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Green Synthesis of AgNPs for Groundwater Remediation: Characterization and Heavy Metal Removal Performance

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Abstract

This study addresses the issue of toxic heavy metal contamination of groundwater and proposes an innovative and sustainable remediation strategy using green synthesized silver nanoparticles (AgNPs). While previous studies have demonstrated the potential of AgNPs in water purification, this study is unique in using a plant-mediated synthesis route using *Vernonia anthelmintica* (L.) and evaluating its effectiveness. This column-based method offers valuable insights into the practical application and scale-up of AgNPs, especially in resource-limited settings. Comprehensive analysis of groundwater samples discovered that although physicochemical parameters such as pH, electrical conductivity (EC), and dissolved solids (DS) were within acceptable limits, while turbidity, arsenic (As), cadmium (Cd), lead (Pb), nickel (Ni), and zinc (Zn) exceeded the World Health Organization (WHO) limits. However, these values were reported in the limits prescribed by Pakistan National Environmental Quality Standards (Pak-NEQS). The eco-friendly AgNPs displayed significant removal capacities, especially for Zn, Cd, and As. This performance is due to their large specific surface area and the presence of active functional groups, as confirmed by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) analysis. The nanoparticles showed antibacterial qualities in addition to their potent adsorptive activity, which increased their suitability for water purification. This study offers a viable and scalable way to reduce groundwater contamination by combining green nanotechnology with economical, ecologically friendly synthesis techniques. In the context of sustainable water treatment technologies, it is a significant advancement toward bridging the gap between laboratory-scale research and field-scale implementation.

Keywords

Groundwater, Heavy metals, Silver nanoparticles, Water purification, Nanotechnology

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1. Introduction

Human activities have become much more intense due to the world's population growth and industrialization, which has contaminated natural water supplies. Heavy metals (HMs) are among the most alarming pollutants, and they are released by a number of industries, such as manufacturing and urbanization [1,2]. There are still major risks to the environment and human health from the effects of urbanization, including resource depletion, increased carbon emissions, and widespread water contamination [3]. The quality of surface and groundwater has drastically declined as a result of industrial expansion, which has also changed socioeconomic landscapes and brought a variety of pollutants into water bodies [4,5].

Water quality is deteriorated and ecological systems are threatened by the toxic HMs and other dangerous elements released by industrial operations [6]. Heavy metal toxicity makes contaminated water sources, particularly drinking water, extremely dangerous for human health [7-9]. Heavy metal poisoning of groundwater continues to be a significant environmental concern despite the many remediation approaches that have been developed [10]. Trace amounts of elements such as nickel (Ni), Copper (Cu), lead (Pb), cadmium (Cd), and zinc (Zn) are necessary for human physiology, but when they build up to dangerous levels, they can be harmful [11-13]. High-density HMs can be extremely harmful, even at low levels, and can lead to energy depletion and major health problems such brain, kidney, and lung damage [14-20]. Some of these metals are also classified as carcinogenic due to prolonged exposure [21,22].

Effective techniques for removing HMs from water systems are therefore desperately needed [23-25]. Many people have employed traditional methods such ion exchange, coagulation, adsorption, oxidation-reduction, and phytoremediation [26,27]. However, these techniques frequently have lengthy treatment periods and significant operating costs, which restricts their usefulness [28]. Nanotechnology, on the other hand, has become a viable and economical substitute for cleaning up polluted water [29,30]. Nanoparticles have improved adsorption capacities and are ecologically beneficial because of their high surface area and reactivity [31,32]. The versatility of this technology in field-scale operations stems from its suitability for both in-situ and ex-situ applications [33]. When contaminated water or soil is treated on-site without excavation or removal, the ecosystem is left intact. This process is known as "in-situ remediation." Ex-situ remediation, on the other hand, entails the removal of polluted soil or water, which is then cleaned offshore or above ground using specially designed equipment [34].

Numerous nanoparticles have been investigated for the treatment of wastewater [35], and they are easily produced in a lab setting [36,37]. The ability of nanoparticles to greatly enhance water quality by removing HMs has been confirmed by earlier studies [38-41]. However, creating silver nanoparticles (AgNPs) via traditional physical and chemical procedures frequently requires hazardous chemicals, a lot of energy, and byproducts that are bad for the environment. On the other hand, by employing phytochemicals as organic stabilizing and reducing agents, plant-mediated green synthesis provides a sustainable, economical, and environmentally beneficial substitute. In order to assess the efficacy of AgNPs made from plant-based extracts in treating arsenic (As), Cd, Pb, Ni, and Zn-contaminated groundwater, this study uses them. The results are intended to aid in the creation of environmentally friendly nanomaterials for the on-site removal of heavy metal contaminants from aquatic ecosystems.

2. Experimental Work

2.1 Sampling Collection and Analysis Period

Over the course of 30 days, ten groundwater samples were gathered from diverse geographically scattered areas in order to analyse the groundwater quality and the effectiveness of biosynthesized AgNPs removal. Ten-day intervals were used for sampling in order to record changes in water quality over time. To ensure higher representativeness of the sampling location and minimize potential local heterogeneity, two 250 mL sub-samples were taken at each site and pooled to generate a single 500 mL composite sample. Acid-washed polyethylene vials that had been previously rinsed with Milli-Q deionized water were used to collect all of the samples. To preserve sample integrity throughout transit, the bottles were labelled, sealed, and put in insulated containers as soon as they were collected. Following collection, the groundwater samples were securely delivered to the University of Peshawar's National Centre of Excellence in Geology (NCEG) for additional examination.

Using Atomic Absorption Spectrometry (AAS), analytical evaluations were conducted in the lab to ascertain the quantities of important HMs, such as As, Cd, Pb, Ni, and Zn. Apart from the study of HMs, a thorough assessment of many physicochemical properties was carried out. These included the concentration of typical inorganic contaminants like fluoride (F^-), nitrate (NO_3^-), nitrite (NO_2^-), and phosphate (PO_4^{3-}), as well as pH, electrical conductivity (EC), total dissolved solids (TDS), and turbidity. To guarantee data accuracy and comparability, the measurements were carried out in accordance with accepted analytical procedures that are advised by the American Public Health Association (APHA).

2.2 Preparation of Plant Extract

In order to eliminate dust, soil particles, and other surface impurities, fresh and healthy *Vernonia anthelmintica* (L.) leaves were gathered and carefully cleaned multiple times using distilled water. To retain the phytochemical ingredients by preventing photodegradation, the cleaned leaves were then spread out on fresh blotting paper and allowed to dry in the shade for seven to ten days at room temperature. A clean, dry mechanical grinder was used to grind the leaves into a fine powder when they had completely dried, and they were then put away in airtight containers for later use.

