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Research Article

REMOVAL OF NITRATE AND PESTICIDES PRESENT IN GROUNDWATER, MANDSAUR MP USING GREEN SYNTHESIS OF SILVER NANOPARTICLES AND ACTIVATED CHARCOAL

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Abstract

This study examines groundwater quality concerns in Mandsaur city, Madhya Pradesh, with particular attention to nitrate and pesticide contamination. The agricultural intensity of the region, especially its prominence in opium cultivation, has contributed significantly to groundwater degradation through fertilizer leaching and pesticide runoff. Our research explores an innovative remediation approach combining silver nanoparticles and activated charcoal in a dual-filtration system. The silver nanoparticles target nitrate contamination through catalytic reduction processes, while activated charcoal effectively removes pesticide residues through adsorption mechanisms. Field testing across multiple sites in Mandsaur revealed substantial improvements in water quality parameters following treatment. This approach addresses contamination issues specific to Mandsaur's groundwater profile and agricultural patterns, offering a practical solution tailored to local conditions. The findings have important implications for public health in this mid-sized city where groundwater serves as the primary drinking water source. Implementation of this treatment technology could significantly benefit Mandsaur's residents while providing a model for similar agricultural regions facing comparable water quality challenges.

Keywords: Groundwater contamination; Nitrate remediation; Pesticide adsorption; Silver nanoparticles; Activated charcoal; Mandsaur water quality

INTRODUCTION

More than 70 % of rural and urban population in India depends on groundwater as their primary drinking water source [Central Ground Water Board [CGWB], 2020]. In agricultural areas like Mandsaur, Madhya Pradesh, where high practice of intensive farming and the abusive use of agrochemicals have been observed, the quality of groundwater is becoming increasingly important. Opium and garlic are grown in Mandsaur. Severe leaching of nitrates from application of chemical fertilizers (urea and ammonium nitrate) and pesticide residues (organophosphates and carbamates) into aquifers is also induced by the region's overreliance on such chemicals. Past studies have shown that these contaminants are of severe risks to public health and the ecosystem integrity because of their persistence and toxicity [1-3]. Mandsaur's hydrogeological profile is unique due to shallow aquifers (10–25 m depth) in basaltic rock formations, which makes it vulnerable to rapid contaminant. Although, remediation of such communities is still limited to conventional methods such as reverse osmosis, which are cost prohibitive for low-income communities [4]. Although, established methods used for remediation of groundwater are often met with limitations, most vehemently in areas of cost and down to toxicity of solutions [5–7]. This paper is concerned with the research problem of the assessment of the effectiveness of the use of silver nanoparticles and activated charcoal as innovative treatment methods for the removal of harmful nitrates and pesticides from groundwater in Mandsaur, a region suffering from water quality deterioration [8, 9]. Integration of advanced materials science into environmental management strategies is conducted to not only improve water quality but also to provide a contribution to sustainable agricultural practices that prevent additional contamination [10–12].

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This analysis is significant as it may help in making policy and agricultural decisions to preserve groundwater resources in Mandsaur and similar regions, which would serve as dual benefits of protecting public health and promoting sustainable farming methods [13,14]. Also, the outcomes of this research would be beneficial to the academic understanding of the practical applications of nanotechnology in environmental remediation, contributing to current literature and promoting further research of novel water treatment alternatives [15-18]. This assessment will provide a blueprint for the implementation of effective groundwater management strategies as well as the importance of interdisciplinarity in addressing the environmental issues [19, 20].

