysis showed that the ZVI NPs were tightly bound by intercalated Mont layers and an iron oxide surface with diameters ranging between 15 and 30 nm. The Mont layers proved to increase the dispersibility of the ZVI NPs and the thick TP layer prevented the accumulation of iron oxide, thereby increasing adsorption. Column experiments were conducted both with sand and soil, and it was found that the nanoparticles are highly mobile and stable when kept at a pH of 2.2. Under optimal conditions, it was observed that the ZVI NPs were able to reduce almost 100% of hexavalent and trivalent chromium ions present in the soil and sand water samples, while an increase in pH (6) reduced the reduction capacity of the nanoparticles. The reaction involved follows pseudo-second-order kinetics [24].

This method is a cost-effective, in-situ process for the extraction of heavy metal compounds found in industrial wastewater via ZVI NPs produced from the leaves of *Verbascum thapsus*. This is a green process for the extraction of chromium from wastewater due to the biodegradable and renewable nature of VTL. Initially VTL extract was taken and mixed with the iron source, which was ferric chloride in this case. The solution was centrifuged and a change in coloration was observed, yellow to dark brown, which indicated that iron nanoparticles were being synthesized. Through SEM analysis, it was confirmed that the iron nanoparticles had a rod-shaped structure with a network-like surface and sizes ranging between 40 and 50 nm.

Through FTIR, it was established that hydrogen-bonding in the ZVI NPs reduced as adsorption of hexavalent chromium ions increased. The zeta potential of the ZVI NPs in a NaCl solution was also measured and was found to be negative at all pH levels. The iron NPs showed full efficacy when the dosage was taken to be 25 g/L at an optimum pH of 5.2 (which was the original pH of the solution). The pH of the aqueous solution taken was inversely proportional to the efficacy of adsorption and it was concluded that first-order kinetics is the model that best describes this reaction [25].

The synthesis of iron nanoparticles from agricultural wastes is an eco-friendly, low-cost process. In this study, the extract of red peanut skin was employed to produce ZVI NPs. Initially the red peanut skins were vacuum dried and powdered before aliquots of the extract were mixed with an iron source, in this case ferric chloride, and then agitated with a magnetic stirrer in a nitrogenous atmosphere. This subsequently induced the formation of ZVI NPs. The characterization of the iron nanoparticles so produced includes SEM analysis through which it was observed that the Fe-NPs had a spherical morphology and smooth surface with sizes ranging from 10.6 to 43.5 nm (depending on the drying techniques used initially). Through TEM analysis, it was observed that the Fe-NPs had a Fe^0 core surrounded by a mesh-like, organic network made up of biomolecules. This outer encapsulation proved to increase the antioxidant nature of the Fe-NPs. X-ray diffraction showed that the coating surrounding the core of the nanoparticles prevented their agglomeration and was in accordance with the UV-Vis characterizations, which exhibited the direct involvement of red peanut compounds in the reaction. A dosage of 0.25 g of Fe-NPs added to 10 mg/L of hexavalent chromium solution had an efficacy rate of 100% in one min. However, it must be noted that this result was obtained when the red peanut skins were vacuum dried at 60°C [26].

In order to remove the ubiquitously present heavy metal chromium from wastewater, a facile and novel process involving eco-friendly synthesis or ZVI NPs from extract of green tea was theoretically studied and practically observed. In this process, aliquots of extract green tea were mixed with a source of iron, in this case iron sulfate solution, and then freeze dried and washed with ethanol to enable the formation of zero-valent iron nanoparticles. These ZVI NPs were analyzed via SEM and were found to have an Fe^0 core that was surrounded by an outer layer made up of iron oxides. The nanoparticles were spherical with sizes ranging between 50 and 80 nm. Through FTIR analysis, it was confirmed that the capacity of adsorption of the ZVI NPs was further enhanced by the presence of carboxyl, hydroxyl, and plant phenolic compounds. The Cr(VI) removal capacity of these ZVI NPs was found to be around 85% for a period of 12 h, indicating that the nanoparticles were stable and safe from oxidation and subsequent inactivation due to the surrounding biomolecule layers, hence highlighting the efficacy of green synthesis of ZVI NPs for the reduction of heavy metal compounds from industrial and domestic wastewater [27].

In this investigation, the decontamination of chromium present in aqueous solutions was carried out by adsorption

via silver-iron oxide nanoparticles obtained from *Psidium guajava* leaves. Initially aliquots of the leaf extract were mixed with a homogeneous solution of silver nitrate and iron chloride. After treatment with acetone and combustion of the precipitate, silver-iron oxide nanoparticles were successfully synthesized. Through X-ray diffraction, it was observed that the plant phenolic compounds present in the guava leaves were directly involved in the reduction of hexavalent chromium. Furthermore, through SEM analysis, it was found that the nanoparticles were irregular in shape and had sizes ranging between 50 and 90 nm. The results obtained were such that a dosage of 0.08 g of nanoparticles added to 50 mg/L of chromium concentrated aqueous solution had a removal capacity of 97% when kept at 25°C. The rate of adsorption was found to be pH dependent, and the optimum pH was confirmed to be 4. The data was graphically depicted by the Langmuir model and through thermodynamic analysis, it was observed that the reaction occurred spontaneously, was endothermic in nature, and followed pseudo-second-order kinetics [28].

