

Valorization of Recent Arsenic Removal Methods and Parameters Controlled for Testing: Mini Review

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ABSTRACT - This study presented the utilisation of an arsenic-ion imprinted polymer as an adsorbent to effectively eliminate arsenic compounds from water. Several variations of arsenic technique approaches have been described and the recent trends have been reviewed. The parameters investigated encompassed pH, temperature, duration of contact, dosage of adsorbent, initial concentration of arsenic ions, presence of competitive ions, and type of eluent in relation to the recovery process. The adsorption capability of the arsenic-ion imprinted polymer can be considerably influenced by pH and temperature.

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1.0 INTRODUCTION

Countless methods for removing arsenic species from water have been developed and implemented. However, the concentration of arsenic in water sources rises over time due to several limitations of each technique. Due to its ability to easily oxidise and reduce, the adsorption method that used iron oxide minerals as an adsorbent was thought to be unstable in the removal of arsenic from water [1]. As a result, conducting research with iron as a sorbent necessitates a very strict environment. Coagulation and biological procedures are used in industries in addition to adsorption, but these treatment methods are unable to meet the mandated level or reduce it to near zero or below 10 parts per billion. Heavy metals are metal elements with a relatively high density in evaluation to water. Heavy metals which include Mercury (Hg), Lead (Pb), Arsenic (As), Nickel (Ni), Cadmium (Cd), and Chromium (Cr) may be risky in combined or elemental forms [2]. Heavy metals are very soluble in the water of our bodies including rivers, lakes, and reservoirs which makes them effortlessly ingested through organic entities. Heavy metals that enter the food chain might also additionally grow to be gathering withinside the human body. Since the maximum of the heavy metals is regularly utilized in industries, people and citizens close to such centres are possible to be uncovered and contaminated. Heavy metals in extra of authorized limits regularly have poor outcomes on humans, different creatures, and the surroundings.

Humans are exposed to high levels of inorganic heavy metals, particularly arsenic, mostly by the ingestion of naturally high quantities of inorganic arsenic in groundwater, food prepared with this water, and food crops irrigated with high-arsenic water sources [3]. Inorganic arsenic that is soluble in water is neurotoxic. Long-term exposure to inorganic arsenic poisoning can lead to chronic arsenic poisoning. According to the levels of exposure, skin cancer and cardiovascular disease are among the impacts that could take decades to emerge. Organic arsenic compounds, which are abundant in seafood, are less hazardous to the body and may be eliminated quickly. As a result, ongoing public health actions to reduce human exposure to arsenic are essential, especially in areas where naturally high levels of arsenic in groundwater exist.

Arsenic, a naturally occurring metalloid, is the 20th most abundant mineral in the earth's crust, the 14th in seawater, and the 12th in the human body, and it is found in over 245 mineral resources, the majority of which are sulfur-containing ores, as well as copper, nickel, lead, cobalt, and other metals [4]. Arsenic and its compounds are extremely mobile in nature [4]. Surface water arsenic contamination is frequently lower than in groundwater. Although groundwater pollution from natural sources is far larger than contamination from anthropogenic sources (human sources), surface water is largely affected by human activities [5]. Concentration of arsenic can vary based on geography, climate, and other factors. Arsenic species are widely present in natural water as a result of distinct inorganic and organic compounds with oxidation states of +5 and +3, the ratio of which is governed by the water's chemical composition and pH levels [6]. Natural/organic arsenic compounds are far more hazardous than inorganic arsenic species, whereas inorganic As(III) is more harmful than As(V) [7] because in natural waters, As(V) is the most stable form, whereas As(III) is oxidised by air oxygen.

Arsenic compounds have been categorised as category 1 carcinogens by the International Agency for Research on Cancer (IARC) [8]. The World Health Organization (WHO) has established a maximum contamination level (MCL) of 10 g/L for arsenic in drinking water. The US Environmental Protection Agency (US EPA) recently reduced the allowable contamination level for arsenic in public water systems to 10 g/L from 50 g/L earlier [9]. However, the allowed maximum contamination level (MCL) of arsenic in drinking water differs by country as shown in Table 1.

