ARSENIC CONTAMINATION IN WATER AND THE RECENT REMOVAL TECHNIQUES

Abstract

Arsenic is found to be one of the most hazardous element in the chemical world and its presence in drinking water is a matter of great concern. There are several reports on contamination of water by arsenic (As) in groundwater as well as in drinking water in different rural and sub-urban areas where expensive water treatment techniques are not affordable. Arsenic exists in organic as well as inorganic forms in aqueous system with varying valence states which is mainly responsible for its variable behaviour and toxicity. Chronic arsenic exposure has devastating health effects such as cardiovascular diseases, cancer and the eventual death. Thus, the removal of arsenic from drinking water is strongly recommended. Many methods of arsenic removal have been studied, but every available process has its own limitations and it can serve to a limited extent only. This chapter summarizes the effects caused by arsenic contamination and the methodologies currently being adopted for its removal from drinking water.

Keywords: toxicity, arsenic, water

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I. INTRODUCTION

Arsenic is a metalloid which is brittle in nature and greyish white in colour. It is generally found in combination with sulphur, oxygen and iron. Arsenic has a capability to mobilize under a wide range of pH values (pH =6.5-8.5) which is typically found in groundwater where it is present mainly in four chemical forms having oxidation states -3, 0, +3 and +5. However, it is mostly found in earth's crust as trivalent arsenite, AsO_3^{3-}, As(III) and pentavalent arsenate, AsO_4^{3-}, As(V). Arsenic in both the forms is found to be poisonous in nature[1](Fig. 1).

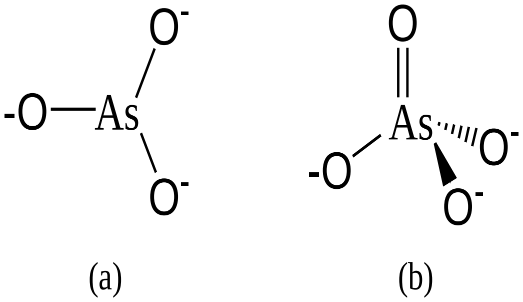


Figure 1: Structures of (a) arsenite and (b) arsenate.

II. SOURCES

Arsenic is released in the environment by both natural and man-made activities. Natural sources of arsenic include volcanic ash and weathering of arsenic containing minerals and ores. However, most of its dispersion in the environment comes from man-made sources which include mining, combustion of fossil fuels and commercial uses. The main uses of metallic arsenic are in strengthening alloys of copper and lead used in car batteries and in smelting processes for ores of many metals such as cobalt, gold, lead and zinc. It is also used as wood preservatives. The greatest threat to public health arises mainly from arsenic which becomes contaminated in drinking water[2].

III. EFFECTS OF ARSENIC POISONING

In recent decades, a huge number of effects have been reported because of the widespread presence of arsenic in groundwater. Human exposure to arsenic occurs through ingestion, inhalation or skin adsorption among which ingestion is the most predominant form of exposure. High doses of arsenic can cause enormous toxic effects either through gastrointestinal symptoms such as poor appetite, vomiting, diarrhoea etc., or through disturbances in cardiovascular and nervous systems such as muscle cramps and heart malfunction leading to even death. The toxic effects are strongly dependant on the form in which arsenic is present.

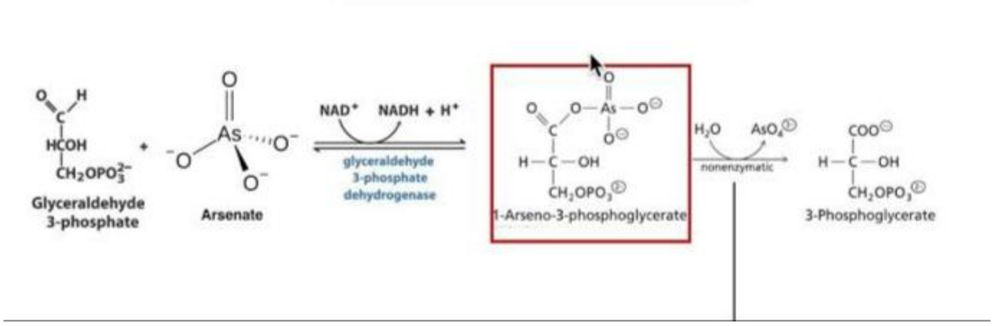
The presence of arsenic is not indicated by any change in taste, odour or visible appearance of water even in high concentrations. The detection of arsenic in drinking water becomes therefore very difficult and requires some particular analytical techniques. In most of the developing countries, the drinking water used is with high arsenic concentrations even several times higher than the recommended limit given by World Health Organization (WHO) which is 10 millionths of a gram per litre of water (10 μg/L)[3].