Ten grams of the dried leaf powder were combined with one hundred milliliters of distilled water in a beaker, and the mixture was heated on a magnetic stirrer equipped with a hot plate at around 80 to 90 degrees Celsius for half an hour in order to allow the active phytochemicals to seep into the water [42]. Following boiling, particle matter was eliminated by filtering the liquid through Whatman No. 1 filter paper after it had cooled to room temperature. For later usage, the clear brownish filtrate that resulted was gathered and kept in a refrigerator at 4 °C. A variety of bioactive chemicals, including flavonoids, alkaloids, phenolics, and terpenoids, were present in this aqueous leaf extract, which acted as a stabilizing and reducing agent during the production of nanoparticles [42].

2.3 Synthesis of Silver Nanoparticles

The aqueous leaf extract of *Vernonia anthelmintica* (L.) was used as a natural stabilizing and reducing agent during the manufacture of AgNPs. The first step in the production procedure was making a 1 mM water solution of the metal precursor, silver nitrate ($AgNO_3$). To find the ideal ratio for nanoparticle generation, the plant extract was subsequently combined with the $AgNO_3$ solution in different volumetric ratios of 1:2, 1:4, 1:6, and 1:8 (plant extract to $AgNO_3$ solution) in different conical flasks. To guarantee even mixing and promote the reduction of silver ions (Ag^+) ions to elemental silver (Ag^0), these mixtures were continuously stirred magnetically at room temperature for around four hours. A gradual color change was observed in the reaction mixtures during the stirring process, which served as a preliminary visual confirmation of nanoparticle synthesis. When surface plasmon vibrations, a distinctive optical characteristic of AgNPs, are excited, the hue shifts from light yellow or dark gray to a deep brown, signifying the creation of AgNPs. A more deep brown hue was seen at higher volumes of the $AgNO_3$ solution among the various ratios tested, indicating better synthesis efficiency. After the reaction was finished, the colloidal solutions were let to settle at room temperature. The produced AgNPs were then kept stable for additional characterisation and to avoid photodegradation in amber-colored bottles at 4°C. Without the use of dangerous chemicals, this green synthesis technique offers an inexpensive, environmentally acceptable way to create nanoparticles [42].

In order to assess the effectiveness of the produced AgNPs in removing HMs, separate stock solutions were made for each target metal, including Cd, As, Pb, Ni, and Zn. Metal ions were obtained from analytical-grade nitrate salts of each metal, namely zinc nitrate [$Zn(NO_3)_2$], lead nitrate [$Pb(NO_3)_2$], nickel nitrate [$Ni(NO_3)_2$], sodium arsenate [Na_2HAsO_4], and cadmium nitrate [$Cd(NO_3)_2$]. To create 1000 mg/L (ppm) stock solutions for every metal ion, precisely weighed amounts of each salt were dissolved in Milli-Q deionized water.

Following the full dissolution of the salts, any remaining particles were removed from the resultant solutions by filtering them if required. After that, the pH of each solution was carefully adjusted to fall between 6.8 and 7.0, which is neutral and thought to be ideal for metal adsorption. This prevents precipitation, which can happen in extremely basic or acidic environments. This pH adjustment was accomplished by adding 1 M sodium hydroxide (NaOH) solution gradually while stirring constantly and keeping an eye on the mixture with a calibrated digital pH meter to guarantee accuracy. Clean, acid-washed polyethylene bottles were used to keep all produced stock solutions at 4 °C in order to guard against chemical deterioration and microbiological contamination. Subsequent adsorption tests, such as batch and column studies, involved diluting these solutions as needed. The presence of metal ions in a free and soluble state is guaranteed by the use of nitrate salts, which makes it easier to obtain reliable and consistent findings from adsorption tests.

2.4 Experimental Setup

To replicate authentic environmental conditions, all adsorption tests were carried out in 250 mL volumetric flasks that were filled with previously collected and filtered groundwater. To get rid of any remaining metal ions or impurities, all glassware–including the volumetric flasks–was meticulously cleaned before use by soaking in 10% nitric acid (HNO_3) for at least 24 hours. Following acid washing, the flasks were repeatedly rinsed with Milli-Q deionized water to get rid of any remaining acid, guaranteeing that there was no contamination or background interference in the experimental setup. Each flask containing groundwater received a precisely calibrated dose of biosynthesized AgNPs. Preliminary optimization studies determined the appropriate number of AgNPs to employ, guaranteeing adequate surface area for efficient heavy metal adsorption. After that, the flasks were carefully sealed and kept for a month at a steady room temperature of 22 ±1 °C. Since no agitation was used throughout this time, the nanoparticles and metal ions were able to interact naturally. To assure accuracy and reproducibility of the results, each experiment was conducted twice. In order to evaluate the baseline metal concentrations and take into consideration potential non-specific changes over time, blank samples (without AgNPs) were also made and observed under the same circumstances.

2.5 Analytical Techniques

Atomic Absorption Spectroscopy (AAS) was used to measure the levels of HMs (Cd, As, Pb, Ni, and Zn) in groundwater samples both before and after they were treated with AgNPs. The study was conducted using an AAS (AAnalyst 600 series,, California, USA), which is widely known for its accuracy and sensitivity in identifying metal ion traces. A fixed wavelength of 195.2 nm, which is appropriate for detecting metals like lead and cadmium, was used for the analysis. To increase flame stability and boost measurement precision, argon gas was employed as the carrier and inert shielding gas.

After removing any particle matter with a filter if needed, each sample was moved into containers that had been acid-washed before examination. For each measurement, a 50 mL sample volume was employed to guarantee uniformity over all experimental runs. To assure dependability, all readings were taken in triplicate, and calibration standards for each metal ion were made fresh using approved standard solutions to create a standard curve. Under carefully monitored laboratory settings, all AAS measurements were carried out at the University of Peshawar's NCEG. The standard procedures were closely adhered to in the analytical process to guarantee data integrity and repeatability.

2.6 Characterization of Silver Nanoparticles

A range of advanced analytical techniques were used to thoroughly characterize the produced AgNPs. A UV-visible spectrophotometer (model UV-1800, Shimadzu, Japan) was used to analyze their optical behavior. Absorbance measurements were taken throughout a wavelength range of 200 to 600 nm. A Shimadzu-6000 diffractometer was used to perform X-ray diffraction (XRD) measurements in order to examine the nanoparticles' crystalline nature. Data collection lasted 1.5 hours, and the scans covered a 2θ angular range between 10° and 70°. The device ran on copper K-alpha (Cu-Kα) radiation with a 50 kV voltage and a 40 mA current. Additionally, Fourier-transform infrared (FTIR) spectroscopy was used to identify the surface functional groups that were involved in the stabilization and reduction of the AgNPs. Spectra were recorded on an IRAffinity-1 FTIR spectrometer (FTIR-8400S, Shimadzu, Japan) in the wavenumber range of 400 to 3000 cm^{-1} using the KBr pellet technique.