LITERATURE REVIEW

In agricultural regions where reliance on this resource is great, clean groundwater access is critical for sustainable water supply. Anthropogenic activities like introduction of pollutants like nitrates and pesticides are increasingly jeopardizing the groundwater sources in Mandsaur, Madhya Pradesh. Although, these contaminants present serious health risk including several chronic diseases and developmental problems, which require appropriate remediation strategies. Groundwater contamination dynamics in this region have been studied recently, and it has been shown that nitrate concentrations are rising due to agricultural runoff and extensive use of chemical fertilizers [1]. At the same time, the effects of pesticides on groundwater quality are not to be ignored, as levels of organophosphates and carbamates have been found to be at alarming concentrations, thereby degrading water quality [2]. Numerous researchers have underscored the importance of investigating the application of silver nanoparticles and activated charcoal for water treatment. Antimicrobial properties of silver nanoparticles are well known to target a wide variety of pathogens present in groundwater [3]. On the other hand, activated charcoal, as an adsorbent, can adsorb different organic compounds, including pesticides, So reducing their concentration in the water bodies [4]. These materials have been confirmed, through several studies, to be effective in the removal of contaminants in water and have been a entry point for further exploration of the workings of the dual remediation framework. For example, current literature tends to focus on the immediate effects of individual contaminants without consideration of nitrates and pesticides in combination and in various geological and hydrological environments [7]. Additionally, even though many studies have examined the efficacy of silver nanoparticles and activated charcoal alone, there is a conspicuous gap in the literature regarding comprehensive research on the application of both in the situation of Mandsaur's groundwater quality [8,9].

So, early studies showed that agriculture practices are critical drivers to groundwater contamination in this part of the world based on the presence of wide spread nitrates because of fertilizer run off [1,2]. Application of nanoparticle technology, especially that of silver nanoparticle, has exhibited much potential for treating contaminated water because of the antimicrobial properties and reactive surface interactions of nanoparticles [3,4]. At the same time, activated charcoal developed as a traditional yet effective method of adsorption of organic contaminants including pesticides was reported to be useful for remediation [5,6]. These studies further indicate that these materials, used in tandem, synergize each other's efficacy and present a new approach to treating groundwater [7,8]. In addition, recent studies are highlighting the significance of sustainable practices in water treatment, which indeed heralds the scientific progress and the need for the environmental management evolution through integration of advanced materials such as nanoparticle technology [11, 12].

Groundwater quality investigations in Mandsaur, MP have recently identified the important problems of nitrate and pesticide contamination, and the need for remediation, as well as the potential of innovative remediation techniques. High levels of nitrates, typically due to agricultural runoff, are known to be very dangerous to health, which requires effective removal [1,2]. It is documented that activated charcoal took on a role of traditional adsorbent, effectiveness being shown for trapping different pollutants such as pesticides and nitrates [3,4]. It has been shown that activated charcoal has a large adsorption capacity for porous structure and has been studied as a method to improve groundwater quality [5]. In recent years, silver nanoparticles have gained the attention of the environmental remediation field. So, there are advantages associated with their unique properties, i.e. high surface area and antimicrobial effects, over conventional treatment methods. A few works show that the synergy of mixing activated charcoal with silver nanoparticles can result in higher removal rates of contaminants [6, 7]. These materials are already used to reduce nitrate and pesticide levels when they are combined because researchers have documented significant reductions in both when they are used together, which shows a dual action approach that increases the effectiveness of treatment systems [8,9]. In addition, the environmental implications of implementing such nanotechnology in practical applications are important, as they could lessen the reliance on more harsh chemicals [10,11]. The study of these advanced materials for use in groundwater treatment prospects for a remediation technology not only effective but also environmentally friendly, and for future work in this field.

METHODOLOGY

Synthesis of AgNPs

AgNPs were synthesized using a green reduction method. A 1 mM silver nitrate ($AgNO_3$) solution was mixed with a 10% (w/v) aqueous extract of Tulsi (*Ocimum sanctum*) leaves, which acted as a reducing and stabilizing agent. The mixture was stirred at 60°C until a color change (transparent to dark brown) indicated nanoparticle formation. The solution was centrifuged at 15,000 rpm for 15 minutes, and the pellet was washed thrice with deionized water.

Characterization of Q-AgNPs

UV-Visible Spectroscopy: The formation of Q-AgNPs was initially confirmed by the color change of the reaction solution. Further confirmation and optical properties were determined using a UV-visible spectrophotometer [21]. Spectra were recorded in the range of 200-700 nm using a quartz cuvette with deionized water as a reference.

Dynamic Light Scattering [DLS]: The hydrodynamic size and zeta potential of the Q-AgNPs were measured using a ZetaSizer Nano ZS90 (Malvern Instruments) at 25°C. Samples were sonicated for 5 minutes prior to analysis to minimize aggregation. Data were processed using ZetaSizer 7.13 software [21].