The first visible symptom caused by arsenic poisoning is abnormal skin pigmentation known as *melanosis* followed by hardening of palms and soles known as *keratosis*. Prolong exposure may result skin de-pigmentation developing white spots known as *leukomelanosis*. Long-term exposure (more than ten years) to arsenic in water can lead to problems in kidney and liver function followed by damage of internal organs including lungs, kidney, liver and bladder, togetherly known as *arsenicosis*. However continuous exposure (more than 20 years) to arsenic may also lead to variant forms of cancer [3,4]. Thus, strategies to avoid and alleviate arsenic contamination in ground water need to be developed to reduce the health risk associated with it.

IV. MECHANISM OF ARSENIC POISONING

The mechanism of arsenic poisoning can be described with the help of the following ways:

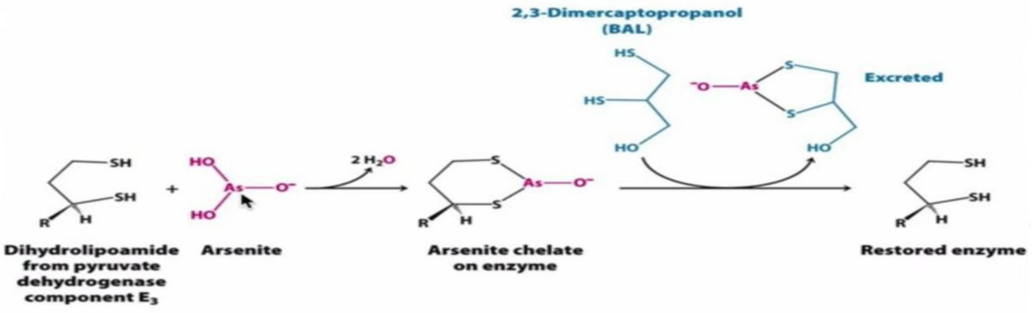
1. **Glycolysis:** In this reaction mechanism, arsenate (AsO_4^{3-}) takes the position of phosphate (PO_4^{3-}) of the Glycolysis cycle and produces 1-arseno-3-phosphoglycerate instead of 1,3-bisphosphoglycerate (Scheme 1). Generally, in glycolysis process, the enzyme phosphoglycerokinase converts 1,3-bisphosphoglycerate to 3- phosphoglycerate by producing ATP. Here arsenate producing 1-arseno-3- phosphoglycerate undergo non-enzymetic hydrolysis to 3-phosphoglycerate by short change glycolysis one ATP per arsenate[5].



↓
Short- change glycolysis
1 ATP per Arsenate

Scheme 1: Glycolysis cycle, arsenate takes the position of phosphate[4].

2. **TCA cycle:** In this mechanism, two thiol groups actually attach to the arsenic and form arsenite chelate on enzyme by removal of water as shown in scheme 2. The arsenite chelate on enzyme is very much poisonous and it stops the TCA cycle. Here 2,3-dimercaptopropanol acts as a antidote and restores the enzyme[6].



Scheme 2: TCA cycle in which arsenite acts as a poison

3. **Removal techniques:** Various methodologies have been developed for arsenic removal from drinking water. The commonly used physical methods include ion-exchange, adsorption, electrochemical techniques and membrane process whereas the chemical methods involve coagulation, ozone oxidation, filtration and precipitation. Some biological methods such as bacterial removals and phytoremediation have been also adopted[7].

- **Adsorption:** Adsorption is found to be one of the most effective methods for arsenic removal from drinking water. In this process, the most commonly used adsorbents are activated alumina, activated carbon, functional resin and metal oxide. In this process of adsorption, purification of water depends on specific surface area and surface energy of the adsorbent. Strong adsorption ability depends on the properties of the material which is being used as the adsorbent. Therefore several researchers are involved in developing high performance adsorbents.