Table 1. MCL of arsenic permitted by different countries [10]

Country	MCL (parts per billion)
European Union	10
Malaysia	10-50
Australia	7
France	15
India	50
Vietnam	50
Mexico	50

2.0 ARSENIC REMOVAL METHOD

2.1 Chemical Precipitation

Chemical precipitation stands out as one of the prominent methods for arsenic removal, offering a reliable and cost-effective solution for water treatment. This method capitalizes on the principle of selective precipitation, where specific chemical agents are employed to induce the formation of insoluble arsenic compounds, effectively separating them from the aqueous phase. Chemical precipitation in water and wastewater treatment refers to the transformation of dissolved elements in water into solid particles [11]. The addition of counter-ions to diminish the solubility of arsenic ionic components in water is employed in chemical precipitation to remove arsenic ionic constituents from water. Chemical precipitation is notably appealing because of its low cost, high purity, quick prep time, high homogeneity, well-crystallized output, and low reaction temperature. A solid separation procedure, such as coagulation, sedimentation, or filtering, is always performed after chemical precipitation because metals are often removed as hydroxides, sulphides, carbonates, or phosphates by adding counter-ions to reduce solubility. Furthermore, in the presence of water and carbon dioxide, such reagents are extremely unstable and can be converted into calcium carbonate and arsenic acid for calcium arsenate, whereas amorphous ferric arsenate and crystalline ferric arsenate have low and high stability, respectively, when subjected to a specific condition [12]. Tuning the pH value is a critical aspect of chemical precipitation for arsenic removal. The solubility of arsenic compounds is highly dependent on the pH of the solution. By adjusting the pH to specific levels, it becomes possible to manipulate the chemical equilibrium and promote the precipitation of arsenic species. At lower pH values (acidic conditions), arsenic tends to remain in its soluble forms, such as arsenite (As(III)) and arsenate (As(V)). However, as the pH increases, certain chemical reactions occur that favor the formation of insoluble arsenic compounds. Under slightly alkaline to neutral conditions, arsenic species can react with hydroxide ions (OH⁻) or other metal hydroxides present in the solution, resulting in the precipitation of arsenic hydroxides or metal arsenates.

2.2 Ion Exchange

The versatility of ion exchange resins allows for the customization of treatment protocols to suit varying water compositions and arsenic speciation profiles encountered in different geographical regions. Factors such as resin type, resin regeneration protocols, flow rates, and pH conditions play pivotal roles in optimizing arsenic removal efficiency and operational performance. Furthermore, recent innovations in ion exchange materials and system designs have expanded the applicability and scalability of this technology, offering cost-effective solutions for arsenic remediation in both centralized water treatment facilities and decentralized community-scale systems. The basic notion of an ion-exchange process has been used to produce ion-exchange membranes. Ion exchange is a reversible and stoichiometric process in which one ionic species displaces the other on the exchanger [13]. Unfortunately, arsenite is not retrieved from water by ion exchange; instead, arsenate is extracted since it is simpler to remove owing to its negative charge [12], while arsenite is typically found in water as an uncharged element. In ion exchange approach, there are two factors that may enhance the efficiency of novelty material fabricated which are regenerative strategies and smart monitoring control systems. Innovations in resin regeneration protocols aim to minimize resource consumption and environmental impact while maintaining effective arsenic removal capacity. Novel regeneration agents, recycling processes, and regeneration optimization algorithms have been developed to enhance the sustainability and cost-effectiveness of ion exchange systems. Advances in sensor technology, automation, and data analytics enable real-time monitoring and optimization of ion exchange processes for arsenic removal. Smart monitoring and control systems facilitate proactive management of system performance, early detection of operational issues, and adaptive process optimization to ensure consistent and reliable treatment outcomes.

2.3 Membrane Filtration

Membrane filtration systems can be engineered to target specific arsenic species, such as arsenite (As(III)) and arsenate (As(V)), by optimizing membrane pore size, surface chemistry, and operating conditions. Membrane filtration is nothing more than a physical process caused by a change in concentration or pressure. Because it depends largely on the selective permeability of a membrane, this method is classed as microfiltration, ultrafiltration, and nanofiltration (based on pore size). In general, this approach removes arsenic from polluted water while preventing bacteria from getting

through the barrier. However according to Zakhar et al., , the strategy is unfavourable because arsenite is oxidised to arsenate, which poses a significant risk of membrane damage [10]. Recent advancements in membrane technology have further enhanced the performance and reliability of arsenic removal systems. Novel membrane materials, surface modifications, and module designs have been developed to improve arsenic rejection rates, reduce fouling tendencies, and extend membrane lifespan, thereby enhancing operational efficiency and cost-effectiveness.