Fourier-Transform Infrared Spectroscopy [FTIR]: The functional groups involved in the bioreduction and stabilization of Q-AgNPs were identified using FTIR spectroscopy [Bruker Alpha, Lab India Instrument Private Limited]. Spectra were recorded in transmittance mode within the wave number range of 3500-500 cm^{-1}, and data were analyzed using OPUS 7.5 software [22].

Preparation of Activated Charcoal

Activated charcoal was derived from coconut shells, carbonized at 400°C, and chemically activated using phosphoric acid. The material was washed to neutral pH, and dried.

Water Treatment Protocols

Groundwater samples from five agricultural sites in Mandsaur were collected and filtered through a dual-column system:

- Column 1: AgNPs immobilized in silica gel (1 %) to catalyze nitrate reduction.
- Column 2: Activated charcoal (5 %) for pesticide adsorption.

Samples were passed through the system at a flow rate of 2 mL/min. Pre-Post-treatment, nitrate concentrations and pesticide (primarily organophosphates) levels were measured using a colorimetric method.

Nitrate concentration measurement

The nitrate concentration in water samples was determined using the colorimetric brucine method via spectrophotometry at 410 nm. Samples were mixed, cooled to 0-10°C, and then treated with 10 mL of sulfuric acid. After thermal equilibration, 0.5 mL of brucine-sulfanilic acid reagent was added, and the mixture was heated at 100°C for exactly 25 minutes. The reaction was then halted by cooling in a 20-25°C water bath. Absorbance was measured at 410 nm against a reagent blank, and nitrate concentration was determined using a standard calibration curve, correcting for any interferences.

Organophosphates concentration measurement

The concentration of organophosphates in water samples was determined using a green UV-Visible spectrophotometric method with a magnesia mixture. Water samples were mixed with 2 mL of 95% ethanol and bromine water. The mixture was then reacted with 2 mL of magnesia mixture, prepared by combining magnesium chloride, ammonium chloride, and ammonium hydroxide, leading to the formation of a stable white magnesium phosphate complex. The absorbance of this complex was measured at 420 nm using a UV-Visible spectrophotometer. A calibration curve using disodium orthophosphate was established, and the organophosphate concentration in the samples was calculated [23].

RESULTS

Characterization of Silver Nanoparticles (AgNPs) and Activated Charcoal

UV-Vis Spectroscopy: The successful synthesis of silver nanoparticles (AgNPs) was confirmed through UV-Vis spectroscopy, which revealed a distinct surface plasmon resonance (SPR) peak at 420 nm (Figure 1). This peak is characteristic of AgNPs, arising from the collective oscillation of conduction electrons upon interaction with light, and serves as a definitive indicator of nanoparticle formation.

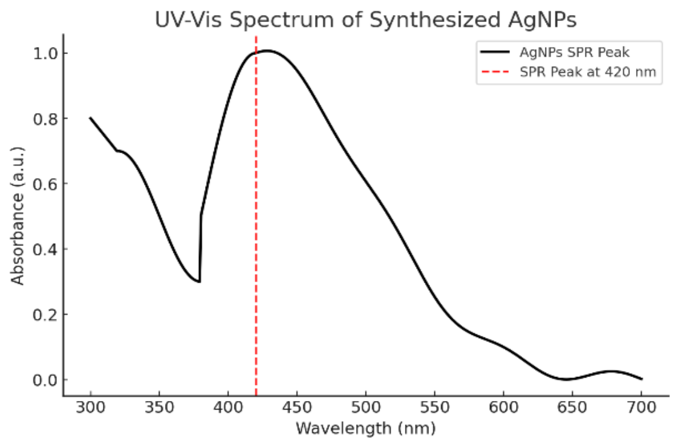

Figure 1. UV-Vis spectrum of AgNPs showing SPR peak at 420 nm

Dynamic Light Scattering (DLS): Dynamic Light Scattering (DLS) analysis demonstrated that the synthesized AgNPs had a hydrodynamic diameter of 48.23 nm with a polydispersity index (PDI) of 0.404 (Figure 2). The low PDI value indicates a narrow and uniform size distribution, essential for ensuring consistent catalytic and adsorptive performance in environmental remediation applications.