  Xiao et al.8 used activated alumina as adsorbent where the soluble arsenic in the water are adsorbed on the aluminous octahedron crystal lattice sites. The maximum adsorptive capacity of activated alumina is 5-24 mg at equilibrium arsenic concentrations of 0.05-0.2 ppm. However, Huang and Vane9 and Reed et al.10 used activated carbon for arsenic adsorption with various metal compounds—impregnating iron compound and zirconium onto activated carbon. Metal oxides show strong adsorption capability due to their high surface area in comparison to many inorganic ions. Manning et al.11 used amorphous hydrous ferric oxide, Raven et al.12 used crystalline hydrous ferric oxide (ferrihydrite), Jackson and Miller13 used α-FeOOH, Jain and Loeppert14 used hematite whereas Goldberg[15] used magnetite and Goethite for arsenate and arsenite removal.

  Altundogan *et al.*[16] used liquid phase of red mud, Brunori *et al.*[17] used red mud and Fuhrman *et al.*[18] used seawater-neutralized red mud (bauxsol)[19] and chemically modified and activated bauxsol (with ferric sulfate or aluminum sulfate)[20] as adsorbents for arsenic removal. Natural zeolites, volcanic stone, cactaceous powder and clinoptilolite-containing rocks are also applied for arsenic removal[20]. Lorenzen *et al*.[21] used coconut-shell carbon as well as pretreated coconut-shell carbon with Fe(III) as adsorbent for As(III) and As(IV).

Buswell[22] first reported the arsenic removal with the help of metal salts. The most commonly used metal salts are aluminium salts (alum) and ferric salts such as ferric chloride or ferric sulphate out of which, ferrous sulphate is found to be less effective. Excellent arsenic removal is possible with both ferric or aluminium salts, with laboratories reporting over 99% removal under optimal conditions[23-25]. However, Bajpai and Chaudhuri reported arsenic removal by oxidizing As(III) to As(V) in contaminated groundwater using greener air, pure oxygen or ozone with 54–57% efficiency[26].

- **Ion exchange:** Various synthesized ion-exchange resins, specially strong base anion exchange resins can be effectively used for arsenic removal from water, with less than 1ppm concentration. Several resins are developed by different groups in this regard, for example Matsunaga[27] and Balaji[28] used an iron(III) and zirconium(IV)-loaded chelating resin containing lysine and diacetic acid based functional groups for the adsorption of As(III) and As(V). Similarly, Peleanu *et al*.[29] also used iron-loaded iminodiacetate chelating resin and a silica/iron (III) oxide composite material for As(V) remediation. Wasay *et al.*[30] used La(III) and yttrium carbonate resin to remove arsenic in a p^H range of 4 and 9 with 98% and 100% efficiency. Chanda *et al.*[31] used impregnated iron whereas Lenoble *et al*.[32] used manganese dioxide, loaded on a polystyrene matrix anionic commercial resin for simultaneous removal of both arsenite and arsenate forms.

- **Coagulation:** Aluminium based coagulation disinfected with chlorination is one of the most commonly used method for arsenic removal[7]. In addition, Yuan et al.[33] investigated a combination method between ferric sulphate coagulation and sand filtration which was found to be much more economic and effective. Scott *et al*.[34] reported the full-scale study of the coagulation process by using ferric sulfate at the Metropolitan Water District of Southern California and achieved high arsenic removal of over 95%. Similarly, Liu *et al*.[35] reported the enhanced co-precipitation of arsenite by the coupling of $FeCl_3$ with permanganate as the coagulant.

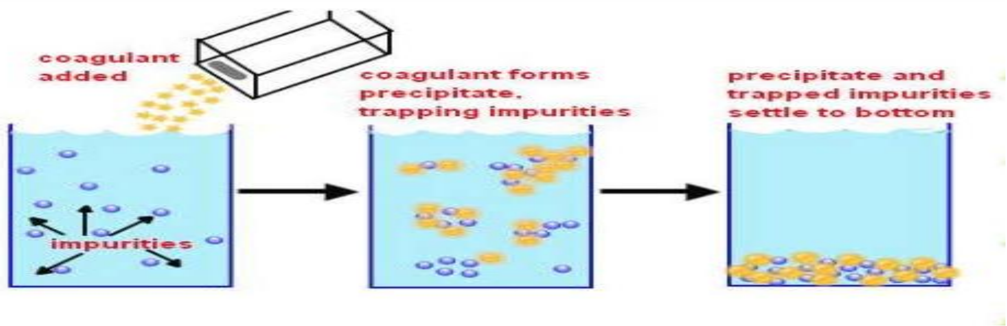


Figure 2: Removal of Arsenic through coagulation[36].