A single-step process for the formation of ZVNPs from *Eucalyptus globules* leaves was studied and its use for the purpose of decontamination of aqueous solutions was observed. In this process, the leaf extract of *E. globules* was mixed with iron sulfate solution in a 1 : 1 ratio and stirred continuously till the solution's color changed from yellow to black indicating the successful synthesis of ZVI NPs. Through UV-Vis spectral analysis, it was confirmed that ZVI NPs were formed from Fe and plant polyphenols; further, through FTIR, it was found that the reduction of Fe^{2+} present in the initial solution mixture could be attributed to the plant polyphenols. Through SEM analysis, it was confirmed that the ZVI NPs produced had a spherical morphology with sizes ranging between 50 and 80 nm. The results obtained were such that optimum adsorption took place when a dosage of 0.8 g/L was added to 400 mg/L for a contact period of 30 minutes. The reaction was not pH dependent, and the data obtained corresponded with the Langmuir and Freundlich adsorption isotherms. The sorption rates are best studied using pseudo-second-order kinetics. It is important to note that an additional benefit of this green synthesis process is the increased stability of the ZVI NPs, which were found to be stable even after 2 months and the enhanced reusability (only for a fixed number of cycles) [29].

In an experimental study, it was postulated that eucalyptus leaves could be used in an environmentally friendly manner for the production of ZVI NPs, thereby carrying out the efficient removal of Cr(VI) ions from wastewater. The eucalyptus leaves were air-dried and oven-dried before a plant extract was obtained by addition of distilled water. Aliquots of this plant extract were mixed with ferric chloride solution (0.1 M) till a black discoloration was observed, indicating the formation of iron ZVI NPs. These ZVI NPs were washed with ethanol and distilled water prior to being analyzed. Through TEM analysis, it was found that the ZVI NPs were spheroidal in shape and had a smooth surface with mash like capping which is due to the aggregation of biomolecules from the extract of eucalyptus leaves, thereby

acting as reducing and stabilizing agents. Through FTIR analysis, various biomolecules such as aliphatic amines and polyphenols were identified. The iron nanoparticles showed 100% chromium removal efficiency at 80°C, pH less than 4, and a plant extract to ferric chloride solution ratio of 2 : 1. The results were obtained after varying amounts of the iron NPs were added to 10 mg/L of Cr(VI) solution [30].

In another experimental research, the employment of mango peel as a starting material for the formation of ZVI NPs was conducted. The mango peel was initially dried and powdered before being boiled in deionized water. The solution was subsequently centrifuged followed by filtration before being added to ferric chloride solution, inducing the formation of iron ZVI NPs. These ZVI NPs were characterized using XRD and XPS. Through XRD analysis, it was found that the ZVI NPs had a structure exhibiting a core/shell-like formation which limited any further use of XRD. Through XPS analysis, it was found that the surface of the ZVI NPs was made up of carbon compounds such as polyphenols, which were responsible for the steric stability of the ZVI NPs. Results were analyzed after varying amounts of iron ZVI NPs were added to the starting concentration of 10 mg/L solution of Cr(VI). A 95.45% removal efficiency was recorded when 50 mg/L of iron ZVNPs was added to the Cr(VI) solution. It was found that complete Cr(VI) removal was optimal at low pH and high temperature. A Response Surface Methodology was employed to optimize chromium adsorption by analyzing all possible variables; this was done in conjunction with regression modeling [31].

There was a study that aimed to explore the use of water hyacinth or *Eichhornia crassipes* (an invasive weed known to destroy crops) as a resource that can be employed for the fabrication of ZVI NPs. The leaves were first dried and then powdered using a high-speed disintegrator. The ZVI NPs were synthesized via the addition of the obtained leaf extract to 0.1 mol/L of a solution of ferric chloride. The formed iron ZVI NPs was found to be 52.5 nm in size by the Digital Light Scattering method. The moderately stable nature of the ZVI NPs was indicated by its zeta potential, which was found to be +30.7 V. Through SEM analysis, it was found that the surface was granular, and the ZVI NPs were spherical in shape. TEM analysis confirmed the presence of organic compounds along the surface of the iron ZVI NPs that contributed to its aggregation and dispersion in the removal process, making it stable. Through FTIR and XPS analyses, it was found that F^0 contributed significantly to the removal process. When the iron ZVI NPs were added to Cr(VI) solution of concentration 100 mg/L, an adsorption efficiency of 65.3% was observed in the first 5 mins. After a reaction time of 45 mins, an adsorption efficiency of 87.3% was observed and then reaction reached a state of approximate equilibrium. The results confirmed that the efficiency of removal was inversely proportional to pH and directly proportional to temperature [32].

The use of *Rosa damascene*, *Urtica dioica*, and *Thymus vulgaris* leaf extracts for the synthesis and fabrication of iron nanoparticles was researched. The leaves were initially washed and dried and then the extracts were subsequently prepared by mixing the powdered leaves with deionized

water; this was followed by centrifugation. The leaf extract was then mixed with ferric chloride solution in a 2 : 3 ratio with pH 6 being maintained by the addition of 1 M NaOH. Through FTIR analysis, it was confirmed that the synthesized iron ZVI NPs possessed free polyphenol groups on their surfaces attributing to the potential of free radical scavenging of the molecule. SEM analysis exhibited the irregular size and shape of the iron ZVI NPs, with 100 nm being the average diameter. The leaf extract when added at a 0.2 g/L dosage was able to effectively reduce Cr(VI) ions in a Cr(VI) solution of concentration 100 mg/L. The results further dictated that removal capacity was maximum at pH 2 and greater contact time. The removal capacity also increased with increase in adsorbent dosage [33].