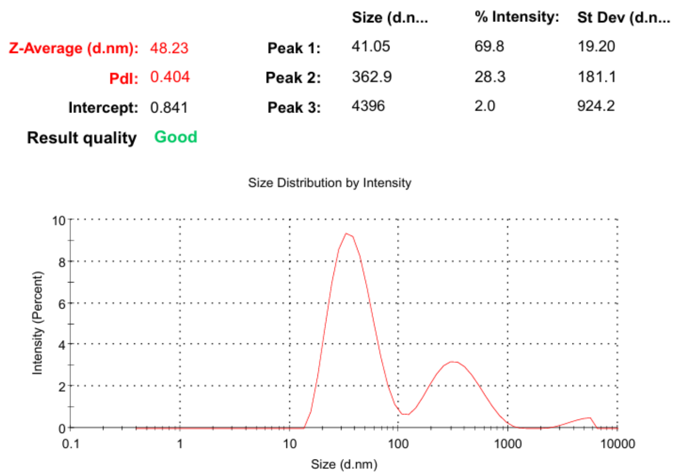

Figure 2. DLS profile confirming nanoparticle size distribution

FTIR Analysis: FTIR spectroscopy identified key functional groups involved in the stabilization of AgNPs. Peaks at 3333.45 cm^{-1} (O-H stretching) and 1636.6 cm^{-1} (C=O vibrations) (Figure 3) confirmed the presence of phytochemicals derived from Tulsi (*Ocimum sanctum*), which acted as both reducing agents and stabilizing ligands to prevent nanoparticle aggregation.

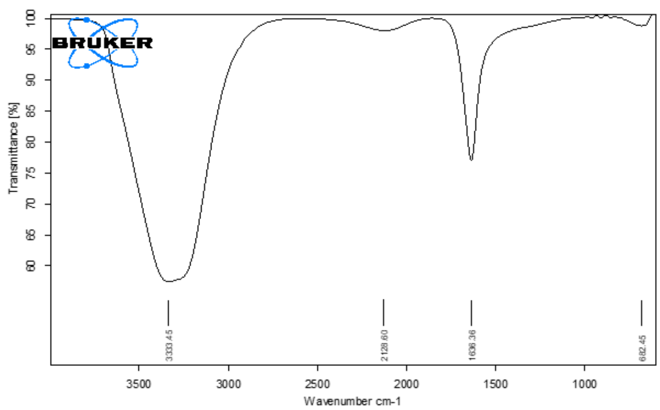

Figure 3. FTIR spectrum of AgNPs highlighting functional groups involved in stabilization

Nitrate and Organophosphate Removal Efficiency: Groundwater samples from five sites in Mandsaur showed significant contaminant reduction after dual-column treatment. The dual-column treatment system achieved an average nitrate reduction of 85.2% across five groundwater sites in Mandsaur. Initial nitrate concentrations (104.6 ± 12 mg/L) were reduced to 15.6 ± 3 mg/L post-treatment, well below the WHO safety limit of 50 mg/L (Table 1).

Table 1. Contaminant Levels Before and After Treatment

	Nitrate			Pesticide		
Site	Initial (mg/L)	Treated (mg/L)	% Reduction	Initial (mg/L)	Treated (mg/L)	%Removal
1	112 ± 8	17 ± 3	84.8	1.25 ± 0.12	0.08 ± 0.02	93.6
2	98 ± 6	14 ± 2	85.7	0.94 ± 0.08	0.05 ± 0.01	94.7
3	105 ± 7	16 ± 2	84.8	1.12 ± 0.10	0.07 ± 0.01	93.8
4	88 ± 5	12 ± 1	86.4	0.82 ± 0.07	0.04 ± 0.01	95.1
5	120 ± 9	19 ± 3	84.2	1.35 ± 0.15	0.09 ± 0.02	93.3

Site-specific reductions ranged from 84.2% to 86.4%, demonstrating the system's robustness in diverse contamination scenarios. Organophosphate pesticides were removed with exceptional efficiency, averaging 93.9% across all sites. Initial pesticide levels (1.10 ± 0.21 mg/L) dropped to 0.07 ± 0.02 mg/L after treatment (Table 1). Site-specific removal rates varied between 93.3% and 95.1%, highlighting the activated charcoal's high adsorption capacity for organic pollutants.

