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# Breakthroughs in Arsenic Remediation: Unveiling Groundwater Treatment by Polymer Technologies

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***Abstract***

*Arsenic (As) is a metalloid characterized by its toxic properties and ability to undergo variations in oxidation state and bonding configuration. Its existence in groundwater has emerged as a subject of worldwide apprehension, primarily due to its detrimental properties and adverse impacts on human health. A significant proportion of the population residing in the Ganga basin relies heavily on groundwater resources that exhibit elevated levels of arsenic (As) for various purposes such as drinking, irrigation, and other domestic and agricultural uses. The mobilization of arsenic in the Central Ganga basin and its subsequent presence in groundwater has become a significant concern. Efforts to address this issue through remediation strategies are of utmost importance. Polymer-based arsenic remediation is the development of highly selective adsorbent polymers specifically designed to target arsenic ions in groundwater. This review addresses several remediation approaches employed for the treatment of As, along with various ex-situ remediation procedures, including precipitation, adsorptive, ion-exchange, and membrane processes. Additionally, it explores in-situ remediation processes such as the immobilization of arsenic by sorption, chemical oxidation, and reduction processes, as well as arsenic biotransformation facilitated by microorganisms.*

**Keywords:** Arsenic Remediation, Groundwater, Ion-Exchange, Bioaccumulation, Polymer.

## INTRODUCTION

Arsenic (N=33, M= 74.92), represented by the chemical symbol falls under the classification of metalloids. It can create colorless and odorless crystalline compounds known as $As_2O_3$ and $As_2O_5$. These compounds possess hygroscopic properties, meaning they tend to absorb moisture from the environment. Additionally, they rapidly dissolve in water, resulting in the formation of acidic solutions. The oxidation states most frequently observed for arsenic include -3, which corresponds to arsenide in the form of alloy-like intermetallic compounds, +3, Arsenic exists primarily in two oxidation states: +3 (arsenites [As III]), and +5 (arsenates [As V]), which are the most secure inorganic arsenic oxy-compounds [1]. Arsenic can potentially occur in both (Inorganic and organic) states. In general, the organic state of arsenic exhibits lower toxicity levels compared to inorganic arsenic. Inorganic arsenic is naturally present in several rock formations and is commonly associated with the sulfide mineral known as arsenopyrite. Inorganic arsenic compounds have been identified as human carcinogens. Elemental arsenic exhibits little solubility in water, while its oxidized derivative demonstrates higher solubility [2]. Furthermore, arsenic is an inherent component found in bedrock and soil. It is frequently discovered within the Earth's crust in moderate quantities (1-5 mg/kg) [3]. However, it has the potential to be more concentrated in specific rock formations, particularly in gold and sulfide-bearing ore deposits. Pyrite ($FeS_2$) and arsenopyrite (FeAsS)

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are commonly occurring sulfide minerals that include arsenic (As). These minerals exhibit a notable degree of stability when present in bedrock and deep soil, particularly in environments characterized by decreasing and near-neutral conditions. The locomotion of arsenic (As) is chiefly affected by alterations in pH and redox conditions, which may arise from natural processes such as microbial activity or human activities [4].

Arsenic contamination in aquifer water is a global issue, causing prominent health challenges for many people in countries including Argentina, Bangladesh, India, Nepal, Pakistan, China, the USA, Vietnam, Mongolia, and Mexico. The toxicity threshold of arsenic in drinking water varies from country to country. In less developed nations such as Bangladesh, India, China, and Taiwan, the permissible concentration is set at 50 mg/l. On the contrary, in developed nations such as the USA, Germany, and Japan, the concentration is more stringent, usually set at 10 mg/l [5]

## THEORIES FOR THE OCCURRENCE OF ARSENIC IN GROUNDWATER

### Microbial Oxidation Theory

Microorganisms are pivotal in the arsenic cycle. They aid in the mobilization of arsenic through both direct and indirect mechanisms. The oxidization of organic matter leads to the formation of peat deposits in groundwater areas, generating a conducive environment for reduction that facilitates the mobilization of arsenic. Similarly, the reduction of sulfate and iron, Additionally, the oxidative dissolution of sulfide minerals contributes to the transport of arsenic. In an environment with anaerobic conditions microorganisms utilize arsenate as an electron donor during the process of arsenate respiration [6].

