



The Significance of Polymeric Ligand Exchange (PLE) Technique for Arsenic Removal from Polluted Groundwater: A Review

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Authors' contributions

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ABSTRACT

Presently, the global concern over the toxic effects of arsenic and its wide distribution is particularly pronounced in India. This study adopts a specialized geochemical perspective to shed light on the issue. Groundwater in the northeastern states of India has been found to contain notably high concentrations of arsenic (ranging from 50 to 986 $\mu\text{g/l}$). This geographical region has come under scrutiny due to the escalating worldwide apprehension about arsenic toxicity and its pervasive presence of particular distress is the substantial disparity between the observed arsenic levels and the recommended limits defined by authoritative bodies such as the World Health Organization (WHO) and the Bureau of Indian Standards (BIS), which have set the acceptable arsenic levels in drinking water at 10 $\mu\text{g/l}$ and 50 $\mu\text{g/l}$, respectively. In response to this critical situation, diverse techniques tailored for targeted removal of arsenic have emerged. These techniques encompass a range of processes including precipitation, adsorption, and modified iron-based and ligand exchange methods.

The inherent characteristics of various arsenic species further compound the challenge of selectively eliminating arsenic, especially when dealing with natural environmental contexts.

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Notably, hydrated Fe(III) oxides have played a vital role in most selective removal techniques through the mechanism of Lewis acid-base interaction. In this context, a pioneering approach known as Polymeric Ligand Exchange (PLE) has surfaced. This method has exhibited promising results by selectively extracting arsenic from drinking water, even in the presence of formidable competing anions such as sulfate. The efficacy of PLE in overcoming this complex chemical milieu marks a significant stride in the ongoing efforts to mitigate the arsenic contamination crisis.

Keywords: Arsenic toxicity; precipitation; adsorption; polymeric ligand exchange; strong base anion exchanges.

1. INTRODUCTION

Arsenic exists primarily in two distinct oxidation states: arsenate (As^{5+}) and arsenite (As^{3+}). These oxidation states, As^{5+} and As^{3+} , are mutually convertible through oxidation, transforming As^{3+} into As^{5+} , and reduction, converting As^{5+} into As^{3+} . Another manifestation of arsenic is in its organic form, resulting from the biomethylation of inorganic arsenic. Within the realm of biology, various organisms including plants, aquatic creatures like fish and crabs, as well as the human body, harbor organoarsenic compounds. Uttar Pradesh comes under upper and Middle Ganga plain. Himalayan Mountain and Tibet plateau, consider as the biggest source of arsenic contamination in the Gangetic region and this contamination are evidently becoming life threatening in almost every year. Geographically Uttar Pradesh situated in the northern region of India and border of Nepal. The river Ganga and Ghaghara are two major river flows from northeast to southeast. First time in UP arsenic introduced as a contaminant in Ballia district. Status of Arsenic Contamination in Eastern U.P.: In U.P. Jal Nigam and UNICEF combinedly reported and identified in 18 districts. Arsenic above the 50 ppb limit for drinking and Arsenic according to WHO limit was found in 31 districts [1]. Times of India also reported "Ground water arsenic contamination of Uttar Pradesh exceeds to the value of BIS(Bureau of Indian Standards) permissible limit of 0.01 mg/liter across 31 districts of the state. Arsenic contamination in Ballia district: District Ballia is located in the eastern part of UP with shared in 17 blocks.

Microscopic life forms, such as bacteria or fungi devoid of chlorophyll, facilitate the biological transformation of inorganic arsenic into the organic form—a phenomenon known as biomethylation. Notably, regions rich in sulfide ores and metal oxides like iron oxide tend to contain heightened concentrations of arsenic. Early research indicated that arsenic-

contaminated groundwater was largely confined to the Ganga basin, originating from areas abundant in sulfide-laden minerals in Bihar and its neighboring deposition basins (Chakraborti, D. et al J. Environ. Monitor, 6: 74–83, 2004). Recent findings, however, have revealed an expanded occurrence of elevated arsenic concentrations in wells across the Indo-Gangetic alluvial region, extending westward and encompassing the Brahmaputra alluvial expanse.

