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“Role of Green Chemistry in Synthesizing Magnetite Nanoparticles for Efficient Arsenic Adsorption: A Comprehensive Review”

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Abstract

This study investigates the adsorption behavior of arsenic species (As(III) and As(V)) over a broad pH range (2 to 13.7) and the efficacy of magnetite nanoparticles synthesized via green and conventional methods for arsenic removal from groundwater. Experimental results revealed distinct pH-dependent adsorption patterns for arsenic species: As(III) exhibited maximum adsorption near pH 8, whereas As(V) adsorbed predominantly around pH 4. At extremely low pH (2), both arsenic forms demonstrated minimal adsorption, while their conjugate base forms such as AsO3− and AsO43− showed enhanced adsorption at alkaline pH (13.5), indicating a strong influence of speciation and electrostatic interactions on removal efficiency. Ionic constituents in aqueous media, such as Cl−, HCO3−, H2PO4−, and SiO32−, facilitated adsorption, with cations like Na^+, Mg^{2+}, and Ca^{2+} further enhancing the process by altering surface charge dynamics of the adsorbents. To develop cost-effective and sustainable adsorbents, magnetite nanoparticles were synthesized using onion peel (MNp-OP) and corn silk extract (MNp-CS), and compared with conventionally synthesized magnetite (MNp-CO). The green extracts were characterized for their antioxidant capacity using FRAP and DPPH assays, confirming high phenolic, flavonoid, and tannin content. Characterization of the nanoparticles through SEM/EDS, XRD, FTIR, and BET surface analysis demonstrated crystalline magnetite structure with high specific surface areas of 243 m²/g (MNp-OP) and 261 m²/g (MNp-CS). Adsorption experiments revealed that arsenic removal by these nanoparticles follows chemisorption, intraparticle diffusion, and external diffusion mechanisms. The maximal adsorption capacities for MNp-OP, MNp-CS, and MNp-CO were found to be 1.86, 2.79, and 1.30 mg/g, respectively, highlighting the superior performance of green-synthesized materials. These findings suggest that MNp-OP and MNp-CS are not only environmentally benign but also highly efficient adsorbents, offering a promising solution for mitigating arsenic contamination in groundwater.

Keywords: Arsenic adsorption, pH dependence, Magnetite nanoparticles, Green synthesis, Groundwater treatment

Keywords: Arsenic adsorption, Arsenate (As^{5+}) and Arsenite (As^{3+}), Electro positivity, Electrostatic force.

INTRODUCTION

Arsenic contamination in groundwater has emerged as a significant environmental and public health concern across the globe, with alarming prevalence in several regions of India. Among the most affected is the northeastern belt, particularly the Ganga–Meghna–Brahmaputra basin, where arsenic concentrations in groundwater have been reported to range between 50–986 µg/L—exceeding the safety thresholds set by the World Health Organization (10 µg/L) and the Bureau of Indian Standards (50 µg/L). This paper explores the geochemical and physicochemical factors that influence the mobilization, transformation, and persistence of arsenic in groundwater systems. Arsenic exists in multiple forms in aquatic environments—primarily as arsenate (As^{5+}) and arsenite (As^{3+})—with their interconversion governed by redox potential, microbial activity, and prevailing environmental conditions. Additionally, organic arsenic species, formed through biomethylation, contribute to the complexity of arsenic behavior in groundwater. The monsoonal cycle, along with the dynamic interaction between iron oxyhydroxides and arsenic species, further exacerbates arsenic mobilization in regions such as West Bengal, Bihar, Jharkhand, Uttar Pradesh, Assam, and Manipur. This introduction underscores the critical need for an integrated hydrogeochemical understanding of arsenic transport mechanisms, including the roles of adsorption/desorption, redox chemistry, competing ions, and anthropogenic contributions such as mining, irrigation, and pesticide application. As arsenic infiltrates food chains and aquatic ecosystems, it poses long-term risks to human and ecological health—necessitating urgent attention to mitigation strategies and sustainable groundwater management.