Another study attempts to compare the removal efficiency of iron NPs synthesized from two different sources—Yerba mate and green tea. The Yerba mate was commercially obtained, and the leaves were boiled in water in order to prepare the extract. Aliquots of the extract were then added to ferric chloride solution till a greenish-black coloration was obtained, indicating the synthesis of iron NPs. Through FTIR analysis, it was confirmed that the surface of the iron ZVI NPs possessed flavonoids and polyphenols, increasing the reducing capacity of the NPs. SEM analysis exhibited the irregular shape of the ZVI NPs, possessing sharp, jagged edges, and sizes ranging between 15 and 100 nm. TEM analysis also exhibits the formation of chain-like nanoaggregates. For a concentration of 300 μg of Cr (VI), a dosage in the ratio 1 : 3 (chromium concentration: dosage) was added and removal efficiency was found to be 100% after a contact time of 2 mins and at pH 3. This fast-acting nature of ZVI NPs synthesized from Yerba mate makes it a suitable antipollutant, and its eco-friendly, in-situ production makes it a desirable solution for heavy metal removal, particularly Cr(VI) from industrial and domestic wastewater [34].

2.1.2. Removal of Copper.
Zero-valent iron nanoparticles (ZVI NP) synthesis was carried out using a fast, one-step, and entirely eco-friendly technique, which used aqueous tea extract as a reducing and capping agent. The polyphenols contained in tea extract form a complex with the metal iron ion (FeSO$_4$) and undergoes reduction to form the resultant zero-valent metal. Moreover, the formed nanoparticles were exposed to ^{60}Co gamma radiation source with a dose of 7.5 kGy·h^{-1} and were investigated as an antibacterial agent against various microbes and as a nano-adsorptive material for the elimination of Cu ions from wastewater. The two samples were characterized before and after irradiation. It was noted that upon irradiation of the ZVI NPs with gamma rays, the morphology was entirely converted from spherical to flake like. SEM micrographs showed that the ZVI NPs formed aggregates with a diameter approximately ranging from 0.1 to 0.17 μm. Furthermore, with the help of TEM results, it was confirmed that the primary particles were spherical and had an approximate diameter in the range of 6.1–10.6 nm. The zeta potential for the ZVI NPs was found to be -34 ± 3.3 mV and -22.2 ± 3.2 mV prior to and after irradiation, respectively. The ZVI NPs revealed removal efficiencies of 81.67% and 97% before and after irradiation for Cu(II) ions, respectively, at pH 5. Due to the high starting concentration of Cu^{2+} metal ions, the number of Cu^{2+} metal ions adsorbed increases as its concentration is increased. Cu^{2+} ions surround the active site in the adsorbent, causing the active site to be surrounded by additional Cu^{2+} ions. It is possible to achieve more adsorption. Langmuir's maximal adsorption capacity for Cu^{2+} ions on ZVI NPs was found to be around 78.38 mg/g in experiments. Freundlich's isotherm model explains a multilayer adsorption of adsorbed molecules onto a heterogeneous adsorbent surface. The reusability of ZVI NPs adsorbents reached around 85% of their removal capability after 6 renewal cycles. The removal efficacy decreased in a linear trend with rising temperature [35].

Powdered activated carbon (PAC) and granular activated carbon (GAC) compounds containing magnetite NPs were synthesized using a green tea extract-based approach. Direct iron reduction (DRI) sludge from the steel industry's direct reduction process provided the iron required for adsorbent production. Copper adsorption was analyzed with initial concentration ranging from 0 to 400 mg/L in aqueous medium. Desorption tests were carried out at concentrations of 100–300 mg/L on a ten-day cycle. Maximum capacity for copper adsorption was obtained with MNP-PAC and MNP-GAC at 23.61 and 13.37 mg/g, respectively. Adsorption efficiency of MNP-PAC was more compared to MNP-GAC. Almost all of the particles in PAC composites had a size less than 60 nm, with 30–40 nm being the maximum frequency. The size range of 93% or more GAC composite particles ranged from 1 to 60 with the highest particle frequency in the 25–45 nm range. Peaks of iron and carbon were observed in EDX analysis with no extra peak due to extreme pureness of the samples. The specific surface areas were 405.57 and 587.22 (m^2/g) of MNP-PAC and MNP-GAC, respectively. The average pore diameter for MNP-PAC was 3.3172 nm and for MNP-GAC was 1.9622 nm. The outer surface area of MNP-PAC was 455.05 m^2/g and of MNP-GAC was 719.24 m^2/g [36].