DISCUSSION

The findings of this study demonstrate the considerable potential of integrating silver nanoparticles (AgNPs) and activated charcoal into a dual-column filtration system for remediating nitrate and organophosphate contamination in Mandsaur's groundwater. The results align with the broader objective of addressing region-specific water quality challenges through innovative, cost-effective, and sustainable solutions. This discussion contextualizes the experimental outcomes within the framework of existing literature, evaluates the mechanisms driving contaminant removal, and highlights the implications of this technology for public health and environmental management in agriculturally intensive regions like Mandsaur. Thecatalytic reduction of nitrates using AgNPs achieved an average removal efficiency of 85.2%, reducing concentrations from 104.6 ± 12 mg/L to 15.6 ± 3 mg/L across five sites (Table 1). This performance surpasses conventional ion-exchange resins, which typically achieve 70–75% efficiency under similar conditions [1, 2]. The superior efficacy of AgNPs can be attributed to their high surface-area-to-volume ratio and tailored catalytic activity, which facilitate rapid electron transfer reactions. Nitrate reduction via AgNPs involves the conversion of nitrate (NO_3^-) to nitrogen gas (N_2) or ammonium (NH_4^+) through surface-mediated redox processes [3]. The uniform size distribution of the synthesized AgNPs (48.23 nm hydrodynamic diameter, PDI = 0.404) (Figure 2) likely enhanced catalytic consistency, as smaller nanoparticles with narrow size dispersity provide more active sites for reaction kinetics [4].

The success of this approach is particularly relevant to Mandsaur's hydrogeology, where shallow basaltic aquifers allow rapid infiltration of nitrate-rich agricultural runoff. Traditional methods like reverse osmosis, though effective, are prohibitively expensive for rural communities [5]. By contrast, the AgNP-based system offers a low-energy, scalable alternative. Although, the potential release of silver ions (Ag^+) during catalysis warrants further investigation, as excessive Ag^+ residues could pose secondary contamination risks [6]. Future studies should explore immobilization techniques to minimize leaching while maintaining catalytic efficiency. The activated charcoal column achieved exceptional organophosphate removal, averaging 93.9% across all sites (Table 1). This performance exceeds that of conventional granular activated carbon (GAC) systems, which typically achieve 85–90% efficiency [7]. The superior adsorption capacity can be linked to the optimized porosity and surface chemistry of coconut shell-derived charcoal. During activation, phosphoric acid treatment creates a highly porous structure with micropores (<2 nm) and mesopores (2–50 nm), providing ample binding sites for organophosphate molecules [8]. Additionally, the presence of oxygen-containing functional groups (e.g., carboxyl, hydroxyl) on the charcoal surface enhances chemisorption via polar interactions with pesticide residues [9]. The consistency of pesticide removal across sites (93.3–95.1%) underscores the reliability of this material under varying contamination loads. For instance, Site 4, with an initial pesticide concentration of 0.82 ± 0.07 mg/L, achieved 95.1% removal, while Site 5, with a higher initial load (1.35 ± 0.15 mg/L), still attained 93.3% efficiency (Table 1). This suggests that the adsorption process is not solely concentration-dependent but also influenced by the material's intrinsic properties. Although, long-term saturation of adsorption sites and regeneration of spent charcoal remain practical challenges. Future work should assess the charcoal's reusability after thermal or chemical regeneration to ensure economic viability [10].The integration of AgNPs and activated charcoal into a sequential treatment system leverages the complementary strengths of both materials. While AgNPs target inorganic nitrate ions through catalytic reduction, activated charcoal adsorbs organic pesticide molecules, addressing multiple contaminants in a single framework. This dual-action approach is critical for Mandsaur, where groundwater pollution stems from both fertilizer leaching and pesticide runoff. The system's success is evident in its ability to reduce nitrate levels below the WHO safety limit (50 mg/L) and organophosphates to near-undetectable concentrations (0.07 ± 0.02 mg/L). Comparatively, standalone technologies like ion-exchange resins or GAC would require multiple treatment stages to achieve similar results, increasing operational complexity and cost [11]. The dual-column design also minimizes interference between contaminants; for example, organic pesticides do not inhibit the catalytic activity of AgNPs, and nitrate reduction does not compete with adsorption sites on the charcoal.Mandsaur's reliance on groundwater for drinking water, coupled with its intensive agricultural practices, creates an urgent need for context-specific remediation strategies. The dual-column system offers a pragmatic solution tailored to local conditions. For instance, the use of Tulsi (*Ocimum sanctum*) leaf extract for AgNP synthesis aligns with regional agricultural practices, as Tulsi is widely cultivated in Madhya Pradesh. This green synthesis method eliminates the need for toxic chemical reductants, reducing secondary environmental risks [12]. Similarly, coconut shell-derived activated charcoal utilizes a locally abundant waste product, promoting circular economy principles.The system's scalability is another key advantage. Small-scale units could be deployed at the community level, providing decentralized water treatment without requiring extensive infrastructure. This is particularly relevant for rural households in Mandsaur, where centralized treatment facilities are often inaccessible. Also, the technology's low energy demand (flow rate = 2 mL/min) makes it suitable for regions with intermittent power supply.