2.4 Activated Carbon

Activated carbon is an adsorption process that is simple to use and has a high removal effectiveness at a cheap cost for removing arsenic from contaminated water. This adsorbent has several advantages, including chemical stability [14], which allows it to be modified with low pH solutions and high temperatures; adequate mechanical resistance, which allows it to be used in a packed column water treatment system. To enhance the number of active sites and, as a result, the arsenic adsorption capacity, shape with a large surface area is sought. Integration of activated carbon with other adsorbents, such as metal oxides, ion exchange resins, or biological materials, has emerged as a promising approach to enhance arsenic removal efficiency and address specific water quality challenges. Hybrid adsorption processes leverage the complementary adsorption mechanisms of different materials to synergistically improve arsenic uptake and minimize the impact of competing ions and organic matter. By combining activated carbon with other adsorbents, it is possible to achieve higher arsenic removal capacities and enhance treatment performance under diverse water chemistry conditions.

2.5 Ion Imprinted Polymer

Ion imprinted polymers (IIPs) are made by first generating a ligand-metal complex with an arsenic ion as a template, then polymerizing around the template arsenic ion in the presence of an initiator and a cross-linker, and then extracting the arsenic ions (target ions) from the polymer matrix [15]. Polymeric chelating ligands could be used to remove the metals from wastewater [16]. The features of arsenic ion-imprinted polymers are notable for their great selectivity towards the target ion (arsenic ion) due to a memory effect caused by the fabrication procedure [17]. Furthermore, they are thermally stable and physically durable [18]. This great selectivity is due to two key factors: the ligand's affinity for the imprinted arsenic ion and the size and shape of the created cavity [19]. Recently, there is a growing interest in integrating ion imprinted polymers into point-of-use devices for decentralized arsenic removal at the household or community level. By leveraging the simplicity and versatility of ion imprinted polymers, point-of-use devices offer scalable and cost-effective solutions for treating arsenic-contaminated water in resource-limited settings, thereby improving access to safe drinking water and public health outcomes. Different approaches of synthesizing give variation of yield of novelty material such as bulk polymerization, suspension polymerization and simple precipitation.

2.6 Bulk Polymerization

Bulk polymerization is the process of combining monomers, cross-linkers, initiators, and templates in a reaction vessel to produce IIPs. This technique of synthesis allows for the production of polymers in a short amount of time using very simple methods and no specialised equipment [20]. However, these activities result in the inability to completely remove ion templates, as well as the loss of certain binding sites and a considerable reduction in process yield [21]. Abu Samah et al. reported about 90% of arsenic able to be removed within 5 minutes of agitation when bulk polymerization was implemented [1].

2.7 Suspension Polymerization

Suspension polymerization is a heterogeneous polymerization method in which two immiscible phases are mixed. The first phase is a continuous phase, which is usually water, and the second phase is a dispersed phase that contains the monomers, cross-linker, initiator, and template ion. In the presence of a stabiliser, droplets of the dispersed phase are suspended in the continuous phase and polymerized. This polymerization is a fast way to make IIPs with precise particle size and shape control. However, no percentage of arsenic removal was reported by Cejner et al. [22].

2.8 Simple Precipitation

This method is quite like bulk polymerization, with the distinction that it requires a much larger amount of solvent. Before the synthesis of the IIPs begins by precipitation method, the reaction mixture is basically made up of a single-phase including monomers, ion template, and initiator all solubilized in a considerable volume of porogen [20]. Jagirani et al. investigated that by utilized this approach, approximately 85% trivalent arsenic has been removed within 15 minutes of agitation [23].

3.0 PARAMETERS THAT AFFECT THE ADSORPTION CAPACITY OF As-IIP

3.1 pH Values

pH is the most significant parameter that could affect the adsorption capacity and surface change of the adsorbent as well as the distribution of the adsorbent in the solution. The optimum pH observed is in the range from pH 8 onwards. At neutral pH, $\text{As}(\text{OH})_3$ is the dominant species while $\text{As}(\text{OH})_2\text{O}^-$ represents a small fraction (1.0%) and the contribution of $\text{As}(\text{OH})\text{O}_2^-$ and AsO_3^- is insignificant [24]. In acidic medium, the solution was rich with H^+ ion which compete with

the arsenic ions to attach on the surface of the arsenic-ion imprinted polymer adsorbent. Meanwhile in alkaline/basic medium, adsorption process reduced because of formation of precipitation of As^{3+} and OH^- ions in solution.