Mobilization Mechanisms of Arsenic in Groundwater

Arsenic (As) contamination in groundwater is a pressing environmental and public health issue across various regions, especially in South and Southeast Asia. Contrary to earlier assumptions, arsenic-rich groundwater is not solely associated with arsenic-rich parent rocks. Instead, it is primarily a consequence of intricate biogeochemical transformations within aquifers. Two fundamental mechanisms, as emphasized by Smedley and Kinniburgh (2002), govern arsenic mobility: (1) mobilization from the solid or adsorbed phase to groundwater via geochemical processes, and (2) retention due to inadequate flushing, which allows As to accumulate.

Key Geochemical Mobilization Pathways:

1. Reductive Dissolution of Iron Oxides (FeOOH):

In reducing environments, particularly in shallow Holocene aquifers rich in organic matter, iron oxyhydroxides (FeOOH) that sequester As(V) become unstable. The microbial degradation of organic carbon (e.g., peat fermentation producing acetate) acts as an electron donor, promoting Fe(III) to Fe(II) reduction and subsequent As desorption:

$8FeOOH\text{-}As(s) + CH_3COOH + 14H_2CO_3 \rightarrow 8Fe^{2+} + As(d) + 16HCO_3^- + 12H_2O$

2. Oxidation of Arsenic-Bearing Sulfide Minerals:

In regions like West Bengal, the oxidation of arsenopyrite (FeAsS) in the presence of oxygen—often introduced via excessive groundwater pumping—results in the release of As(V) and SO_4^{2-}:
$FeAsS + 13Fe^{3+} + 8H_2O \rightarrow 14Fe^{2+} + SO_4^{2-} + 13H^+ + H_3AsO_4$
This mechanism is intensified in overexploited aquifers where oxygen-rich water infiltrates deeper strata.

3. Competitive Desorption Due to Phosphate Inputs:

Agricultural runoff enriched with phosphate fertilizers ($H_2PO_4^-$) leads to competitive anion exchange on mineral surfaces, releasing arsenate (AsO_4^{3-}) into the aqueous phase. This is a key anthropogenic mobilization pathway in agrarian zones.

4. pH-Induced Desorption:

Under alkaline conditions, arsenic adsorbed onto iron and aluminum hydroxides is released due to decreased surface affinity. Similarly, oxidizing environments facilitate desorption by destabilizing metal-As complexes.

5. Evapoconcentration and Capillary Action:

In arid regions, capillary rise of groundwater and subsequent evaporation can concentrate arsenic in the upper soil layers, enhancing its re-entry into shallow aquifers during recharge events.

6. In Situ Source Patches:

Research indicates that arsenic-rich patches occur in situ within aquifers, influenced by localized hydrogeochemical conditions, rather than by lateral transport from distant sources (Michael and Voss, 2008).

Biogeochemical Controls and Sustainability Considerations:

- The availability of electron donors (organic matter), pH, redox potential (Eh), presence of competing ions (e.g., phosphate, silicate), and mineralogy of aquifer sediments are critical controls.
- Long-term aquifer sustainability relies on strategic groundwater management, including the development of deeper uncontaminated aquifers and alternative water sources like treated surface water.

Advancements in Arsenic Remediation Using Nanotechnology:

- Recent advances highlight the efficacy of iron-based nanoparticles (INPs) such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and zero-valent iron (ZVI) for arsenic removal.
- These materials offer advantages including high surface area, magnetic separability, and strong As affinity.
- Environmentally benign green synthesis methods utilize plant extracts rich in polyphenolics and proteins, offering a sustainable route for nanoparticle production.