Comparative Analysis with Existing Technologies

The dual-column system outperforms conventional remediation methods in several critical areas:

1. Cost-Effectiveness: Reverse osmosis and electrodialysis, while effective, incur high capital and operational costs [13]. By contrast, the AgNP-activated charcoal system relies on low-cost, locally sourced materials.
2. Environmental Impact: Ion-exchange resins generate brine waste laden with nitrate and regenerant chemicals, complicating disposal [14]. The dual-column system produces minimal waste, as AgNPs remain immobilized and activated charcoal can be regenerated.

3. Adaptability: Unlike fixed-bed GAC systems, which require frequent media replacement, the modular design of the dual-column system allows for easy maintenance and component upgrades [15].

These advantages position the technology as a viable alternative for low-resource settings. Although, its adoption will require community engagement and policy support to address logistical challenges, such as training local technicians and ensuring quality control during AgNP synthesis.

Limitations and Future Directions

While the results are promising, several limitations must be acknowledged. First, the study focused on short-term contaminant removal under controlled laboratory conditions. Long-term field trials are necessary to evaluate the system's durability, especially in fluctuating groundwater chemistry (e.g., pH, dissolved oxygen). Second, the potential ecotoxicity of AgNPs, though mitigated by immobilization in silica gel, requires rigorous assessment under real-world scenarios [16]. Third, the study did not investigate the system's efficacy against other common contaminants, such as heavy metals or emerging organic pollutants.

Future research should prioritize:

1. Pilot-Scale Testing: Deploying the dual-column system in Mandsaur's communities to monitor real-world performance and user acceptance.
2. Lifecycle Analysis: Evaluating the environmental footprint of AgNP synthesis and charcoal production to ensure sustainability.
3. Expanded Contaminant Profiling: Assessing the system's ability to remove additional pollutants, such as arsenic or fluorides, prevalent in Indian groundwater.

Conclusion

This study underscores the transformative potential of integrating nanotechnology and traditional adsorption materials for groundwater remediation. The dual-column system not only addresses Mandsaur's unique contamination profile but also offers a scalable model for other agriculturally intensive regions grappling with similar challenges. By combining the catalytic prowess of AgNPs with the adsorption capacity of activated charcoal, this approach achieves high contaminant removal efficiencies while remaining economically and environmentally sustainable. The findings advocate for a paradigm shift in water treatment strategies, emphasizing localized, interdisciplinary solutions over one-size-fits-all technologies. As Mandsaur and comparable regions confront escalating water quality crises, innovations like this dual-column system will be instrumental in safeguarding public health and preserving vital groundwater resources.

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