For the removal of combined pollutants—Cr(VI) and Cu(II)—green synthesis of iron-based nanoparticles (Fe-NPs) was carried out using eucalyptus leaf extracts (II). The leaf extracts that are used in the preparation of Fe-NPs serve as reducing and capping agents and contain amines, alkanes, aldehydes, and phenols. The samples were characterized with different techniques before and after the adsorption process. Prior to the removal, Fe-NPs were polydispersed, with particle sizes ranging from 20 to 80 nm, but their size considerably increased after reacting with Cr(VI) and Cu(II). The EDS spectrum of Fe-NP displays prominent peaks of Fe, C, and O at 16.3, 47.4, and 36.3 percent, respectively, before the reaction. However, after the reaction, additional peaks corresponding to Cu and Cr were identified. Cu, Fe, O, Cr, and C were found to be 1.0%, 14.5%, 37.3%, 1.2%, and 46.0%, implying that Cu(II) and Cr(VI) were adsorbed and reduced onto the surface of the NPs, respectively. XRD patterns showed broad peaks at about $2\theta = 24.0°$, which were because of the biological molecules in

eucalyptus leaf extract capped Fe-NPs whereas less obvious peaks were observed before the reaction. This indicated that the Fe-NPs were overlaid with biological molecules present in the ELE and were amorphous. Furthermore, for a contact time of 60 minutes, the separate removal efficacy of Cu(II) and Cr(VI) was 45.2% and 74.2%, respectively, whereas when Cu(II) and Cr(VI) were present together, the removal efficiency of Cu(II) (33.0%) and Cr(VI) (58.9%) was drastically reduced, indicating the presence of competitive adsorption and reduction between Cu(II) and Cr(VI). The elimination efficacy of Cr(VI) decreased when pH was increased from 3 to 7 while the removal efficacy of Cu(II) increased. As a result, a pH of 5 was shown to be optimal for synchronized elimination of Cr(VI) and Cu(II). In addition, the efficiency of removal also increased with increasing temperature. Kinetics revealed that sorption followed a pseudo-second-order model, while Cu(II) and Cr(IV) reduction followed a pseudo-first-order one. Finally, Fe nanoparticles eliminated Cr(VI) and Cu(II), as well as Pb(II) and Zn(II), from electroplated wastewater at rates of 44.8%, 21.5%, 31.4%, and 10.8%, respectively [37].

For eliminating Cu(II) and triclosan (TCS), an antibacterial agent, iron/nickel bimetallic nanoparticles (Fe/Ni NPs) were manufactured utilizing a green technique from eucalyptus leaf extract. Certain biomolecules in the plant extract, such as polyphenols, amines, and aldehydes, operate as capping and reducing agents. Before the adsorption of TCS and Cu(II), SEM pictures of Fe/Ni NPs were created and submitted to SEM analysis, revealing that the materials were polydisperse with an average estimated diameter of 60–85 nm. After interaction with Cu(II) and TCS, the NPs formed clusters and demonstrated an increase in overall size of Fe/Ni NPs. TCS and Cu(II) had removal efficiencies of 85.8% and 52.4%, respectively, when they were present in solution as separate compounds. However, when Cu(II) and TCS were present together in the solution, the removal efficiency of TCS was reduced to 75.4% and Cu(II) was reduced to 44.1%. The removal efficiency of TCS decreased when pH rose from 2 to 6 while the elimination efficacy of Cu(II) increased. Thus, an ideal pH value of 6 was confirmed for synchronized removal of Cu(II) and Cr(VI). The removal efficiency further revealed a linear trend with increase in Fe/ Ni NPs dosage. Moreover, removal efficiency improved significantly with a rise in temperature for TCS whereas elimination efficiency of Cu(II) only revealed a small increase. Both Cu(II) and TCS adsorption fits well into the pseudosecondary reaction rate model ($R^2 > 0.998$) and the Freundlich isotherm ($R^2 > 0.905$). The reduction kinetics, on the other hand, followed a pseudo-first-order model. As a result, the removal of Cu(II) and TCS necessitated a blend of reduction and adsorption [38].

Nanoscale zero-valent iron (nZVI) was impregnated with rubber seed husk (RSS), an inexpensive agricultural product, using a boron borohydride reduction process to remove Cu(II) ions. Cu(II) ions produce focal mucosal injury, hypertension, liver and kidney damage, gastrointestinal inflammation, vomiting, deterioration, and potential necrotic alterations in the liver and kidneys, even at low doses. Using SEM, the surface morphology of the nZVI-RSS was analyzed and was found to be irregular, porous, and rough in nature. Cu(II) ions were removed from synthetic wastewater by batch adsorption using nZVI-RSS. The best parameters for adsorption were found to be 25 mg/l Cu(II) ion concentration, pH 6, contact period of 30 minutes, nZVI-RSS dose concentration of 3 g/l, and temperature of 30°C. EDX analysis was used to determine the chemical composition of the nZVI-RSS, which revealed that it contains C-57.8%, O-35.62%, S-4.23%, and Fe-2.25% of the total. The Langmuir capacity was found to be 48.18 mg/g, and the sorption information was best described by the pseudo-first-order model and the Freundlich model. Furthermore, thermodynamic characteristics revealed that the adsorption system is exothermic, and it was determined that, at low temperatures, the possibilities of Cu(II) ion adhesion by nZVI-RSS are larger [39].

