

Biopolymer based hydrogels for arsenic removal

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Water contamination by arsenic has led to serious human-health hazards. Millions of people die every year in several countries of the world because of arsenic-rich groundwater. To date, adsorption by activated carbon, iron-based adsorbents, zeolite and hydrogels have been widely used for arsenic-ion removal. Among these, adsorption by renewable resource-based hydrogels has ignited great interest because of biocompatibility, biodegradability, low cost and non-toxicity properties. This article discusses the biopolymer-based hydrogels like cellulose, chitin, pectin and chitosan for arsenic removal. It also discusses the arsenic chemistry, health hazards caused by arsenic, pros and cons of various techniques used for arsenic removal and different mechanisms involved in arsenic adsorption. Though hydrogels are capable of bringing down the arsenic level below the WHO limit, their reusability, recovery of industrially important metal ions from hydrogels and the mechanical stability of hydrogels under harsh conditions should be given more focus in future research.

Keywords: Adsorption, arsenic, biopolymer, hydrogels, reusability.

AMONG the topmost 20 hazardous heavy metals, arsenic (As) occupies the first place¹. The name 'arsenic' is derived from the Latin arsenicum, meaning pigment, as it is mainly found as a compound in the earth's crust, like iron arsenide sulphide. Arsenic exists in four oxidation states: As^{5+} , As^{3+} , As^0 and As^{3-} ; however, the most common states of arsenic found in water are As(III) and As(V) species. Arsenic exists in organic and inorganic forms. Organic forms of arsenic are mainly found in surface water, produced by biological activity, while the inorganic form is most likely to be found in reducing anaerobic environments (such as groundwater)².

Arsenate and arsenite exist in the ratio of about 70 : 30 in natural water. The arsenate/arsenite ratio can differ in groundwater (depending on oxidizing or reducing conditions). As^{3+} is a hard acid while As^{5+} is a soft acid; they form complexes with hard bases (sulphides) and hard acids (oxides and nitrogen) respectively. Environmental forms of As include arsenious, arsenic acids, arsenites, arsenates, methylarsenic acid, dimethylarsenic acid,

arsine, etc.^{3,4}. Nowadays, research is mainly focused on the removal of As^{3+} and As^{5+} ions from contaminated water because these ions are more common in water and are more toxic in nature (Figure 1).

Among the two forms, arsenite is more toxic than its coexisting form because of the high mobility of the former in water. Redox potential and pH are the important factors that control arsenic adsorption. Under reducing atmosphere, the uncharged H_3AsO_3^0 predominates (at pH less than 9.2), while under oxidizing condition H_2AsO_4^- and HASO_4^{2-} dominate, depending on the pH value. Figure 2 shows the distribution of As(III) and As(V) species as a function of pH^{5,6}.

More than 150 million people are at high risk because of arsenic-contaminated water. The most affected countries across the world are Bangladesh, India, China, Myanmar, Nepal, Pakistan and Vietnam countries. Arsenic-contaminated water is considered to be the most serious problem in Bangladesh and hence, much of the research has been focused in this area. The population in Bangladesh is mostly affected by arsenic-contaminated water⁷. Arsenic ranks 20th in natural abundance and is mainly found in combination with sulphur, oxygen and iron. Weathering reactions, biological activity, volcanic emissions and anthropogenic activities (mining activity, fossil-fuel combustion, use of insecticides, pesticides and herbicides) are some of the pathways for environmental arsenic contamination in nature^{8,9}.

Arsenic is toxic in nature, especially the inorganic forms such as AsCl_3 and H_3AsO_3 . Arsenic enters into the human body either by direct or indirect consumption (Figure 3). Effects of toxicity of arsenic on human health have been studied in various As-contaminated regions. High levels of arsenic exposure leads to arsenicosis, and its severity depends upon the dose and number of years of exposure to arsenic^{10,11}. Table 1 gives the allowable limits for As in potable water for various countries. According to the World Health Organization (WHO), the permitted arsenic level in potable water is 10 $\mu\text{g}/\text{l}$. However, in Bangladesh and China, the allowed arsenic level in potable water is 50 $\mu\text{g}/\text{l}$ according to earlier WHO guidelines^{3,12}.