- **Filtration:** The conventional filtration process uses sand, activated carbon or paper that retains the solid on its surface and allows the liquid to pass through it. In case of filtration processes for arsenic removal, red soil (rich in oxidized iron), clay minerals, iron ore, scrap iron or fillings and cellulose materials (containing jute and cotton fibers) are generally used. Nikolaidis and Lackovic[37] reported iron filing filter system with 95% efficiency.

- **Membrane process:** Several natural and synthetic membranes are highly used for arsenic removal as they are easy to produce, simple to operate and even easy to maintain. These membranes have a huge number of microscopic pores that act as selective barriers and allow only some particular constituents to pass through. Membrane filtrations are classified on the basis of applied pressure. High driven pressure (50 to 1,000 psi) processes include Reverse Osmosis (RO) and Nano Filtration (NF), while low-pressure processes (5 to 100 psi) include Micro Filtration (MF) and Ultra Filtration (UF).

  Clifford *et al.*[38], Fox[39] and Waypa *et al.*[40] used cellulose acetate based RO membrane for arsenic removal. Similarly, Sato *et al.*[41] also used cellulose acetate and polyamide type membrane. However, Waypa *et al.*[42] reported arsenic removal by a thin-film composite film NF membrane which is found to be much more efficient. Vrijenhoek and Waypa[43] also used porous polyamide thin-film composite membrane (NF-45) for the removal of arsenic. Han *et al.*[44] reported the use of mixed ester of cellulose acetate and cellulose nitrate MF membrane with a pore size of 0.22 and 1.22 μm as well as a combination of both ferric chloride and ferric sulfate and cationic polymeric flocculants as a membrane for arsenic removal.

- **Electrocoagulation:** Electrocoagulation is a simple and effective method where the flocculating agent is formed by electrooxidation on anode, which is made up of metal, generally iron or aluminum. Parga *et al.*[45] and Hansen *et al.*[46] reported maximum arsenic removal (more than 99.6%) with aluminum and iron electrodes. Maldonado-Reyse *et al.*[47] reported a system where both aluminum and iron are used in the same electrochemical cell and found 78.9% to more than 99.6% efficiency for different arsenic concentrations. Kumar *et al.*[48] and Parga *et al.*[49] reported the removal efficiency of both arsenic species with the help of iron electrode forming amorphous iron oxide and hydroxide complexes which was more than 90% at different p^H values at a constant current of 0.5-30 μA.

- **Oxidation methods:** Oxidation method is accompanied by conversion of soluble arsenite to arsenate in the solution which is particularly important for groundwater, followed by removal methods such as adsorption, coagulation or ion exchange. In addition to atmospheric oxygen, different oxidants such as activated chlorine, chlorine dioxide, hydrogen peroxide etc. have been used by different groups for the oxidation of arsenite in water[50-52].

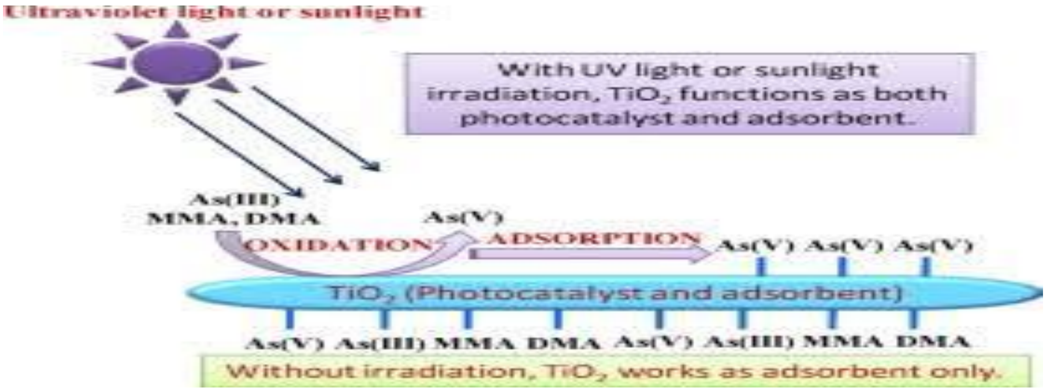


Figure 3: As removal by TiO_2 beads using UV rays[54].

Kim *et al*.[53] reported oxygen and ozone for the oxidation of As (III). Miller et al synthesised a TiO_2 coated chitosan bead and applied in the oxidation process. They observed a higher efficiency for the solution with an exposure to UV radiation than that for the solution which was not exposed to UVlight(Fig. 3)[54].