3.2 Temperature

Temperature has a significant influence on the mobility of ions in solution, as well as the contact and collision between ions and adsorbent when they move freely in the solution, therefore a suitable temperature is essential for optimal adsorption. Maximum adsorption was usually obtained at room temperature, and as the temperature rose, adsorption decreased [25]. The reason is as the temperature rises, the active sites expand, making selective adsorption more difficult, as well as the formation of unstable bonds between the arsenic-ion imprinted polymer (As-IIP) adsorbent and arsenic ions [26].

3.3 Contact Time

As the contact time between the arsenic-ion imprinted polymer (As-IIP) and the arsenic ions grew, the adsorption process increased as well. Because arsenic ion adsorption is highly influenced by contact time, this is the case. However, Song et al., found that the removal rate of As(III) reached more than 40% in the first 0.5 hours and gradually neared the balance of adsorption and desorption in roughly 11 hours when they ran an experiment from 0 to 25 hours at different temperatures (313K, 303K, and 293K) [27]. The adsorption rate is initially high due to many adsorption sites on the arsenic-ion imprinted polymer adsorbents' surface, great affinity of the imprinted cavities for the target analyte (arsenic ions), and structural matching between the target analyte and the imprinted cavities. The adsorption rate remains constant because there are more readily available adsorption sites, and the adsorbent surface has a lower mass transfer constraint.

3.4 Adsorbent Dose

The percentage of adsorption capacity increased proportional with the adsorbent dosage, as the adsorption mass per unit of adsorbent drops. As the dosage increases, the unsaturated adsorption active site decreases, resulting in a decrease in adsorption per unit. Sadani et al. did an experiment using As(V)-IIP under the fixed condition of a starting concentration of As^{5+} of 6 mg/L, found that introducing more adsorbent increases adsorption efficacy from 30% to 80% because more adsorption sites are available [28]. Furthermore, the adsorbent surface may saturate, resulting in a lower percentage of adsorption capacity, or a longer contact time may be necessary to adsorb all existing ions.

3.5 Initial Concentration of Arsenic Ion

The initial concentration is usually measured in parts per million (mg/L) or parts per billion (g/L), but unit parts per million is preferred. Because of interaction or collision between the arsenic ions and the arsenic-ion imprinted polymer adsorbent increases, the concentration of the solute (arsenic ions) increases, thus the adsorption capacity.

3.6 Competitive Ions

Some ionic species are apparently naturally present in water, and they may obstruct arsenic adsorption through complexation or competitive binding. The tolerance limits of foreign ions, according to [29] Abdullah et al., show a consistency of less than 5%. Because it was determined that synthesised As-IIP has the potential to extract and pre-contrast the hazardous arsenic ions from genuine samples containing many ions, the foreign ions had almost zero effect under the given conditions [29].

3.7 Eluent Type on The Recovery Process

Hydrochloric acid (HCl), nitric acid (HNO_3), sodium hydroxide (NaOH), methanol (CH_3OH), and acetonitrile (CH_3CN) are common desorption agents used in the recovery process. [25] Mafu et al. found that the mixture of hydrochloric acid and nitric acid (1:1, v/v) showed the highest percentage of arsenic recovery in an experiment using various eluent mixtures on the recovery process of adsorbent As-imprinted polymer (97%) [25].

4.0 CONCLUSION

In conclusion, valorisation of arsenic removal method has been extensively researched and discussed. The potential of arsenic removal method is due to its characteristics, which allow for selective identification of target ions. In addition, the effects of pH, temperature, contact time, adsorbent dosage, initial concentration of arsenic ion, competitive ions, and eluent type on the recovery process were addressed in this review work.

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6.0 CONFLICT OF INTEREST

The authors declare no conflicts of interest.

7.0 AUTHORS CONTRIBUTION

N. A. A. Halem (Writing - original draft; Formal analysis)

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