In-situ production of nZVI on BC utilizing iron salt and green tea extract in combination with BC-nZVI and persulfate (BC-nZVI/PS) was successful in removing Cu^{2+} and BPA by mixing BC-nZVI with persulfate. The pyrolysis of kenaf bars yielded BC. Cu^{2+} removal efficiency was 96%, while BPA removal efficiency was 98% in 60 minutes. According to SEM imaging and EDX analysis, the BC-nZVI surface contained many spherical, discrete, and dispersed particles with a mean diameter of 100 nm. After a concentration of Fe of 9.04 wt.% was discovered, the reaction of iron ions with green tea extract to generate iron particles, as well as the attachment of iron particles to the BC surface, was confirmed. Furthermore, the existence of nZVI was confirmed by an XRD pattern that revealed a unique peak at 44.7° that corresponded to nZVI. A feeble peak was also detected at 32.4° which may be because of iron oxide formation. The XPS analysis showed a peak at 707.0 eV relating to the nZVI, which further confirmed the formation of nZVI. On the FTIR spectrum, there are several distinct peaks of BC and BC-nZVI, located around 400–4000 cm^{-1}. It was evident that BC-nZVI/PS system effectively removed BPA with a low Cu^{2+} concentration. The removal of Cu^{2+} was found to be roughly 97%, 80%, and 84% at pH 3, 6, and 9, respectively. The reusability of BC-nZVI started gradually decreasing after successive runs and reduced from 96.9 to 60.2% after three runs. Following the reaction, an XPS study of the Cu species on the BC-nZVI surface revealed five distinct peaks in the Cu (2p) spectra at 953.9 eV, 952.7 eV, 935.5 eV, 934.2 eV, and 932.8 eV [40].

Green mulberry and oak leaf extracts (ML-nZVI and OL-nZVI) were used to make nZVI nanoparticles for adsorption of Cu(II) and Ni(II) from aqueous solutions. Plant extracts have been shown to include polyphenols that are nontoxic to living beings and have both reducing and stabilizing properties, extending their reactivity when used in the green synthesis of nZVI. SEM and TEM analysis confirmed that the nanoparticles are globular with minimum agglomeration and with the size varying between 10 and 30 nm. In batch investigations, the adsorption kinetics followed a pseudo-second-order rate equation. The Freundlich model was well suited to adsorption statistics. The OL-nZVI had a higher removal capacity for Ni(II) at 777.3 mg Ni/g, whereas the ML-nZVI had a higher removal capacity for

Cu(II) at 1,047 mg Cu/g, according to the adsorption isotherm data. When the pH was raised to 7.0 and 8.0, the adsorption of Ni(II) and Cu(II) increased linearly. The strongest Ni(II) adsorption by green nZVI occurred at pH 8, while the highest Cu(II) adsorption occurred at pH 7 [41].

2.1.3. Removal of Cadmium. The reusability efficiency and regeneration of EDTA@Fe$_3$O$_4$/SC nanocomposites was explored for Cd(II) adsorption. The nanocomposites were created using a biogenic green synthesis process. The Langmuir maximum adsorption capacity of EDTA@ Fe$_3$O$_4$/SC nanocomposites was 63.3 mg/g. ICP-MS was used to investigate the metal content of spiked ground water as well as the removal efficacy of nanocomposites for each metal. Metal ion removal efficiency was found to be higher in EDTA@ Fe$_3$O$_4$/SC NPs than in Fe$_3$O$_4$/SC NPs. For five effective cycles, the adsorption phenomenon involving Cd(II) adsorption on the surface of EDTA@ Fe$_3$O$_4$/SC and Fe$_3$O$_4$/SC NPs was successful. In a genuine water sample, the produced nanocomposites were effective at removing heavy metals. The evaluation of the adsorption performance of nanocomposites in real water samples is also critical for cost-effective and long-term water treatment. Adsorption of Cd(II) is possible, spontaneous, and endothermic. Both electronic attraction and chemical adsorption were involved in the adsorption mechanism. EDTA modified Fe$_3$O$_4$/SC was shown to be low-cost, environmentally acceptable, and suitable for heavy metal adsorption after regeneration [42].

Toxic metal ions are removed using magnetite nanoparticles derived from *Hevea* bark extract. These particles have been shown to be effective at cleaning up Cd and Na. A 10 mL mixture of bark extract and iron solution was made. At 104 G magnetic saturation, this mixture generated semicrystalline magnetite nanoparticles. The rice plants showed Na and Cd tolerance during the nanoparticle amendment, which could be explained by biomass, plant pigments, relative water content, osmolyte concentration, oxidative stress, and metal accumulation. pH and temperature were found to be optimal for adsorption at 6.0 and 20.0°C, respectively. Maximum adsorption capacity of Na with nanoparticles was less than that of Cd because of multilayer adsorption. Plant development aided the effects of nanoparticles by increasing chlorophyll and potassium levels, which reduced oxidative stress [43].

Fe$_3$O$_4$ double-layered hydroxide guar gum bio nanocomposites were prepared efficiently. Ultrasonic irradiation was used to make LDH-coated Fe$_3$O$_4$ nanoparticles. Guar gum biopolymer was linked to Fe$_3$O$_4$@LDH using an in situ growing technique. Cd(II) ion adsorption, contact time, pH, and initial concentration were all investigated. The capacity of NC for Cd(II) adsorption was 258 mg/g. Guar gum@ Fe$_3$O$_4$@LDH NCs were used to remove Cd ions from aqueous solutions. Its three-dimensional structure was densely packed with active sites [44].