Criscuoli et al. reported MnO_2 coated nanostructured capsules with higher efficiency than conventional oxidation methods when the arsenic concentration of the water is low. More than 99% oxidation of arsenite was achieved by this method at 100 to 300 ppb of arsenic concentration. However, with increased arsenic concentration (700 and 1000 ppb), oxidation efficiency is found to be decreased[55].

- **Bioremediation:** There are two types of biological methods for arsenic removal from water. The first of these uses cultured bacteria to oxidize whereas in the second method, anaerobic sulphate-reducing bacteria and other reducing bacteria are used to precipitate arsenic as insoluble arsenic sulphide complexes. Elson *et al*.[56] and Mcafee *et al*.[57] used chitosan, chitin, chitosan/chitin mixture and biomass from *Rhizopus oryzae* for arsenic removal from contaminated water.

Dead fungal biomass of *Lessonia nigrescens* (an algae), *Aspergillus niger* (fungus) coated with iron oxide, *Penicillium purpurogenum* were used for arsenic removal by several workers[58-63]. In addition, pre-treatment of these species with hexadecyl-trimethyl ammonium bromide dodecylamine and several cationic polyelectrolyte was also applied to improve the arsenate biosorption[58-63]. Most commonly used bacterial species include *Geospirillum arsenophilus*, *Geospirillum barnesi, Desulfutomaculum auripigmentum, Bacillus arsenicoselenatis and Crysiogenes arsenates*[64-68] which are known as dissimilatory arsenate reducing bacteria or arsenate respiring bacteria. Specific indigenous bacteria known as "iron and manganese oxidizing bacteria" are also used effectively for the biological oxidation[69-71](Fig. 4). The biological oxidation by two bacteria, *Gallionella ferruginea and Leptothrix ochracea,* has also been found to be very effective for the removal of arsenic from groundwater[72].

Figure 4: Removal of arsenic by using coliform bacteria[73].

- **Phytoremediation:** Phytoremediation is a new technique adopted for arsenic removal from groundwater where certain plant species are used to accumulate arsenic in their aerial tissue. Visoottiviseth *et al*.[74] used cottonwood, sunflower, Indian mustard, maize, ryegrass, prairie grasses and hyper-accumulating ferns for the purpose. Young plants of water lettuce, *Garcinia combogia* (indigenous plant), *Pista stratiotes* L. (aquatic plant), water hyacinths (*Eichhornia crassipes*) and dried roots of water hyacinths (harvested from a pollution free pond and hydroponically cultured) are also used for the simultaneous and rapid remediation of arsenic along with other heavy metals from polluted water at effective concentration[75,76].

  Recently *Pteris vittata, P. cretica,* orange juice waste (containing cellulose, pectins, hemicellulose, chlorophyll pigments and other low molecular weight compounds like limonene) residue and phosphorylated cross-linked orange waste are also used for arsenic removal[77-79]. Murugesan *et al*.[80] reported the use of industrial waste autoclaved tea fungal mats as well as tea fungal with pretreated $FeCl_3$ for arsenic removal from groundwater. Wasiuddin *et al*.[81] reported the application of human hair to remove arsenic due to their ability to absorb arsenic from contaminated water.

- **Nanotechnology:** Now-a-days, nano particles are highly used in the arsenic removal in drinking water. Tang *et al*.[82] synthesized ultrafine α-Fe_2O_3 nanoparticles and applied in the removal of arsenic from contaminated water. The kinetics study revealed that both forms of arsenic, As(III) and As(V), can be removed rapidly and very effectively with the help of these nanoparticles.

V. CONCLUSION

Arsenic contamination in drinking water emerges as a major problem around the world. As the presence of arsenic in drinking water has a huge impact on human health, in present literature survey, we tried to elaborate various remediation method based on conventional as well as modern technologies for the removal of arsenic. But we should bear in mind that the various approaches described have their own advantages and disadvantages. The various methods described are quite effective and safe for removal of arsenic from water, but need more promotion for wider implementation in the needy areas. In addition, care must be taken in cleaning the arsenic removing filters regularly and disposing off the sledge generated by these filters properly.

Arsenic-free drinking water is a necessity for human health, so we should emphasize on the purification of water through the several discussed techniques. Among all the techniques, the polymeric support technique is found to be more effective which offers innovative materials for arsenic separation. In this technique, designing functional polymers is a key requirement; it can be assisted by chemical modification and graft modification as well. High degree of binding groups may be incorporated through this technique. However, research efforts are still needed to develop cost-effective, rapid, beneficial and reproducible technologies for arsenic removal.

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