3. Results and Discussion

3.1 XRD Analysis

In order to determine the average particle size and examine the crystalline structure of the produced AgNPs, XRD) analysis was utilized (Figure 1). The phase purity, crystallinity, and structural properties of nanomaterials can all be ascertained using the popular XRD technique. In this study, the aerial portions of *Vernonia anthelmintica* (L.) were used to produce AgNPs. The resulting XRD pattern verified that Ag^+ were successfully bioreduced to Ag^0. The (111), (200), (220), and (311) crystallographic planes of face-centered cubic (FCC) silver are shown by the different peaks in the diffraction profile at 2θ values of roughly 37.95°, 41.12°, 64.30°, and 76.85°. These reflections demonstrate the creation of pure, crystalline metallic AgNPs and are in good accord with the standard data from the Joint Committee on Powder Diffraction Standards (JCPDS card No. 04-0783).

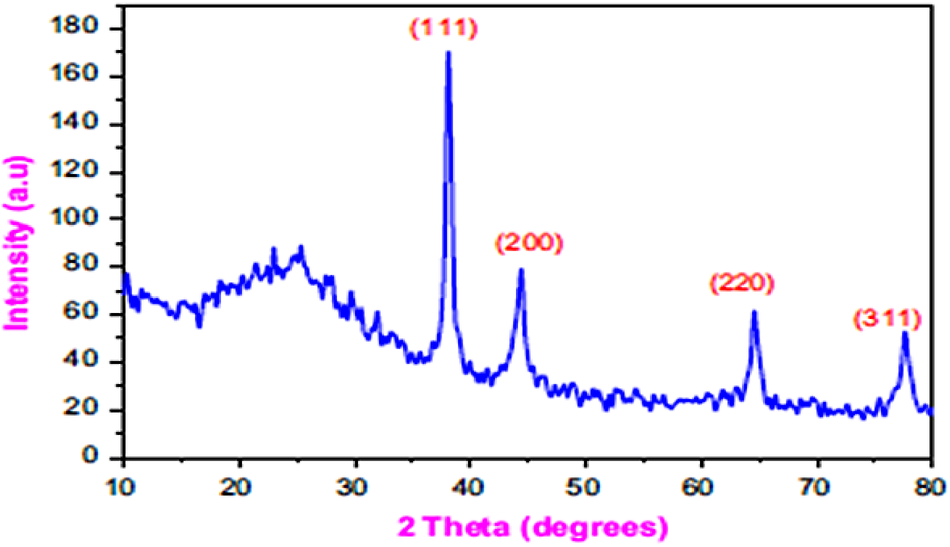

Figure 1. XRD analysis of AgNPs with 1mM $AgNO_3$ (from Shaukat S. et al. [42], Digest Journal of Nanomaterials and Biostructures, 2022, CC BY 4.0).

A high degree of crystallinity is indicated by the diffraction peaks' sharpness and intensity. The physical and chemical characteristics of nanoparticles, including optical activity, thermal stability, and catalytic effectiveness, are significantly influenced by crystallinity. By using the Scherrer equation to the full width at half maximum (FWHM) of the (111) peak typically the most intense reflection for silver it was possible to estimate the average crystallite size of the produced AgNPs. With a computed average size of roughly 21 nm, the generation of nanoscale particles with a comparatively uniform distribution was demonstrated.

These results are in line with earlier studies that used plant extracts to create green-synthesized AgNPs and found comparable ranges in crystallinity and particle size. Overall, the XRD data support the prospective use of crystalline AgNPs in antibacterial, catalytic, and environmental technologies by confirming the effective biosynthesis of these particles and offering crucial details on their structural integrity and nanoscale dimensions.

3.2 FT-IR Spectroscopic Analysis

The functional groups in charge of the reduction, capping, and stability of the biosynthesized AgNPs were examined using Fourier-transform infrared (FT-IR) spectroscopy. FT-IR spectra of AgNPs showed multiple distinct absorption bands at 3295.50, 3275.12, 2894.14, 2898.08, 2351.12, 2355.11, 1640.22, 1643.32, 768.56, and 424.35 cm^{-1}, as shown in Figure 2(b). Usually found in alcohols or alkanes, the broad band seen at 3295.50 cm^{-1} is suggestive of O–H or C–H stretching vibrations. The existence of aromatic phytochemicals is suggested by the absorption peak at 2894.14 cm^{-1}, which correlates to C–C stretching in aromatic structures. Furthermore, the stretching vibrations of phosphonic acid groups, notably (O=)P–OH, which are known to aid in metal ion chelation and nanoparticle stability, could be the cause of the band at 3275.12 cm^{-1}.

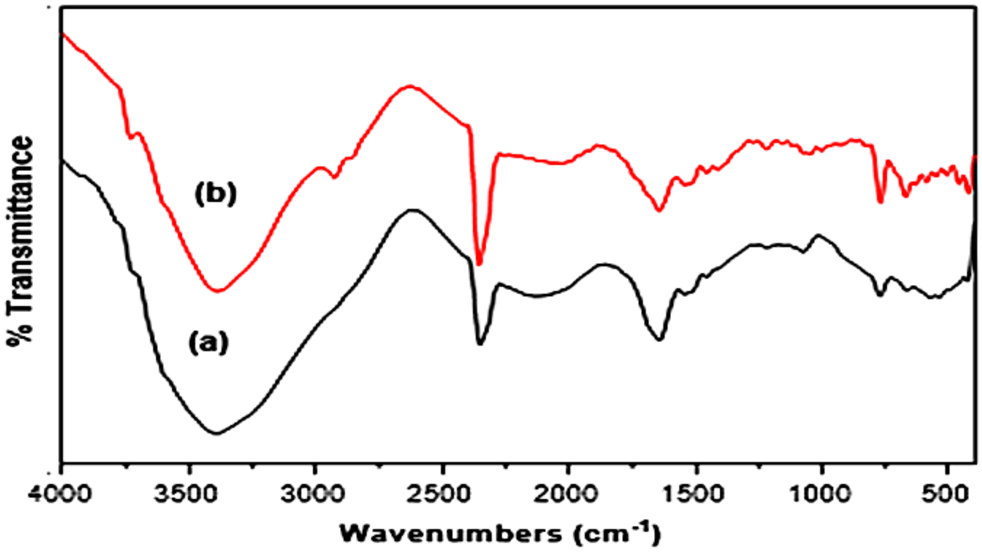

Figure 2. (a) FT-IR spectra of plant extract and (b) FT-IR spectra of AgNPs (from Shaukat S. et al. [42], Digest Journal of Nanomaterials and Biostructures, 2022, CC BY 4.0).