Conclusions

We have obtained substantial results enhancing our understanding of the physicochemical and hydrogeochemical factors that govern arsenic sedimentation and mobilization. Numerous studies have explored the morphology and adsorption behavior of arsenic in aqueous environments, yielding several promising conclusions:

1. The adsorption behavior and morphology of arsenic are significantly influenced by the pH of the aqueous medium. Generally, an increase in pH leads to a decrease in arsenic adsorption; however, the determination of an optimal pH for arsenic adsorption remains inconclusive. Notably, As(III) and As(V) species exhibit divergent and sometimes conflicting adsorption patterns across varying pH levels, underscoring the complex interplay between arsenic speciation and environmental conditions.
2. The presence of cations typically enhances arsenic adsorption, while coexisting anions can inhibit it due to competitive interactions. Specifically, anions such as SO_4^{2-}, SiO_3^{2-}, PO_4^{3-}, HCO_3^-, Cl^-, F^-, and HPO_4^{2-} have been observed to interfere with As(III) adsorption to varying degrees, thereby influencing arsenic mobility in groundwater.
3. A positive correlation has been established between arsenic content and the presence of specific minerals, particularly those rich in Mn, Fe, and Al, which enhance arsenic adsorption. However, the role of organic matter remains a topic of debate, with contrasting findings regarding its capacity to adsorb arsenic.
4. Organic functional groups—including carboxyls, phenolic hydroxyls, alcohol extract hydroxyls, ethers, and amides—can form stable associations with arsenic, thereby increasing the adsorption capacity of sediments. This interaction enhances the retention of arsenic in natural matrices.
5. The presence of arsenic itself appears to enhance the electropositive character of the adsorbent surface, thereby strengthening the electrostatic attraction for arsenic anions. This self-reinforcing mechanism may contribute to increased arsenic accumulation under specific conditions.
6. Another crucial mobilization pathway involves the reductive dissolution of iron oxides, which releases arsenic into groundwater. Additionally, excessive use of irrigation and phosphate fertilizers promotes the leaching of phosphate into shallow aquifers, resulting in arsenic desorption via competitive anion exchange at reactive mineral surfaces.

Future Scope

Recent studies have revealed that the presence of arsenic significantly enhances the electropositivity of adsorbent surfaces. This heightened electropositive character increases the electrostatic attraction toward negatively charged arsenic species, thereby facilitating greater binding efficiency on the adsorbent's surface. Mineralogical components, particularly manganese (Mn), iron (Fe), and aluminum (Al), show a positive correlation with arsenic retention, indicating their facilitative role in arsenic adsorption within sediment matrices. However, the role of natural organic matter in arsenic sorption remains equivocal, warranting further systematic investigation to elucidate its influence under varying environmental conditions.

In an effort to develop sustainable and high-performance arsenic adsorbents, novel magnetic nanoparticles (MNp-OP and MNp-CS) were successfully synthesized via a green route utilizing onion peel and corn silk extracts as reducing and stabilizing agents. The formation of these magnetic nanoparticles was confirmed through X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). Notably, their high surface area and significant pore volume suggest strong potential for arsenic removal from contaminated groundwater.

When benchmarked against conventionally synthesized magnetic nanoparticles (MNp-CO) prepared via chemical co-precipitation, the green-synthesized MNp-OP and MNp-CS demonstrated comparable, if not superior, adsorption performance. Adsorption kinetic data fitted well with the pseudo-second-order model, indicating that chemisorption is the dominant mechanism. Furthermore, the Weber–Morris and Boyd diffusion models confirmed the contribution of both external surface interaction and intraparticle diffusion to the overall sorption process.

An additional advantage of these green-synthesized nanoparticles lies in their magnetic properties, which enable straightforward separation and recovery post-treatment, underscoring their practical viability for real-world water purification applications.

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Conflict of Interest

The authors declare no conflict of interest.