### Arsenical Pyrite Theory

Based on the proposed idea, the liberation of arsenic occurs because of the percolation of surface water, leading to the occurrence of oxidation of arsenical pyrite within the alluvial deposits. The method allows for the infiltration of air oxygen into the aquifer. During the monsoon season, the replenishment of the water table occurs through the infiltration of rainwater, this process leads to the liberation of arsenic from sediments into the aquifer. [7]

### Anion Exchange Theory

The process of ion exchange occurs when sorbed arsenic ions are displaced by phosphate ions derived from the administration of aquatic mineral fertilizer. This displacement is a result of the competitive exchange between the two ions. The act of withdrawing groundwater from shallow aquifers for irrigation purposes has the potential to induce the release of phosphate from fertilizers. The degradation of naturally occurring organic materials can also have a similar effect. The concept suggests that extracting groundwater for irrigation leads to the toxication of water levels, resulting in the presence of arsenic within the aquifer. Natural processes significantly contribute to water pollution, particularly the interaction between water and rocks, which can lead to the accumulation of arsenic. Favorable physical and geochemical conditions within the aquifer further contribute to groundwater contamination with arsenic. Groundwater pH values are commonly seen to range from 6.5 to 8.5 in both oxidizing and reducing environments. Therefore, the mobilization of arsenic occurs inside this aquifer. In specific regions of India, geological factors have been pinpointed as the primary cause of arsenic contamination in aquifer water. The prevailing hypothesis posits that the rocks harboring arsenic experienced erosion originating from the Himalayas, thereafter, undergoing deposition within the deltaic and Gangetic plains. The deposition of these sediments over a prolonged period results in the formation of an aquifer [8].

### Reduction Dissolution Theory

According to the reduction dissolution theory, the process of dissolving occurs in sediments that have been previously accumulated in the Himalayan plain region. The conveyance of materials occurred through the utilization of wind, glacial, and river systems. The arsenic that was adsorbed onto

 

the fine-grained iron, manganese, and hydroxide materials underwent sedimentation and deposition in the flood plains. The reductive breakdown of iron oxyhydroxide (FeOOH) leads to the liberation of arsenic ions into the aquifer water [9].

## ORIGIN OF ARSENIC

The primary origin of arsenic in aquifer water can be attributed to two main factors: anthropogenic activities and geogenic processes. The mineral arsenopyrite has been widely recognized as the primary contributor to groundwater contamination. Chemical industries involved in the production of paint, plastics, pesticides, and fertilizers have the potential to contribute to groundwater contamination by increasing arsenic levels [10]. Many districts in India demonstrate high concentrations of arsenic in their aquifer water, exceeding the threshold of 50 parts per billion (ppb) [11]. Arsenic exists in diverse configurations in the Earth's crust, including organic, inorganic, and gaseous states. Groundwater acts as a significant reservoir of inorganic arsenic, which poses substantial risks to human health due to its tendency for bioaccumulation and its adverse effects on several bodily organs. The existence of arsenic has been associated with the rising incidence of various diseases. The relative toxicity of arsenic compounds can be ranked as follows: arsenic gas exhibits the highest toxicity, followed by inorganic As (III), organic As (III), inorganic As(V), organic As(V), and elemental As.

## ARSENIC'S IMPACTS ON HUMAN HEALTH

Exposure to arsenic has been found to result in adverse health consequences in humans, plants, and animals. The medical risks linked to arsenic exposure normally emerge after a duration of 5 to 10 years, although symptoms may become evident within 3 years in instances of high arsenic ingestion by humans. Inorganic arsenic possesses the capacity to operate as a genotoxic agent, capable of eliciting chromosomal abnormalities that have an impact on the occurrence of sister chromatid exchange and the formation of micronuclei. Additionally, arsenic acts as an epigenetic regulator of genetic material, leading to modifications in the functioning of crucial enzymes including DNA methyltransferases, histone deacetylase, and histone acetyltransferase [12] levels of arsenic in drinking water, exceeding 50 μg/L, have been observed to induce carcinogenic effects in various human organs such as the skin, bladder, lungs, and kidneys.

## REMEDIATION STRATEGIES

The current scenario of groundwater contamination with arsenic offers an opportunity to explore remediation techniques. Arsenic can be effectively treated using traditional methods involving oxidation, where soluble As (III) is changed into less soluble As (V). The resulting insoluble As (V) can then be separated by exploiting various physico-chemical characteristics. However, the addition of chemical substances during the oxidation process can increase the associated costs. Physico-chemical methods, including sorption, ion exchange, precipitation, coagulation, membrane filtration, permeable reactive barriers, as well as biological techniques such as phytoremediation and microbial degradation, have been identified as effective means of arsenic removal [13].

### Physicochemical Strategies for Remediation

#### *Precipitation-coagulation*

This process involves converting soluble arsenic into an insoluble state, followed by settling. Arsenic's presence in water can also lead to its adsorption onto external surfaces and subsequent co-precipitation with other substances. Coagulation can also be employed to remove dissolved arsenic. The efficiency of this arsenic elimination technique is notably influenced by factors like pH. Common reagents used in this process include copper sulfate, manganese sulfate, ammonium sulfate, ferric salts, and alum [14]. Lime softening offers an alternative precipitation technique utilizing limestone and calcium hydroxide for the elimination of arsenic [15].