During the deposition of sedimentary layers in the Holocene period, hydroxides precipitate, and arsenic, released during the weathering of sulfide minerals, becomes adsorbed. Subsequent redox processes result in the dissolution of iron oxides, facilitating the migration of arsenic into aquifers through complex biogeochemical mechanisms. Over the late Quaternary and Holocene eras, sedimentary deposits in river systems transport arsenic within the aqueous phase of the Ganga-Brahmaputra river basin. Recent global research has introduced a novel geochemical paradigm to address the issue of groundwater arsenic contamination in the Eastern Gangetic River Basin [2,3]. This concern has gained significant attention due to its far-reaching implications, not only for the safety of drinking water but also for its impact on irrigation efforts. Azam A.'s pioneering work in [4] illuminated the prevalent oxidation states of arsenic, primarily existing as arsenate (As^{5+}) and arsenite (As^{3+}), as further elucidated in subsequent research by Azam A. and Kunwar in [5] (Azam A. and Kunwar [6] JOWPPR Pg. no. 1-4, 2018)

The intricate interplay of multiple factors intricately regulates the concentration and movement of arsenic within groundwater systems. These factors encompass the redox potential (Eh), the dynamic equilibrium of adsorption and desorption processes, precipitation and dissolution phenomena, as well as the crucial arsenic speciation [7]. The pH level, alongside the presence and concentration of competitive ions, along with biologically-

mediated transformations, also exert substantial control over arsenic behavior, as articulated in publication [6]. The potential for arsenic contamination in surface waters is due to the increased release of arsenic into water from sediments. During the dry season, arsenic in sediments has a poor ability to resuspension. Therefore, little arsenic is transported downstream. During the wet season, flooding upsets the sediment and water balance, allowing arsenic to resuspension and downstream transport of pollution [8,9].

A captivating temporal pattern emerges in the realm of arsenic dynamics across various seasons, as revealed in Azam A. [10] study. During the monsoon season, there is a notable increase in arsenic content, attributed to the breakdown of Fe(III)-oxy hydroxides. In contrast, the pre-monsoon period witnesses the reversible adsorption of arsenic onto Fe(III) oxy hydroxides [11,12]. Significantly, Azam A. investigation in the same year established a clear connection between arsenic behavior and the intensity of rainfall, emphasizing the crucial link between environmental conditions and arsenic mobilization [13].

2. INNOVATIVE GEOCHEMICAL APPROACH FOR TARGETED ARSENIC REMOVAL

Water and wastewater treatment facilities worldwide grapple with a significant challenge in effectively removing trace elements like Arsenic (As), particularly when faced with high concentrations of competing major ions in the background (Mandal et al., 2013; Ramana and Sengupta, 1992). The conventional methods to eliminate *As(Arsenic)* often struggle to counteract the impact of these background ions, leading to reduced cost-efficiency (Korngold et al., 2001; Pincus et al., 2019). This situation hinders their practicality due to economic, environmental, and societal factors, resulting in gaps in achieving the desired selective removal of *As(Arsenic)*. This challenge becomes more pronounced in scenarios where water sources have only minimal *As(Arsenic)* contamination, which is exacerbated when compared to the abundance of other dissolved chemical species crucial for safe drinking water. Consequently, there is an urgent need for mechanisms that exclusively target *As(Arsenic)* removal while focusing on maximizing efficiency and selectivity [14,15].

Moreover, the behavior of As in aqueous environments complicates its removal efficiency, often diminishing as the initial As concentration increases. Hence, an effective selective removal strategy should have a strong affinity for As, regardless of its initial concentration. Additionally, a key goal is to find methods that eliminate the need for pre-oxidation and post-treatment steps typically required for removing As(III), thus reducing energy usage, process complexity, and costs. Equally important is the minimization of waste generation. Non-selective treatment approaches often lead to unintended removal of significant amounts of other solutes, resulting in substantial costs associated with waste management on both ecological and economic fronts. Consequently, a selective As removal process aims to significantly reduce the volume of waste enriched with As.

Given the distinct behaviors of the two primary As species, As(V) and As(III), achieving targeted removal in natural settings poses heightened challenges. Remediation strategies can be broadly categorized into four main groups: ion-exchange processes, membrane separation processes, precipitative processes, and adsorptive processes, often requiring pre-oxidation for As(III) removal [16,17], (Bundschuh et al., 2011; Jadhav et al., 2018; Yüksel et al., 2018).