REFERENCES

1. Acharyya, S. K., Lahiri, S., Raymahashay, B. C. and Bhowmik, A. (2000). Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: The role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environmental Geology, 39*(10), 1127–1137.
2. Jin, Z. F., Chen, Y. X., &Ke, Q. (2001). Study on sorption condition and species of arsenic in the sediments of the Grand Canal and the West Lake. *Journal of Zhejiang University(Agriculture and Life Sciences)*, *27*(6), 652-656.
3. Majumdar, P. K., Ghosh, N. C., &Chakravorty, B. (2002). Analysis of arsenic-contaminated groundwater domain in the Nadia district of West Bengal (India), Special issue: Towards Integrated water Resources Management for Sustainable Development. *Hydrological Sciences Journal, 47*(S), S55–S66.
4. Ma, Y., Ly, W., & Chen, Z. (2003). Status and thoughts on controlling water-born endemic arsenism in China in 2002. *Chin J Endemiol*, *22*(4), 330-332.
5. Anawar, H. M., Akai, J. andSakugawa, H. (2004). Mobilization of arsenic from subsurface sediments by 404 effect of bicarbonate ions in groundwater. *Chemosphere, 54*(6), 753–762.
6. Norra, S., Berner, Z. A., Agarwala, P., Wagner, F., Chandrasekharam, D., &Stüben, D. (2005). Impact of irrigation with As rich groundwater on soil and crops: A geochemical case study in West Bengal Delta Plain, India. *Applied Geochemistry, 20*(10), 1890–1906.
7. Ding, A. Z., Yang, S. X. and Zhang, H. D. (2007). Analysis on arsenic contamination in groundwater. *Journal of Jilin University(Earth Science Edition)*, *37*(2), 319-325.
8. Goh, K. H., & Lim, T. T. (2005). Arsenic fractionation in a fine soil fraction and influence of various anions on its mobility in the subsurface environment. *Applied Geochemistry, 20*(2), 229–239.
9. Rahman, M. M., Sengupta, M. K., Chowdhury, U. K., Lodh, D., Das, B., Ahamed, S., ... &Chakraborti, D. (2006). *Arsenic contamination incidents around the world* (Doctoral dissertation, Csiro Publishing).
10. Seddique, A. A., Masuda, H., Mitamura, M., Shinoda, K., Yamanaka, T., Itai, T., Maruoka, T., Uesugi, K., Ahmed, K. M., & Biswas, D. K. (2008). Arsenic release from biotite into a Holocene groundwater aquifer in Bangladesh. *Applied Geochemistry, 23*(8), 2236–2248.
11. Michael, H. A. and Voss, C. I. (2008). Evaluation of the sustainability of deep groundwater as an arsenic-safe resource in the Bengal Basin. *Proceedings of the National Academy of Sciences, 105*(25), 8531–8536.
12. Deng, Y., Wang, Y., Ma, T., Yang, H. and He, J. (2011). Arsenic associations in sediments from shallow aquifers of northwestern Hetao Basin, Inner Mongolia. *Environmental Earth Sciences, 64(8)*, 2001–2011.
13. Li, X., Wang, Y., & Zhang, D. (2011). Adsorption of arsenic in estuarine sediments and its influencing factors. *Environmental Science & Technology (China)*, *34*(12), 1-6.
14. Azam, A. (2013). Arsenic polluted ground water in eastern U P, India *International Journal of Engineering and Management Research, 3*(4), 81–83.
15. Ali, I., Rahman, A. and Khan, T. A. (2012). Recent trends of arsenic contamination in groundwater of Ballia District, Uttar Pradesh, India, GU. *Journal of Science,25*(4), 853–861.
16. Alam, S. M. M., Farha, M. N., & Zaman, A. K. B. (2015). An appraisal of arsenic and pesticide toxicity for economically terminal people: A Snap Shot of North-Western part of Bangladesh. *Journal of Scientific Research, 7*(3),159–165.