C–F stretching is indicated by another peak at 2898.08 cm^{-1}, which points to the presence of carboxylic acids, particularly when proteins serve as capping agents to stabilize nanoparticles. The overlapping vibrations that cause the peak at 2355.11 cm^{-1} include the C–N stretching of amines, the C–H stretching of alkanes and aromatic compounds, and perhaps the C–Br stretching of alkyl halides. It is thought that the bioactive substances found in the plant extract used for synthesis are the source of all of these functional groups. Their existence demonstrates that the extract serves as a capping and reducing agent. By stabilizing the nanoparticles, this bio-reduction process helps turn Ag^+ into Ag^0 while also avoiding aggregation. The synthesis and stability of AgNPs were directly impacted by the unique functional groups identified by FTIR investigations [43].

3.3 UV–Visible Spectroscopic Analysis

A noticeable change in the reaction mixture's hue served as visual confirmation that AgNPs had formed. The hue of the $AgNO_3$ solution changed from pale black to deep brown when *Vernonia anthelmintica* (L.) aerial extract was added. This alteration is explained by the surface plasmon resonance (SPR) phenomenon, which is a defining feature of the production of AgNPs and arises from the collective oscillations of conduction electrons on the surface of the nanoparticles in response to light.

Ag^+ were completely reduced to Ag^0 as the reaction proceeded, as evidenced by the solution's steady dark brown color. By showing a distinctive absorption peak at 420 nm, a value frequently linked to spherical AgNPs, UV–visible spectroscopy further supported this observation. AgNPs were successfully synthesized utilizing *Vernonia anthelmintica* (L.) extract, as indicated by the identified SPR band.

The dependability of this spectral indication has been confirmed by previous research including the green synthesis of AgNPs utilizing plant species such as Azadirachta indica, which found similar absorbance peaks around 420 nm. Therefore, this study's 420 nm peak confirms that the produced nanoparticles are, in fact, silver-based and stabilized by phytochemicals originating from plants (Figure 3).

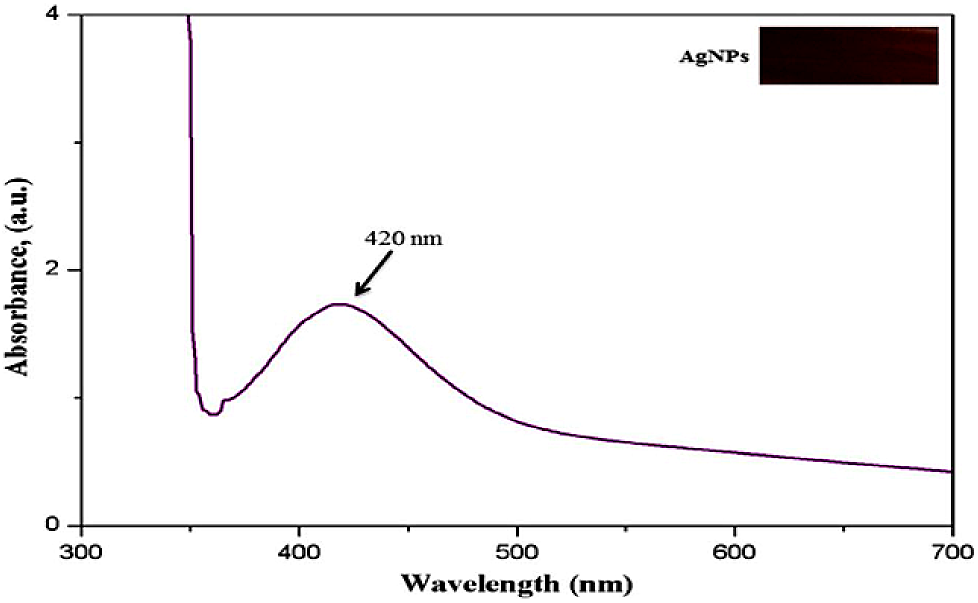

Figure 3. UV-visible spectra of synthesized AgNPs (from Shaukat S. et al. [42], Digest Journal of Nanomaterials and Biostructures, 2022, CC BY 4.0).

3.4 Removal of Heavy Metals Using AgNPs

According to an analysis of groundwater samples taken from the approved study area, numerous HMs had noticeably higher quantities. It was found that the amounts of Cd, As, Pb, Ni, and Zn were 20.00, 15.20, 17.60, 120.28, and 131.12 µg/L, respectively. The maximum permissible limits established by the World Health Organization (WHO) for safe drinking water are exceeded by these detected amounts [43]. There are major worries about the region's groundwater quality and safety when these hazardous substances are present in such high concentrations. Long-term exposure to HMs can have serious negative effects on human health, including increased risk of cancer, neurological disorders, and renal damage, even at low doses.

Furthermore, because these pollutants can build up in soil and aquatic systems, upsetting ecosystems and endangering biodiversity, the ecological ramifications are also significant. In order to guarantee the preservation of the environment and public health, the results thus point to the urgent necessity for efficient monitoring and repair techniques. The contaminated water samples were treated with biosynthesized AgNPs for 30 days in order to evaluate the remediation capability of AgNPs. Ten-day intervals were used for sampling in order to assess variations in HM concentrations. As shown in (Figure 4), the first results on day 1 showed modest removal efficiency, with Zn showing the largest reduction at 43%, followed by Pb (36%), Cd (34%), Ni (32%), and As (31.2%).

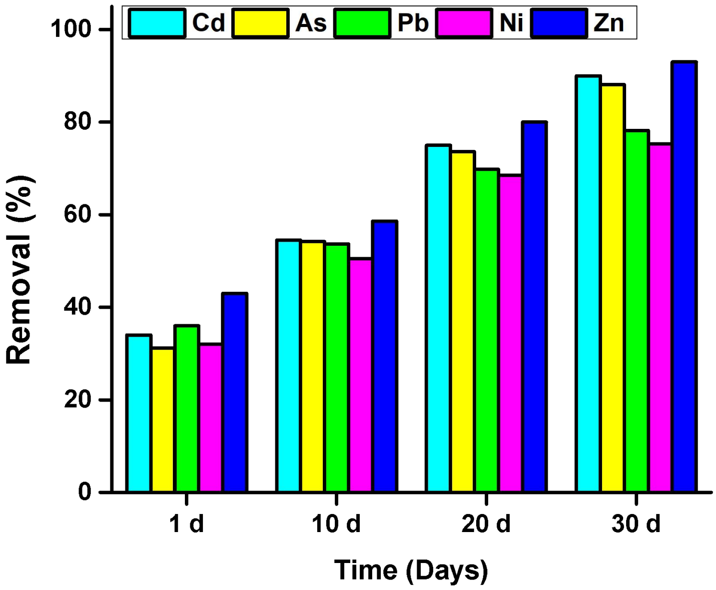

Figure 4. Heavy metals removal efficiency from water using AgNPs.