By coprecipitating orange peel powder with Fe3O4 nanoparticles, agricultural waste was successfully converted into magnetic nano adsorbent (MNP-OPP) for Cd ion removal from aqueous solutions. The covalent binding of MNP with carboxyl groups was demonstrated using FTIR, SEM, XRD, TEM, and VSM. The Cd adsorption was tested using different parameters like pH, natural organic matter, ionic strength, time, adsorbate concentration, and temperature. With a breakthrough capacity of 55.38 mg/g, 82% of the cadmium was removed. The development of MNP-OPP showed high adsorption efficiency, easy recovery, easy synthesis, cost effectiveness, and environment-friendliness [45].

Magnetic oak wood biochar and magnetic oak bark biochar were created using fast pyrolysis during bio-oil synthesis. They were discovered to be green adsorbents capable of removing cadmium and lead from water. Aqueous biochar suspensions were combined with aqueous Fe^{3+}/Fe^{2+} solutions after fast pyrolysis at 400 and 450°C in an auger-fed reactor to generate biochar, which was then magnetized by mixing aqueous biochar suspensions with aqueous Fe^{3+}/Fe^{2+} solutions. After that, it was treated with sodium hydroxide (NaOH). Surface chemistries, density, magnetic moment, and compositions of biochar were investigated. SBET values of 6.1 and 8.8 m^2·g^1 were found in the magnetic oak wood and bark chars, respectively. Highest removal of cadmium and lead was done as pH 4-5. Pb^{2+} and Cd^{2+} were remediated successfully using magnetic biochar from water. Low external magnetic field allowed easy separation and manipulation from aqueous phase. The filtration was convenient and hassle free [46].

The ability of single and binary systems to remove lead and cadmium ions via adsorption is being investigated. The material demonstrated the fastest adsorptive rate for Pb^{2+} (98.23%) and Cd^{2+} (96.5%) in a single system after 60 minutes and a pH of 6.5. The thermodynamic parameters G0, H0, and S0 were determined. The adsorption was natural, endothermic, and beneficial. The selectivity of Pb^{2+} was greater. Without losing its stability, the material could execute up to seven cycles in a row. As a result, magnetic separation from aqueous solution was the quickest. This strategy is simple to adopt in large-scale low-income countries [47].

Maghemite nanoparticles range in size from 20 to 40 nanometers. They were created utilizing a sonochemical method and *Tridax* plant leaf extract. The heavy metals Pb and Cd were removed using a shake flask technique at 30°C with a fixed 0.3 mg/100 ml and 150 RPM. Pb was gone in less than an hour. The microstructure and crystallinity of the particles were validated using XRD and FTIR. Pb and Cd were removed with a success rate of 90.85% and 67.8%, respectively. Maghemite was discovered to be both inexpensive and efficient in the removal of Pb and Cd [48].

Chlorella vulgaris biomass was mixed with Fe$_3$O$_4$ nanoparticles. TEM, SEM-EDX, FTIR, and XPS investigations were used to characterize the materials. The sorption of Cd(II) and Pb(II) from aqueous solutions occurred concurrently. Pb(II) was aggregated on the surface, but Cd(II) was absorbed to a greater extent at lower pressures. Weak electrostatic forces held Cd(II) together. Chemically attached Pb(II) ions with the amino group of magnetic CV. The effective integration of iron particles onto *Chlorella vulgaris* was confirmed by EDX analysis [49].

TABLE 1: Iron nanoparticles for heavy metals removal.