For example, coagulation with ferric chloride followed by microfiltration can remove both As(III) and As(V), but it may not be suitable for waters with low As content due to the formation of sludge containing As (Koby et al., 2020; Sarkar et al., 2012). Traditional ion-exchange strategies often have limited As removal capabilities due to competition with other anions in water. Among these strategies, adsorption has gained attention due to its simplicity and relatively moderate cost, especially when using natural adsorbents [18,19]. Modifying these natural adsorbents chemically has yielded successful As removal outcomes [20], (Kumar et al., 2019).

Various materials have been employed for As removal, including soil minerals, impregnated ceramic adsorbents, agricultural and industrial waste materials, plant and aquatic biomass, and activated carbon substances. Notably, the electronic structure of As, particularly arsenate (As(V)), is similar to that of phosphorus/phosphate, potentially causing interference with phosphate chemistry (Bui et al.,

2019). Other interfering ions include silicate, sulfate, chloride, and bicarbonate, which, if unaddressed, could increase waste production and costs while shortening the operational lifespan of removal units [21], (Gu et al., 2005).

Many established and modified As treatment methods often require additional removal techniques, such as microfiltration, to comply with regulatory standards, which could impact cost-effectiveness [22]. Despite their effectiveness, commercially available ion-exchange resins often lack the selectivity needed for competitive economic feasibility in As removal efforts.

3. INNOVATIVE GEOCHEMICAL APPROACH FOR PRECISE ARSENIC EXTRACTION

In the realm of global water and wastewater treatment facilities, a formidable conundrum arises in the meticulous eradication of trace elements, with a specific focus on Arsenic (As), amid the concurrent presence of predominant major ions (Mandal et al., 2013; Ramana and Sengupta, 1992). Traditional methodologies, while displaying competence in As elimination, grapple with the coexistence of background ions, leading to diminished cost efficiency (Korngold et al., 2001; Pincus et al., 2019). This constraint not only poses economic, environmental, and societal impediments but also engenders gaps in the attainment of targeted As removal. The complexity deepens in scenarios where water systems harbor marginal As concentrations vis-à-vis other indispensable dissolved compounds in potable water. Consequently, a strategic maneuver exclusively centered on As removal emerges as a pursuit, underscored by its efficiency and precision.

The intricate behavior of As complicates its removal, particularly as initial concentrations surge. Therefore, an efficacious approach should manifest a robust inclination toward As, irrespective of its preliminary concentration. Furthermore, the objective revolves around circumventing pre-oxidation and post-treatment phases, thereby curtailing energy consumption and process intricacy. A paramount focus lies in waste minimization; non-selective techniques tend to expunge other solutes, thereby necessitating onerous waste management protocols. Ergo, a selective As removal process aspires to curtail the presence of As-rich waste.

Given the disparate behaviors of As(V) and As(III), accomplishing selective removal under natural conditions presents a challenge. The arsenal of remedial techniques encompasses ion-exchange, membrane separation, precipitation, and adsorption, often entailing As(III) pre-oxidation [16,17]; (Bundschuh et al., 2011; Jadhav et al., 2018; Yüksel et al., 2018). Coagulation with ferric chloride followed by microfiltration can facilitate the removal of both As(III) and As(V), yet it proves cost-prohibitive for waters with low As concentrations (Kobyas et al., 2020; Sarkar et al., 2012). Conventional ion-exchange suffers from decreased As removal due to the influence of competing anions. The realm of adsorption, particularly utilizing modified natural adsorbents, garners attention [20]; (Kumar et al., 2019). Materials encompassing soil minerals, impregnated ceramics, waste products, biomass, and activated carbon are harnessed. Notably, As(V) shares similarities with phosphate, raising the specter of potential interference (Bui et al., 2019). Concurrently, interfering ions like silicate and sulfate demand meticulous consideration [21], (Gu et al., 2005). Several methodologies necessitate supplementary steps such as microfiltration to align with regulatory norms [22]. Commercial ion-exchange methods lack the requisite As selectivity, thereby impinging on cost-effectiveness.

4. INNOVATIVE GEOCHEMICAL STRATEGY FOR TARGETED ARSENIC ELIMINATION

In the realm of global water and wastewater treatment, a significant and intricate challenge revolves around effectively eliminating trace elements, particularly Arsenic (As), in the presence of high concentrations of other competitive solutes, mainly major ions (Mandal et al., 2013; Ramana and Sengupta, 1992). Traditional methods for As removal, while generally effective, struggle to handle the coexistence of these major ions efficiently, leading to cost-effectiveness limitations (Korngold et al., 2001; Pincus et al., 2019). This issue restricts their widespread adoption due to economic, ecological, and societal considerations, creating gaps in achieving the desired selective As elimination. This challenge becomes more pronounced in situations where water systems have low As contamination relative to the prevalence of other essential dissolved compounds crucial for safe drinking water [23]. This necessitates the development of

strategies exclusively targeting As removal to enhance both effectiveness and selectivity.