Day 10 saw a notable improvement in removal performance, with Cd, As, Pb, Ni, and Zn reaching 54.5%, 54.2%, 53.7%, and 50.5%, respectively. The adsorption capability was further increased by the AgNPs' ongoing contact with the HM ions. A progressive adsorption mechanism that is getting close to saturation is indicated by the observed removal rates increasing to 75% for Cd, 73.6% for As, 69.8% for Pb, 68.5% for Ni, and 80% for Zn on day 20. Maximum removal efficiencies were attained after 30 days of treatment; Zn had the greatest removal rate at 93%, followed by Cd at 90%, As at 88.1%, Pb at 78.2%, and Ni at 75.3% (Table 1). These findings show how well AgNPs work over time to lower harmful heavy metal concentrations. Nevertheless, it was also noted that after 30 days, the adsorption efficiency started to level off, presumably as a result of the nanoparticle surfaces' accessible binding sites becoming saturated. These results demonstrate that AgNPs provide a dependable, affordable, and environmentally friendly way to clean up HMs-polluted groundwater.

Table 1. Removal of selected HMs from water using AgNPs.

HMs	HMs in water (µg/L)	1 d	%	10 d	%	20 d	%	30 d	%
As	15.20	4.75 ± 0.02	31.2	8.25 ± 0.02	54.2	11.2 ± 0.02	73.6	13.4 ± 0.02	88.1
Cd	20.00	6.20 ± 0.02	34.0	10.9 ± 0.02	54.5	15.0 ± 0.02	75.0	18 ± 0.02	90.0
Pb	17.60	6.35 ± 0.02	36.0	9.45 ± 0.02	53.7	12.3 ± 0.02	69.8	13 ± 0.02	78.2
Ni	120.28	38.6 ± 0.02	32.0	60.8 ± 0.02	50.5	82.4 ± 0.02	68.5	90.6 ± 0.02	75.3
Zn	131.12	56.4 ± 0.02	43.0	76.9 ± 0.02	58.6	104.9 ± 0.02	80.0	122.0 ± 0.02	93.0

To increase the dependability of the findings, all experimental data in this study are presented as the mean of three independent replicates. To show the variability in the data, standard deviations were computed and displayed as error bars in the appropriate graphs. Regression analysis was used to fit curves and display the trends in adsorption efficiency for each metal ion. The coefficient of determination (R^2) was used to assess the goodness of fit, and the results showed a significant connection between the fitted curves and the experimental data. The statistical consistency of the data confirms the precision and reproducibility of the AgNPs' removal performance, even though specific error percentage calculations were omitted for the sake of conciseness.

3.5 Decontamination Mechanism

It has been demonstrated that AgNPs effectively remove HMs from water because of their unique physical and chemical properties. The process by which AgNPs remove HMs in our investigation is adsorption (Figure 5). Heavy metal ions may be adsorbed onto the surfaces of AgNPs when they are added to a solution containing these metal ions due to a variety of interactions, including surface chemical bonding, van der Waals forces, and electrostatic attraction. AgNPs' negatively charged surface frequently uses electrostatic forces to draw in positively charged HM ions. Furthermore, the overall adsorption effectiveness is improved by possible chemical bonding and weak van der Waals interactions between the metal ions and functional groups on the nanoparticle surface.

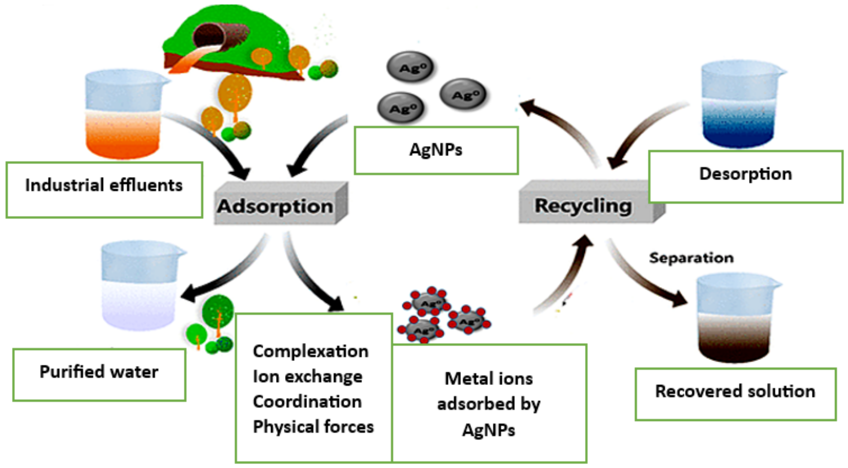

Figure 5. Heavy metals adsorption from water using AgNPs.

The efficient removal and immobilization of HMs from tainted water is made possible by these combined forces. The AgNPs act as a kind of magnet, drawing the HM ions to their surface [1]. Once the HM ions have been adsorbed onto the AgNPs' surface, they may be effectively extracted from the solution. Among the factors influencing AgNPs' capacity to adsorb HMs are the solution's size, shape, composition, and pH. The kind and concentration of HM ions is other factors. All things considered, employing the adsorption mechanism of AgNPs for HMs to remove HMs from contaminated water sources is a promising approach since it is a simple and effective procedure that doesn't require complex equipment or chemicals.

Although AgNPs showed good adsorption of HMs, it is crucial to remember that there is still a chance of desorption in the presence of shifting environmental factors like pH or variations in ionic strength. Filtration procedures were used in this study to remove AgNPs and adsorbed pollutants from purified water; however, to assure safe implementation in actual water treatment systems, future research should examine long-term stability and potential leaching issues.

Due to the presence of suspended particulates, oxidized iron and manganese particles, and other heavy metal precipitates, the untreated groundwater sample showed obvious turbidity and a brownish-yellow coloring. The samples showed a discernible decrease in color intensity and turbidity after 10 and 20 days, and almost total optical clarity after 30 days, as the treatment went on (Figure 6). This visual trend supports the effectiveness of the AgNPs therapy by correlating with the quantitative data for heavy metal elimination.

(a) Before treatment (b) After 10 days

(c) After 20 days (d) After 30 days

Figure 6. Visual representation of groundwater samples during treatment process using AgNPs (a) untreated sample, (b) after 10 days, (c) after 20 days, (d) after 30 days.

3.6 Activity Regeneration of AgNPs

Potential alterations in the physicochemical characteristics of AgNPs make their regeneration and reuse after usage in water treatment a major concern. Depending on the particular use, exposure to the environment, and operational circumstances, AgNPs may oxidize, agglomerate, or get contaminated on the surface while in use. These changes may lessen their surface area, active binding sites, and general efficacy for additional catalytic or adsorption uses.

According to earlier research, AgNPs can be regenerated with the use of appropriate reducing agents, which aid in the restoration of their nanoscale properties. Sodium borohydride ($NaBH_4$) and hydrogen gas (H_2) are often employed reducing agents because they help turn Ag^+, which may be produced during oxidative degradation, back into Ag^0. In the regeneration process, the reducing agent is added to a solution that contains the spent or oxidized AgNPs. The reduction reaction is then allowed to occur under regulated circumstances, frequently with stirring or mild heating to increase efficiency.