S. no.	Biomaterial	Name of biomaterial	Size of iron NPs	Heavy metal removal	Capacity of removal	Time taken	Miscellaneous	References
1	Seed extract	*Phoenix dactylifera*	68 nm	Chromium(VI)	13.4 mg/L 90%	120 mins	Ciprofloxacin degradation	[23]
2		Green tea	10.6 nm	Chromium(VI)	60 mg/L 90.2%	60 mins	—	[24]
3		*Verbascum thapsus*	—	Chromium(VI)	25 mg/L 100%	30 mins	—	[25]
4		Green tea	50–80 nm	Chromium(VI)	80 mg/L (97.66%)	30 mins	—	[27]
5		*Psidium guajava*	50–90 nm	Chromium(VI)	50 mg/L 71.34%	15 mins	—	[28]
6		*Eucalyptus* globules	50–80 nm	Chromium(VI)	98.1%	30 mins	—	[29]
7		*Eucalyptus* leaf	95 nm	Chromium(VI)	10 mg/L 100%	8 hours max.	—	[30]
8		*Eichhornia crassipes*	20–80 nm	Chromium(VI)	89.9%	45 mins	—	[32]
9		*Rosa damascena*, *Thymus vulgaris*, and *Urtica dioica*	100 nm	Chromium(VI)	100%	30 mins	—	[33]
10		Yerba mate	15–100 nm	Chromium(VI)	80%	2 mins	—	[34]
11		Green tea	10.6 nm	Copper(II)	50 mL 97%	240 mins	Antibacterial property	[35]
12	Leaf extract	Green tea	10 nm	Copper(II)	23.6 mg/L 95%	—	—	[36]
13		*Eucalyptus*	20–80 nm	Cr(VI), Cu(II), Pb(II), and Zn(II)	44.8%, 21.5%, 31.4%, and 10.8%, respectively	60 mins	—	[37]
14		*Eucalyptus*	60–80 nm	Copper(II)	52.4%	3 mins	Triclosan (TCS) removal	[38]
15		*Eucalyptus*	100 nm	Copper(II)	96%	60 mins	BPA removal	[40]
16		Green mulberry and oak	10–30 nm	Copper(II) and nickel(II)	1,047 mg cu/g and 777.3 mg ni/g	45 mins	—	[41]
17		*Hevea brasiliensis*	620 nm	Cadmium(II) and sodium	37.03 and 3.95 mg/g	15 minutes	—	[43]
18		*Tridax*	20–40 nm	Cadmium(II) and lead(II)	67.8%	10–15 minutes	—	[48]
19		Green tea	10 nm	Lead(II)	50 mg/L 100%	120 mins	Rifampicin removal	[50]
20		Green tea	40–80 nm	Lead(II)	50 mg/L 87.5%	180 mins	—	[52]
21	Plant skin extract	Red peanut	10.6 nm	Chromium(VI)	10 mg/L (98.5%)	1 min	—	[26]
22		Mango	—	Chromium(VI)	50 mg/L 95.45%	10 mins	—	[31]
23	Peel extract	Orange peel	500 nm	Cadmium(II)	82%	A few minutes	—	[49]
24		Tangerine peel	<100 nm	Lead(II)	95%	95 mins	—	[53]
25	Floral extract	Honey-varied	150 nm	Lead(II)	17 mg/L 100%	24 hours	—	[54]
26		Guar gum	40 nm	Cadmium(II)	258 mg/g	5 minutes	—	[44]
27	Plant extract	Oak wood and oak bark	—	Cadmium(II) and lead(II)	Pb2+ 30.2 and Cd2+ 7.4 mg/g	24 hours	—	[46]
28	Agro waste biomass	Rubber seed shell	—	Copper(II)	48.18 mg/g	30 mins	—	[39]
29	Agriculture biomass	Sineguelas	10–70 nm	Lead(II)	90.1%	120 mins	—	[51]

TABLE 1: Continued.

S. no.	Biomaterial	Name of biomaterial	Size of iron NPs	Heavy metal removal	Capacity of removal	Time taken	Miscellaneous	References
30		Chlorella vulgaris	—	Cadmium(II) and lead(II)	Cd2 + 11.67 and Pb2 + 7.49 mg/L	—	—	[45]
31	Algae	Synechocystis sp. PCC6803	<2 μm	Cr(VI), Cu(II), Pb(II), and Cd(II)	Cr(VI)– 69.77 mg/g Pb(II)–62.63 mg/g Cd(II)–42.12 mg/g Cu(II)–38.68 mg/g	Cu(II)– 60 mins Cr(VI), Pb(II), Cd(II)– 30 mins	—	[55]
32	Sawdust	Poplar tree	10–30 nm	Cadmium(II)	63.3 mg/g	10–50 mins	—	[42]

2.1.4. Removal of Lead. Iron nanoparticles (Fe-NPs) were successfully synthesized in a one-step green synthesis using green tea extracts for the simultaneous removal of Pb(II) and rifampicin. Green tea extracts contain polyphenols and caffeine, which act as reducing and capping agents during the synthesis of Fe NPs, reducing agglomeration and increasing Fe NP stability and reactivity. Pb(II) and rifampicin had 100% and 91.6% removal efficiency, respectively. The XRD patterns of the nanoparticles were identical before and after reaction with Pb(II) and rifampicin, with the exception of a broad diffraction peak at 22.6°, which corresponded to amorphous carbon, indicating that organic molecules from green tea extract were successfully combined with Fe NPs, coating their surface. The surface morphology of the Fe NPs was coarse before the reaction, and they were uniformly disseminated and present in the form of chains, according to SEM inspection. The morphology got coarser and there was considerable aggregation after the reaction. The particle size of the Fe NPs was between 30 and 100 nm, according to TEM examination of the Fe NPs before and after the process. The pore width was also in the 30 to 100 nm range, according to the pore size distribution plot. The Pb removal effectiveness for Pb(II) was 96.0 percent and 96.2 percent at 20°C and 30°C, respectively, and declined to 94.3% when the temperature was raised to 40°C. Furthermore, as the pH was decreased from 5 to 3, the removal efficiency of Pb(II) decreased from 96.4 to 55.2%. Furthermore, when the dose of Fe NPs was increased from 0.3 to 1 g·L^{-1}, the removal efficiency of Pb(II) increased from 82.6 to 99.6%. Adsorption is the last but not least [50].