#### *Adsorption*

This method is extensively utilized in water purification applications. During this process, arsenic species undergo binding to the adsorbent surface through a combination of physical and chemical interactions.

 

***Ion exchange method***

It affects the electrostatic retention of arsenic ions which are present on the surface of the strong alkali ion exchange resin. Arsenic ions undergo replacement by ionized particles of similar charge present in the solution, which then react with the resin. The ionized particle exchange process involves the exchange of ions between the solution phase and the solid phase through physical and chemical mechanisms. The presence of As (III) necessitates its oxidation to As (V) for effective operation. Resins typically feature elastic 3D hydrocarbon networks containing numerous ionizable groups that electrostatically bond to the resin. One method for softening and removing nitrates involves employing the ionized particle exchange process This process facilitates the exchange of ions of identical charge in the solution, with the resin exhibiting a high affinity for ion exchange. The arsenic removal procedure entails the continuous flow of water through one or more strong base anion (SBA) exchange resin columns. The pH insensitivity of these resins ranges from 6.5 to 9.0 [16].

***Membrane filtration***

This technique entails the extraction of arsenic from water through the use of a semi-permeable membrane and barrier. The membrane employed in this method is composed of synthetic material with numerous pores acting as a selective barrier, effectively preventing the passage of specific arsenic compounds. A crucial aspect driving the system is the pressure difference between the input and output streams [17]. Permeable sides are essential for facilitating water transfer across the membrane.

***Bacterial remediation***

The utilization of microorganism-assisted remediation processes has emerged as the main method of heavy metal storage. These organisms possess the ability to remediate arsenic from contaminated sites due to their small size and rapid doubling time. Moreover, they possess genes and plasmids that are responsible for the process of metal detoxification. These organisms possess the ability to endure highly contaminated environments through their inherent adaptive mechanisms. Microorganisms are pivotal in the detoxification, mobilization, and immobilization of arsenic species through various methods like oxidation-reduction, biomethylation, absorption, methylation, and complexation. According to Mitra and its colleagues [18], arsenic enters bacterial cells through the phosphate transporter. Once inside, the arsenic can undergo either oxidation or reduction, depending on the specific mechanism employed by the bacterial species.

Various kinds of bacteria, such as alpha, beta, and gamma proteobacteria, have demonstrated the capacity to effectively mitigate arsenic contamination. Bacteria such as *Corynebacterium glutamicum* are known to engage in the remediation of arsenic through a process called arsenate reduction. On the other hand, bacteria like *Bacillus subtilis* have been shown to utilize thioredoxin as a reductant, so facilitating the remediation of arsenic. Several studies have documented the involvement of *Pseudomonas, Psychrobacter, Citrobacter, Vibrio,* and *Enterobacter* in the process of remediation [19].

Recently, there has been increased interest in using sulfate-reducing bacteria to facilitate arsenic remediation. This interest stems from the ability of these bacteria to generate biogenic pyrite, which serves as a highly efficient absorber of dissolved arsenic [20]. Microorganisms have also been employed in conjunction with physicochemical techniques to augment and optimize the effectiveness of remediation processes. Pous *and their colleagues.,* [21], employed bacteria for the conversion of arsenite to arsenate. This approach was chosen due to the high mobility of arsenite, which poses challenges in its removal. The proposed methodology entails a sequential process consisting of the conversion of arsenite to arsenate, followed by the absorption of the produced arsenate species into various materials.

***Mycoremediation***

Fungi exhibit a wide range of functions within the ecosystem and make substantial contributions to

 

the cycling of nutrients. Due to their large biomass in the soil and their long life, they are widely used to clean up various pollutants. Fungi can assimilate various heavy metals, such as arsenic, via mechanisms of bioaccumulation, biotransformation, and biomethylation. Various surface proteins, peptides, and polysaccharides are utilized by organisms to uptake arsenic and other metalloids from their surrounding environment. To provide more insight, there are three distinct transporter proteins present. According to Chen *and its colleagues* [22], several types of fungi can promote the process of methylation of inorganic arsenic, leading to the production of volatile derivatives. It helps in lowering levels of arsenic pollution. Certain fungal species, such as *Aspergillus, Rhizomucor, Fusarium*, and *Emericella* have demonstrated the capacity to tolerate elevated concentrations of arsenic. This capability possesses the potential to effectively remediate contaminated regions. Concurrently, this species can contribute to the development of soil physicochemical properties and soil enzyme activity. Several more fungi that have been employed for arsenic removal include *Trichoderma, Penicillium sp., P. verrucosum, Ascomycetes,* and *Basidiomycetes* [23]. Multiple studies have documented the presence of fungal species such as *Sacrosphaera coronaria, Fomitopsis meliae, Absidia cylindroslora*, and *Rhizopus microsporus*, which have demonstrated the ability to tolerate elevated levels of arsenic. This characteristic holds potential for their application in remediation strategies [24-25].