To recover the regenerated AgNPs, the resultant solution is filtered after the reduction stage. Any remaining reducing agents or byproducts are then repeatedly washed away with ethanol or deionized water. Following regeneration, the nanoparticles are dried and kept for later use. The performance of AgNPs may be impacted by repeated regeneration cycles, which could change the particles' size distribution, shape, or surface chemistry. Constant characterization and optimization are therefore necessary to guarantee their efficacy in long-term uses.

3.7 Comparison of AgNPs with Other Nanoparticles for HMs Removal

The exceptional capacity of AgNPs to remove HMs from tainted water has drawn significant attention in recent years. Key physicochemical characteristics, such as a wide surface area, a high number of active binding sites, and a great propensity to create persistent chemical interactions with different heavy metal ions, are responsible for their remarkable effectiveness. AgNPs are very effective adsorbents in water treatment applications because of these properties.

Although AgNPs are quite effective, other nanomaterials have also been investigated for this purpose. For the cleanup of HMs, a variety of additional nanoparticles have been studied. Iron oxide (FeO_4), titanium dioxide (TiO_2), zinc oxide (ZnO), copper oxide (CuO), magnesium oxide (MgO), carbon-based structures such as carbon nanotubes (CNTs), and gold (Au) nanoparticles are among the nanomaterials that have been investigated for environmental applications. All of these nanomaterials have shown encouraging results in eliminating harmful metals including As, Pb, Cd, Hg, and Cr from aqueous solutions and exhibit high adsorption capabilities under particular circumstances.

According to numerous studies, these nanoparticles' effectiveness is usually maximized at or close to neutral pH, where surface interactions and metal ion solubility are at their best. AgNPs work better than many of these alternatives, notably for metals like Zn, Cd, and As, as shown in Table 2, even though many of these alternatives have demonstrated great removal rates that frequently surpass 80% efficiency. The ease of green synthesis and AgNPs' exceptional performance make them an appealing option for sustainable and scalable water filtration systems.

Table 2. Removal capacity of different HMs using various nanoparticles.

Nanoparticles Type	Heavy Metals Removed	Removal Efficiency (%)	Specific pH Values	Reference
Iron oxide NPs	Mercury, lead, arsenic, cadmium, nickel, chromium and copper	>80%	7.0	[44]
Titanium dioxide NPs	Lead, zinc, copper, cadmium, arsenic and chromium	>82%	6.5	[45]
Zinc oxide NPs	Mercury, chromium, cadmium, arsenic, and lead	>85%	7.2	[46]
Copper oxide NPs	Lead, cadmium, mercury, arsenic and chromium	>75%	7.5	[47]
Gold NPs	Lead, cadmium, mercury, arsenic and chromium	>78%	6.8	[47]
Carbon nanotubes	Lead, chromium, cadmium, arsenic, copper, zinc and nickel	>80%	8.0	[48]
Magnesium oxide NPs	Lead, cadmium, chromium, arsenic, mercury, copper and zinc	>82%	7.7	[49]
Zirconium oxide NPs	Arsenic, cadmium, lead, zinc, mercury, chromium, copper	>81%	6.5	[50]
Cerium dioxide NPs	arsenic, lead, cadmium, mercury, chromium	>75%	6.0	[51]
Silver NPs	Arsenic, cadmium, lead, nickel and zinc	>90%	7.0	This study

3.8 Limitation of the Study

Microbial water quality testing is not included in this study, despite the fact that it offers a thorough evaluation of the physicochemical characteristics and heavy metal concentrations in groundwater. In groundwater systems, bacterial contamination especially from pathogens like *Salmonella* and *Escherichia coli* represents a serious public health risk. In order to offer a more comprehensive assessment of groundwater safety, future research should address the study's limitation the lack of microbiological analysis. However, the use of AgNPs in this study may have two advantages: the elimination of HMs and possible bacterial disinfection. AgNPs are known to have antibacterial qualities.

To confirm the antibacterial effectiveness of biosynthesized AgNPs in practical settings, future research should combine physicochemical testing with microbiological assays. The lack of SEM analysis for a thorough examination of the surface morphology and particle size distribution of the produced AgNPs is another drawback of this work. Although the removal effectiveness of HMs was successfully measured using AAS, SEM might have offered important information about the form, dispersion, and surface roughness of the nanoparticles. Understanding the physical interaction that occurs during the adsorption process between AgNPs and heavy metal ions requires knowledge of this information. We acknowledge this restriction and suggest that in order to improve the structural characterization of biosynthesized nanoparticles, future research should use SEM or sophisticated imaging methods like Field Emission SEM (FESEM) or Transmission Electron Microscopy (TEM).

4. Conclusions

In this study, we tested AgNPs to verify the removal of harmful metals like cadmium, arsenic, lead, nickel, and zinc from groundwater. We found that how much metal was removed depended on how much of it was there in the beginning. Zinc had the highest removal rate at 93%, then cadmium at 90%, arsenic at 88.1%, lead at 78.2%, and nickel at 75.3%. These results show that AgNPs are good at taking out certain metals, especially cadmium and zinc. Since they are cheap to make, work well, and are not harmful to the environment, they could be a good option for cleaning water on a larger scale. This could be useful in places with fewer resources, like rural areas. Future studies should try to improve how they work in systems where water flows continuously and also figure out safe ways to throw them away after use.

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Conflict of Interest

The authors confirm that there are no known financial or personal conflicts of interest that could have influenced the findings or interpretations presented in this study.

Generative AI statement

The authors declare that no Gen AI was used in the creation of this manuscript.

References

[1] Ullah S, Shams DF, Ur Rehman SA, Khattak SA, Noman M, Rukh G, et al. Application of visible light activated thiolated cobalt doped ZnO nanoparticles towards arsenic removal from aqueous systems. Digest Journal of Nanomaterials & Biostructures (DJNB), 2022, 17(2). DOI: 10.15251/DJNB.2022.172.443

[2] Nawab J, Din ZU, Ahmad R, Khan S, Zafar MI, Faisal S, et al. Occurrence, distribution, and pollution indices of potentially toxic elements within the bed sediments of the riverine system in Pakistan. Environmental Science and Pollution Research, 2021, 28(39), 54986-55002. DOI: 10.1007/s11356-021-14783-9

[3] Megahed H, El Mahallawy N. A comprehensive model for enhancing productivity of a decentralized desalination unit. Journal of Cleaner Production, 2022, 368, 133105. DOI: 10.1016/j.jclepro.2022.133105