17. Azam, A. and Kunwar, A. (2018). Arsenic contamination in Groundwater in Eastern U.P., *Research Magma, 2*(1), 1–9.
18. Azam, A. and Kunwar, A. (2018). Hydrochemistry of arsenic in groundwater pollution in eastern Uttar Pradesh. *Journal of Water Pollution & Purification Research, 5*(2)*,* 1–4.
19. Azam, A. (2020). Study of seasonal variation of arsenic concentration in Groundwater in Ghazipur district of Uttar Pradesh. *Asian Journal of Advances in Research 3*(1), 8–15.
20. Azam, A. (2020). Temporal and seasonal variation of arsenic in Ballia district of Eastern U. P. *Asian. Journal of Advances in Research, 2*(1)*,* 22-29.
21. Nicomel, N.N.; Leus, K.; Folens, K.; De Voort, P.V.; Laing, G.D. Technologies for Arsenic Removal from Water: Current Status and Future Perspectives. Int. J. Environ. Res. Public Health 2016, 13, 62. [CrossRef] [PubMed]
22. Pathan, S.; Bose, S. Arsenic Removal Using "Green" Renewable Feedstock-Based Hydrogels: Current and Future Perspectives. ACS Omega 2018, 3, 5910–5917. [CrossRef]
23. Mukherjeea, D.; Ghosha, S.; Majumdar, S.; Annapurnaa, K. Green synthesis of-Fe2O3 nanoparticles for arsenic(V) remediation with a novel aspect for sludge management. J. Environ. Chem. Eng. 2016, 4, 639–650.
24. Poguberovi´ c, S.; Krˇ cmar, D.; Maleti´ c, S.; Kónya, Z.; Tomaševi´ c Pilipovi´ c, D.; Kerkez, Đ.; Ronˇ cevi´ c, S. Removal of As(III) and Cr(VI) from aqueous solutions using "green" zero-valent iron nanoparticles produced by oak, mulberry and cherryleaf extracts. Removal of As(III) and Cr(VI) from aqueous solutions using "green" zero-valent iron nanoparticles produced by oak, mulberry and cherryleaf extracts. Ecol. Eng. 2016, 90, 42–49.
25. Medina-Ramirez, A.; Gamero-Melo, P.; Ruiz-Camacho, B.; Minchaca-Mojica, J.I.; Romero-Toledo, R.; Gamero-Vega, K.Y. Adsorption of Aqueous As(III) in Presence of Coexisting Ions by a Green Fe-Modified W Zeolite. Water 2019, 11, 281. [CrossRef]
26. Asere, T.G.; Stevens, C.V.; Laing, G.D. Use of (modified) natural adsorbents for arsenic remediation: A review. Sci. Total Environ. 2019, 676, 706–720. [CrossRef]
27. Habuda-Stani´ c, M.; Nuji´ c, M. Arsenic removal by nanoparticles: A review. Environ. Sci. Pollut. Res. 2015, 22, 8094–8123. [CrossRef]
28. Siddiqui, S.I.; Chaudhry, S.A. Arsenic removal from water using nano-composites: A review. Curr. Environ. Eng. 2017, 4, 81–102. [CrossRef]
29. Wong, W.W.; Wong, H.Y.; Borhan, A.; Badruzzaman, M.; Goh, H.H.; Zaman, M. Recent advances in exploitation of nanomaterial for arsenic removal from water: A review. Nanotechnology 2017, 28, 1–31. [CrossRef] [PubMed]
30. Song, K.; Kim, W.; Suh, C.Y.; Shin, D.; Ko, K.S.; Ha, K. Magnetic iron oxide nanoparticles prepared by electrical wire explosion for arsenic removal. Powder Technol. 2013, 246, 572–574. [CrossRef]
31. Lunge, S.; Singh, S.; Sinha, A. Magnetic iron oxide (Fe3O4) nanoparticles from tea waste for arsenic removal. J. Magn. Magn. Mater. 2014, 356, 21–31. [CrossRef]
32. Roya, P.K.; Choudhury, M.R.; Ali, M.A. As (III) and As (V) Adsorption on Magnetite Nanoparticles: Adsorption Isotherms, E ect of pH and phosphate, and Adsorption Kinetics. Int. J. Chem. Environ. Eng. 2013, 4, 55–63.
33. Tuutijärvi, T.; Lu, J.; Sillanpää, M.; Chen, G. As(V) adsorption on maghemite nanoparticles. J. Hazard. Mater. 2009, 166, 1415–1420. [CrossRef]