The complex behavior of As in aqueous environments further complicates its removal efficiency, often decreasing as initial concentrations rise. Consequently, an effective selective removal approach should exhibit a strong affinity for As, irrespective of its initial concentration. Additionally, there's a need to explore methods that eliminate the need for conventional pre-oxidation and post-treatment steps required for removing As(III), thus reducing energy consumption, process complexity, and costs. Minimizing waste generation is also crucial. Many non-selective treatment methods inadvertently remove significant amounts of other solutes, leading to substantial costs for waste management, both environmentally and economically. Thus, a selective As removal process aims to significantly reduce the volume of waste containing As [24,25].

A variety of materials have been employed for As removal, including soil minerals, impregnated ceramic adsorbents, agricultural and industrial waste materials, plant and aquatic biomass, and activated carbon substances. Notably, the electronic structure of As, particularly arsenate As(V), closely resembles that of phosphorus/phosphate, which could potentially interfere with phosphate chemistry (Bui et al., 2019). Other interfering ions include silicate, sulfate, chloride, and bicarbonate, all of which, if left unaddressed, could escalate waste production and costs while shortening the operational lifespan of removal units [21], (Gu et al., 2005).

5. CONCLUSIONS

In the realm of geochemical approaches, addressing the selective removal of arsenic (As) from aqueous solutions is a complex undertaking, driven by multiple factors. The prevalence of common anions in natural waters and wastewater at substantially higher concentrations poses a challenge by competing with As for adsorption sites. Furthermore, the dynamic interplay of solution pH and redox potential triggers a transformation of As into diverse oxidation states—ranging from As(V) oxyanions to neutral As(III) species—in most natural water sources. These distinct chemical forms exhibit disparate physical and chemical behaviors, rendering a universal removal method elusive.

Nevertheless, an intriguing solution emerges from the recognition that hydrated granular or amorphous Fe(III) exhibits remarkable efficacy in selectively sequestering both As(III) and As(V) in aqueous solutions. This exceptional affinity sets the stage for enhancements in both mechanical strength and adsorption capacities through the incorporation of robust materials alongside hydrated Fe(III), as illustrated by examples like chitosan and ion-exchange resins. The secure integration of hydrated Fe(III) within the chosen matrix stands as a pivotal phase in the preparation process, amplifying the success of selective As removal [26].

Beyond the realm of Fe(III), alternative metal ions such as Cu^{2+} , La^{3+} , and Al^{3+} ions have demonstrated their prowess in selectively extracting As, showcasing promising As removal capabilities. Presently, strong base anion exchange methods are deployed in the treatment of drinking water to mitigate arsenic contamination. However, the efficacy of these approaches is hampered by the presence of competitive anions like sulfate, curtailing the capacity of SBA (strong base anion exchange) resins [27].

Enter the innovative frontier of anion exchange polymeric ligand exchange (PLE), a recent development offering an augmented arsenal for arsenic removal from drinking water. PLE exhibits greater selectivity and capacity in the presence of formidable competing anions—chloride, sulfate, bicarbonate, and phosphate. This breakthrough holds the potential to overcome the limitations of traditional approaches and provide a more effective solution for arsenic removal, addressing a critical concern in water treatment and environmental preservation [28].

6. FUTURE SCOPE

1. The challenge of selectively extracting arsenic (As) from aqueous solutions is a complex endeavor shaped by various geochemical factors. Within natural waters or wastewater, a multitude of common anions coexist, often at significantly elevated concentrations, creating a competitive environment for As adsorption processes. Consequently, unraveling efficient techniques for arsenic separation stands as a prominent realm of research.
2. An innovative avenue in addressing this challenge involves the utilization of anion

exchange through polymeric ligand exchange (PLE) materials. This pioneering approach showcases heightened selectivity and capacity for eliminating arsenic from potable water, even amidst the presence of robust competing anions such as chloride, sulfate, bicarbonate, and phosphate. The pursuit of analogous facile methodologies is imperative, underscoring the need to identify techniques that share comparably advantageous attributes.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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