[4] Xie P, Zahoor F, Iqbal SS, Ullah S, Noman M, Din ZU, et al. Elimination of toxic heavy metals from industrial polluted water by using hydrophytes. Journal of Cleaner Production, 2022, 352, 131358. DOI: 10.1016/j.jclepro.2022.131358

[5] Hubeny J, Harnisz M, Korzeniewska E, Buta M, Zieliński W, Rolbiecki D, et al. Industrialization as a source of heavy metals and antibiotics which can enhance the antibiotic resistance in wastewater, sewage sludge and river water. PloS one, 2021, 16(6), e0252691. DOI: 10.1371/journal.pone.0252691

[6] Qadri R, Faiq MA. Freshwater pollution: effects on aquatic life and human health. In Fresh water pollution dynamics and remediation, Springer: Singapore, Singapore, 2020, pp. 15-26. DOI: 10.1007/978-981-13-8277-2_2

[7] Noman M, Haziq MA, Safi BU, Ullah S, Rukh G, Faiq ME, et al. Lead (II) adsorption from aqueous systems using visible light activated cobalt doped zinc oxide nanoparticles. Digest Journal of Nanomaterials & Biostructures (DJNB), 2022, 17(3). DOI: 10.15251/DJNB.2022.173.839

[8] Khan RA, Khan NA, El Morabet R, Alsubih M, Qadir A, Bokhari A, et al. Geospatial distribution and health risk assessment of groundwater contaminated within the industrial areas: an environmental sustainability perspective. Chemosphere, 2022, 303, 134749. DOI: 10.1016/j.chemosphere.2022.134749

[9] Scanlon BR, Fakhreddine S, Rateb A, de Graaf I, Famiglietti J, Gleeson T, et al. Global water resources and the role of groundwater in a resilient water future. Nature Reviews Earth & Environment, 2023, 4(2), 87-101. DOI: 10.1038/s43017-022-00378-6

[10] Ahoulé DG, Lalanne F, Mendret J, Brosillon S, Maïga AH. Arsenic in African waters: A review. Water, Air, & Soil Pollution, 2015, 226(9), 302. DOI: 10.1007/s11270-015-2558-4

[11] Hussain T, Akhter N, Nadeem R, Rashid U, Noreen S, Anjum S, et al. Biogenic synthesis of date stones biochar-based zirconium oxide nanocomposite for the removal of hexavalent chromium from aqueous solution. Applied Nanoscience, 2023, 13(9), 6053-6066. DOI: 10.1007/s13204-022-02599-z

[12] Ghani J, Nawab J, Faiq ME, Ullah S, Alam A, Ahmad I, et al. Multi-geostatistical analyses of the spatial distribution and source apportionment of potentially toxic elements in urban children's park soils in Pakistan: A risk assessment study. Environmental Pollution, 2022, 311, 119961. DOI: 10.1016/j.envpol.2022.119961

[13] Nawab J, Idress M, Ullah S, Rukh G, Zainab R, Sher H, et al. Occurrence and distribution of heavy metals in mining degraded soil and medicinal plants: A case study of Pb/Zn sulfide terrain Northern Areas, Pakistan. Bulletin of Environmental Contamination and Toxicology, 2023, 110(1), 24. DOI: 10.1007/s00128-022-03673-6

[14] Arroyo-Ortega G, Paz JF, Armendariz IO, Camacho-Montes H, León C, Reyes-Blas H, et al. Photocatalytical degradation of methyl orange (MO) using ZnO nanoparticles from alkaline wasted batteries. The effect of the MO, catalyst, and organic loads. Digest Journal of Nanomaterials & Biostructures (DJNB), 2022, 17(4). DOI: 10.15251/DJNB.2022.174.1241

[15] Mustapha S, Ndamitso MM, Abdulkareem AS, Tijani JO, Shuaib DT, Ajala AO, et al. Application of TiO2 and ZnO nanoparticles immobilized on clay in wastewater treatment: A review. Applied Water Science, 2020, 10(1), 49. DOI: 10.1007/s13201-019-1138-y

[16] Bednar AJ, Garbarino JR, Ferrer I, Rutherford DW, Wershaw RL, Ranville JF, et al. Photodegradation of roxarsone in poultry litter leachates. Science of The Total Environment, 2003, 302(1-3), 237-245. DOI: 10.1016/S0048-9697(02)00322-4

[17] Nico PS, Fendorf SE, Lowney YW, Holm SE, Ruby MV. Chemical structure of arsenic and chromium in CCA-treated wood: implications of environmental weathering. Environmental Science & Technology, 2004, 38(19), 5253-5260. DOI: 10.1021/es0351342

[18] Baidya K, Raj A, Mondal L, Bhaduri G, Todani A. Persistent conjunctivitis associated with drinking arsenic-contaminated water. Journal of Ocular Pharmacology & Therapeutics, 2006, 22(3), 208-211. DOI: 10.1089/jop.2006.22.208

[19] Arun KB, Madhavan A, Sindhu R, Emmanual S, Binod P, Pugazhendhi A, et al. Probiotics and gut microbiome− Prospects and challenges in remediating heavy metal toxicity. Journal of Hazardous Materials, 2021, 420, 126676. DOI: 10.1016/j.jhazmat.2021.126676

[20] Reddy KJ, McDonald KJ, King H. A novel arsenic removal process for water using cupric oxide nanoparticles. Journal of Colloid and Interface Science, 2013, 397, 96-102. DOI: 10.1016/j.jcis.2013.01.041

[21] Rahman MA, Hasegawa H. Aquatic arsenic: phytoremediation using floating macrophytes. Chemosphere, 2011, 83(5), 633-646. DOI: 10.1016/j.chemosphere.2011.02.045

[22] Abernathy CO, Thomas DJ, Calderon RL. Health effects and risk assessment of arsenic. The Journal of Nutrition, 2003, 133(5), 1536S-1538S. DOI: 10.1093/jn/133.5.1536S

[23] Saha JC, Dikshit AK, Bandyopadhyay M, Saha KC. A review of arsenic poisoning and its effects on human health. Critical Reviews in Environmental Science and Technology, 1999, 29(3), 281-313. DOI: 10.1080/10643389991259227

[24] Ng KS, Ujang Z, Le-Clech P. Arsenic removal technologies for drinking water treatment. Reviews in Environmental Science and Biotechnology, 2004, 3(1), 43-53. DOI: 10.1023/B:RESB.0000040054.28151.84

[25] Garelick H, Jones H, Dybowska A, Valsami-Jones E. Arsenic Pollution Sources. In Reviews of Environmental Contamination Volume 197. Reviews of Environmental Contamination and Toxicology; Springer: New York, USA, 2008; vol 197, 17-60. DOI: 10.1007/978-0-387-79284

[26] Ahn JS. Geochemical occurrences of arsenic and fluoride in bedrock groundwater: a case study in Geumsan County, Korea. Environmental Geochemistry and Health, 2012, 34(Suppl 1), 43-54. DOI: 10.1007/s10653-011-9411-5