**Uses of Polymer in the Process of Water Purification [26, 27]**

Polymers are used in the process of water purification for several reasons:

i. **Coagulation and Flocculation**: Polymers are often used as coagulants or flocculants in water treatment processes. They help in aggregating small particles suspended in water, allowing them to settle out more efficiently during sedimentation or filtration processes.
ii. **Enhanced Particle Removal**: Polymers can improve the efficiency of particle removal by binding fine particles together into larger clumps (flocs), which can then be more easily removed by filtration or settling.
iii. **Improved Water Clarity**: By aiding in the formation of larger, denser flocs, polymers contribute to clearer water quality, reducing turbidity and improving overall water aesthetics.
iv. **Reduced Chemical Dosage**: Using polymers can sometimes reduce the overall dosage of traditional coagulants like alum or ferric chloride, thereby potentially lowering chemical costs and minimizing the environmental impact of water treatment processes.
v. **Versatility**: Polymers come in various types and formulations, allowing for flexibility in addressing specific water quality challenges such as organic matter removal, color reduction, and disinfection byproduct control.

***Technologies Used for the Cleaning of Groundwater [28, 29]***

Several technologies are available for the cleanup of groundwater contaminated by various pollutants. These technologies can be broadly categorized into physical, chemical, and biological methods. Here are some common technologies used for groundwater cleanup:

i. *Pump and Treat Systems:* This is a traditional method where groundwater is pumped to the surface, treated (often using air stripping, filtration, or chemical treatments), and then re-injected or discharged.
ii. *Air Sparging:* Air sparging involves injecting air or other gases into the groundwater to volatilize contaminants, which are then removed using vapor extraction systems.
iii. *Bioremediation:* Biological processes can be used to degrade contaminants in groundwater. This can involve stimulating natural microbial activity or introducing specific microorganisms that can break down contaminants.
iv. *Activated Carbon Adsorption:* Groundwater is passed through activated carbon filters, which adsorb organic contaminants and certain dissolved chemicals.
v. *Chemical Oxidation:* Chemical oxidation involves injecting oxidizing agents (like ozone, hydrogen peroxide, or permanganate) into the groundwater to chemically degrade contaminants.
vi. *Permeable Reactive Barriers (PRBs):* PRBs are installed underground and filled with reactive materials (such as zero-valent iron or activated carbon) that chemically degrade or immobilize

 

contaminants as groundwater flows through them.

vii. *Electrokinetic Remediation:* This method uses electrical currents to move charged contaminants in groundwater towards electrodes for collection or degradation.

viii. *Phytoremediation:* Certain plants are used to uptake, degrade, or immobilize contaminants from groundwater through their roots and metabolic processes.

ix. *In Situ Chemical Reduction (ISCR):* ISCR involves injecting reducing agents (such as zero-valent iron) into contaminated groundwater to chemically reduce contaminants to less harmful forms.

x. *Thermal Treatment:* Techniques like thermal desorption or steam injection can be used to vaporize and remove volatile contaminants from groundwater.

***Polymer as a coagulant or a flocculant?***

Polymers can be classified as flocculants rather than coagulants in the context of water treatment processes.

**i.** *Coagulants:* Coagulants are typically inorganic chemicals like alum (aluminum sulfate) or ferric chloride. They work by neutralizing the electrical charges of particles in water, causing them to destabilize and clump together (coagulate) into larger aggregates. These larger aggregates are then more easily removed through processes like sedimentation or filtration.

ii. *Flocculants:* Polymers, on the other hand, are typically used as flocculants. Flocculants help in the formation of larger, denser flocs by bridging between particles or by adsorbing onto particle surfaces, which enhances particle agglomeration. These flocs settle out more efficiently during sedimentation or can be removed more effectively during filtration, leading to clearer water.

While both coagulants and flocculants aid in the removal of suspended particles from water, they function differently in terms of particle destabilization and aggregation. Polymers are particularly useful as flocculants due to their ability to create stable flocs that can improve water clarity and enhance the efficiency of subsequent treatment processes.

## CONCLUSION

The presence of arsenic in the ecosystem has given rise to significant environmental apprehensions owing to its toxic and carcinogenic properties. Considerable research and development endeavors have been undertaken to address the remediation of As from water sources. These efforts have focused on the implementation of sustainable technologies that are both environmentally benign and readily applicable in areas affected by contamination. The utilization of adopted technologies may have some limitations, and the resulting by-products could potentially contribute to the secondary contamination of arsenic. Hence, to enhance environmental remediation efforts, the implementation of novel technologies, including hybrid technologies, is important to effectively address the issue of As contamination. Additional study is required to devise more effective methodologies that do not possess any limitations.

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