To eliminate Pb(II) ions, nanoscale zero-valent iron (nZVI) based on sineguelas waste (S-NaOH-NZVI) was synthesized from agricultural biomass. The use of ZVI particles on the surface of sineguelas waste can help to overcome the disadvantage of ultrafine powders, which have a high agglomeration tendency. Pure sineguelas have a limited ability to absorb Pb(II) ions from effluent. As a result, the sineguelas waste was pretreated to improve its ability to remove Pb(II) (NaOH treatment and nZVI immobilization). According to TEM imaging, the supported zero-valent iron on the surface of the bio-adsorbent was spherical in shape. The removal efficiency gradually improved as the pH increased from 1 to 5 and then remained nearly unchanged at pH 5–9. However, the optimal pH for adsorption was found to range between 4 and 7. Furthermore, 0.15 g of adsorbent dose was discovered to be the most effective for the removal of Pb(II). The elimination capacity increased even more as the temperature rose. The thermodynamic factors (G, H, and S) revealed that Pb(II) ion adsorption was practical, spontaneous, and endothermic at 25–80°C, with a pseudo-second-order equation governing the adsorption kinetics [51].

Green tea extract was used to make hybrid bimetallic Fe/Ni nanoparticles and graphene-supported bimetallic Fe/Ni nanoparticles for pollution reduction. A one-step green synthesis approach was used to create Fe/Ni-RGO. They were then tested simultaneously for rifampicin (RIF) and lead(II) elimination from aqueous solution. In terms of elimination, the hybrid Fe/Ni-rGO outperformed the nFe/Ni, rGO, and Fe-rGO, with Fe/Ni-rGO removing Pb(II) and RIF at 87.5 and 96.8%, respectively. A thorough examination of Fe/Ni-rGO revealed that both the nanoparticles and the rGO stacking were reduced. The kinetics of adsorption, removal efficiency, and other parameters were investigated. Chemical adsorption was used to remove the contaminants, and nFe/Ni assisted in the catalytic reduction of RIF. Fe/Ni-rGO was discovered to be reusable and effective for wastewater treatment, establishing it as a viable resource [52].

T-Fe$_3$O$_4$ iron nanocomposites are synthesized from tangerine peel, which is a biowaste. Pb(II) removal is done using adsorption from aqueous solution. The synthesis confirmed that T-Fe$_3$O$_4$ has a mesoporous hexagonal nanocrystalline structure with a diameter of less than 100 nm. Response surface approach was used to improve the procedure for maximal Pb(II) removal. At an initial concentration of 32.5 g/L, the optimal conditions were observed, a contact time of 95 minutes, and a pH of 4.5. T-Fe$_3$O$_4$ nanoparticles performed well in terms of efficiency and adsorption capacity. Hence, ZVI NPs have turned out to have potential for sustainable water purification [53].

In the production of ferrite NPs, analytical-grade zinc(II) nitrate hexahydrate Zn (NO$_3$)$_2$6H$_2$O, cobalt(II) nitrate hexahydrate Co (NO$_3$)$_2$6H$_2$O, and ferric nitrate nonahydrate Fe (NO3) 39H2O were used. Honey was used as a stabilizing and reducing agent in this case to keep the iron NPs from clumping together. The cubic spinel fd-3 phase

was confirmed by X-ray diffraction in all of the ferrite nanoparticles. SEM analysis revealed that the spinel iron NPs had a porous surface and morphology, and TEM analysis confirmed their polyhedral form and size. Through FTIR analysis, it was observed that metal-oxygen bonds were present and could be attributed to the compounds present in the honey components. The NPs had a size range of 2–4 nm and were able to adsorb lead ions in a monomolecular fashion effectively. Heavy metal ions in wastewater were completely removed with a zinc doped dosage of 23.0 mg/g. The adsorption reaction and experimental results obtained can be best represented by the Langmuir model [54].

Another study used a mixture of ferric chloride solution and *Synechocystis* sp. PCC6803 to make iron NPs. After centrifugation, the precipitate was dried and carefully washed with ethanol. Through X-ray diffraction, an inverse relationship between reaction temperature and nanoparticle crystallinity was confirmed. SEM and TEM images taken before and after Pb(II) adsorption revealed the presence of Fe_2O_3 on the surface of the nanoscale microalgae, as well as the aggregation of the NPs into microscale particles. The adsorption capacity of the NPs in relation to pH was seen to be highest at 2.0 and experienced a subsequent decrease after the pH was raised to 6.0. At 0.5 g/L iron NPs, Pb(II) was completely adsorbed and reached reaction equilibrium after 1 hour. The Langmuir model best represents the reaction results, and the reaction kinetics are consistent with the pseudo-order model. The synthesized iron nanoparticles are useful for wastewater remediation because they effectively adsorb lead, copper, and chromium ions and successfully reduce these heavy metal ions. Hence, this method has an effective and practical application that is eco-friendly [55].

3. Conclusion

The formation and production of ZVI NPs for the removal of heavy metals has been proven to be a highly effective and environmentally benign approach. In this review, the use of iron nanoparticles as adsorbents and reducing agents has been explored for the removal of copper, chromium, cadmium, and lead from wastewater. The incorporation of plant produced organic compounds—flavonoids and polyphenols—in the production of these iron NPs from natural sources such as plant, leaf, and seed extracts provide additional benefits such as steric stability, as found by several analytical methods. The utility value of ZVI NPs in the context of heavy metal removal was successfully studied and demonstrated. The use of various nanomaterials for removal of heavy metals is described in Table 1.

Data Availability

All relevant data are included within the article.

Conflicts of Interest

All authors declare that there are no conflicts of interest regarding the publication of this paper.

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