[27] Yoshizuka K, Nishihama S, Sato H. Analytical survey of arsenic in geothermal waters from sites in Kyushu, Japan, and a method for removing arsenic using magnetite. Environmental Geochemistry and Health, 2010, 32(4), 297-302. DOI: 10.1007/s10653-010-9300-3

[28] Natasha, Shahid M, Imran M, Khalid S, Murtaza B, Niazi NK, et al. Arsenic environmental contamination status in South Asia. In Arsenic in drinking water and food, Springer: Singapore, Singapore, 2019; pp. 13-39. DOI: 10.1007/978-981-13-8587-2_2

[29] Hung DQ, Nekrassova O, Compton RG. Analytical methods for inorganic arsenic in water: A review. Talanta, 2004, 64(2), 269-277. DOI: 10.1016/j.talanta.2004.01.027

[30] Khosravi-Darani K, Rehman Y, Katsoyiannis IA, Kokkinos E, Zouboulis AI. Arsenic exposure via contaminated water and food sources. Water, 2022, 14(12), 1884. DOI: 10.3390/w14121884

[31] Yaqoob AA, Parveen T, Umar K, Mohamad Ibrahim MN. Role of nanomaterials in the treatment of wastewater: A review. Water, 2020, 12(2), 495. DOI: 10.3390/w12020495

[32] Vonnie JM, Rovina K, Mariah AM, Erna KH, Felicia WX, ‘Aqilah MN. Trends in nanotechnology techniques for detecting heavy metals in food and contaminated water: A review. International Journal of Environmental Science and Technology, 2023, 20(7), 8041-8072. DOI: 10.1007/s13762-022-04487-z

[33] Nasrollahzadeh M, Sajjadi M, Iravani S, Varma RS. Green-synthesized nanocatalysts and nanomaterials for water treatment: Current challenges and future perspectives. Journal of Hazardous Materials, 2021, 401, 123401. DOI: 10.1016/j.jhazmat.2020.123401

[34] Shukla S, Khan R, Daverey A. Synthesis and characterization of magnetic nanoparticles, and their applications in wastewater treatment: A review. Environmental Technology & Innovation, 2021, 24, 101924. DOI: 10.1016/j.eti.2021.101924

[35] Sarkar B, Sao S, Ghosh SK. Smart production and photocatalytic ultraviolet (PUV) wastewater treatment effect on a textile supply chain management. International Journal of Production Economics, 2025, 283, 109557. DOI: 10.1016/j.ijpe.2025.109557

[36] Mandal BK, Suzuki KT. Arsenic round the world: A review. Talanta, 2002, 58(1), 201-235. DOI: 10.1016/S0039-9140(02)00268-0

[37] Singh R, Ullah S, Rao N, Singh M, Patra I, Darko DA, et al. Synthesis of three-dimensional reduced-graphene oxide from graphene oxide. Journal of Nanomaterials, 2022(1), 8731429. DOI: 10.1155/2022/8731429

[38] Ullah S, Noman M, Ali KS, Siddique M, Sahak K, Hashmi SK, et al. Treatment of industrial wastewater (IWW) and reuse through advanced oxidation processes (AOPs): A comprehensive overview. IOSR Journal of Environmental Science Toxicology and Food Technology, 2021, 15(1), 4-14. DOI: 10.9790/2402-1501010414

[39] Qin Q, Zhou Q, He LL, Zhu XD, Feng W, Wang J. Influences of Sn/Cu single doping and CO-doping on the structure and photocatalytic property of anatase/rutile mixed crystal TiO 2 nanomaterials under UV-visible light. Digest Journal of Nanomaterials & Biostructures (DJNB), 2022, 17(1), 65. DOI: 10.15251/DJNB.2022.171.65

[40] Jain K, Patel AS, Pardhi VP, Flora SJ. Nanotechnology in wastewater management: a new paradigm towards wastewater treatment. Molecules, 2021, 26(6), 1797. DOI: 10.3390/molecules26061797

[41] Crini G, Lichtfouse E. Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters, 2019, 17(1), 145-155. DOI: 10.1007/s10311-018-0785-9

[42] Shaukat S, Hassani MA, Yadgari MY, Ullah S, Iqbal MS, Khan F, et al. Green synthesis of silver nanoparticles and its application towards As (V) removal from aqueous systems. Digest Journal of Nanomaterials & Biostructures (DJNB), 2022, 17(4). DOI: 10.15251/DJNB.2022.174.1385

[43] Guidelines for drinking-water quality (Vol. 1). World health organization. 2004. https://iris.who.int/bitstream/handle/10665/42852/9241546387.pdf (accessed on 23 June, 2025).

[44] Khin MM, Nair AS, Babu VJ, Murugan R, Ramakrishna S. A review on nanomaterials for environmental remediation. Energy & Environmental Science, 2012, 5(8), 8075-8109. DOI: 10.1039/C2EE21818F

[45] Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG, et al. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. Ecotoxicology and Environmental Safety, 2018, 148, 702-712. DOI: 10.1016/j.ecoenv.2017.11.034

[46] Abuzeid HM, Julien CM, Zhu L, Hashem AM. Green synthesis of nanoparticles and their energy storage, environmental, and biomedical applications. Crystals, 2023, 13(11), 1576. DOI: 10.3390/cryst13111576

[47] Abbas A, Al-Amer AM, Laoui T, Al-Marri MJ, Nasser MS, Khraisheh M, et al. Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. Separation and Purification Technology, 2016, 157, 141-161. DOI: 10.1016/j.seppur.2015.11.039

[48] Deng R, Huang D, Wan J, Xue W, Wen X, Liu X, et al. Recent advances of biochar materials for typical potentially toxic elements management in aquatic environments: A review. Journal of Cleaner Production, 2020, 255, 119523. DOI: 10.1016/j.jclepro.2019.119523

[49] Olivera S, Chaitra K, Venkatesh K, Muralidhara HB, Inamuddin, Asiri AM, et al. Cerium dioxide and composites for the removal of toxic metal ions. Environmental Chemistry Letters, 2018, 16(4), 1233-1246. DOI: 10.1007/s10311-018-0747-2

[50] Labulo AH, David OA, Terna AD. Green synthesis and characterization of silver nanoparticles using Morinda lucida leaf extract and evaluation of its antioxidant and antimicrobial activity. Chemical Papers, 2022, 76(12), 7313-7325. DOI: 10.1007/s11696-022-02392-w

[51] Stozhko N, Tarasov A, Tamoshenko V, Bukharinova M, Khamzina E, Kolotygina V. Green silver nanoparticles: Plant-extract-mediated synthesis, optical and electrochemical properties. Physchem, 2024, 4(4), 402-419. DOI: 10.3390/physchem4040028