Several techniques are available for arsenic removal like ion exchange, filtration, floatation, etc. (Figure 4)^{13,14}. Table 2 lists the advantages/disadvantages of the above-mentioned strategies³. There is an urgent need for the

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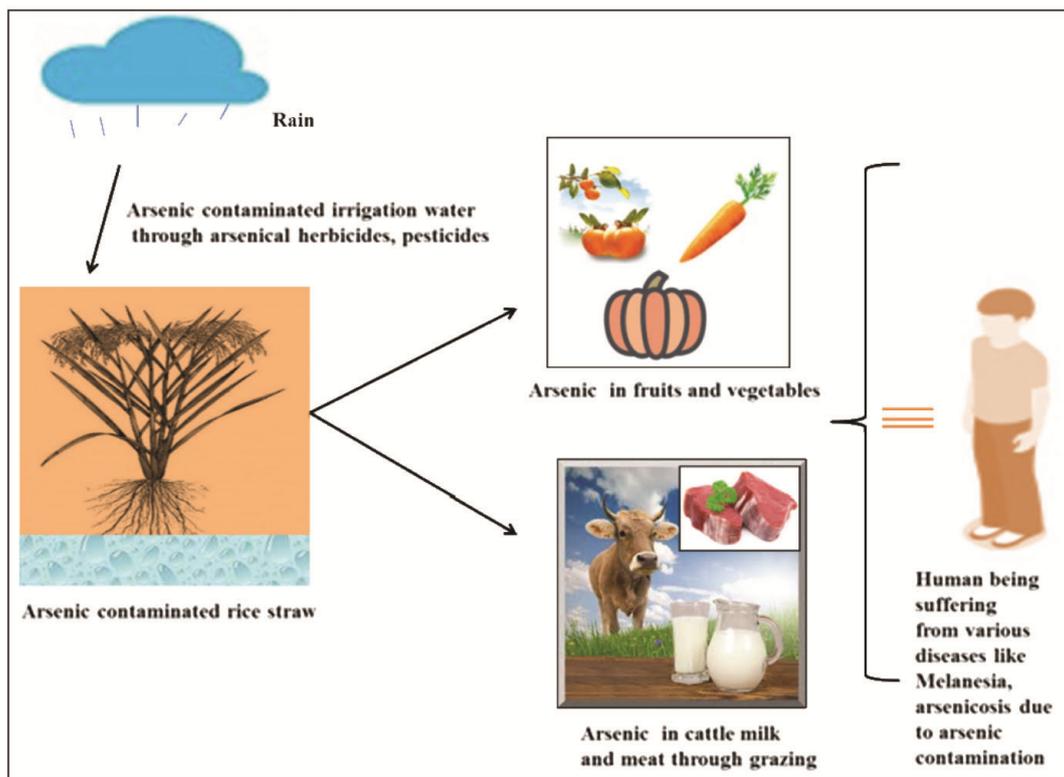


Figure 3. Schematic diagram showing the transfer of arsenic to human beings through the food chain.

Table 2. Pros and cons of various technologies used for arsenic removal³

Technology	Advantages	Disadvantages
Oxidation/precipitation	Simple, low-cost, can oxidize other impurities and kills microbes	Effective for As(V) removal
Coagulation/co-precipitation	Low cost, easy to operate, effective at various pH values	Further treatment is required, pH adjustment is required
Sorption and ion-exchange techniques	pH-independent, exclusive ion-specific resin to remove arsenic	High cost, high-tech operation and maintenance, difficult to remove As ³⁺
Membrane techniques	Highly efficient, no solid waste is produced	

used for arsenic removal^{18–25}. Table 3 gives the pros and cons associated with different adsorbents other than hydrogels.

Arsenic remediation by hydrogels

Recently, biopolymeric hydrogels for arsenic adsorption have gained considerable perception because of unique advantages like low cost, non-toxicity, biocompatibility and biodegradability properties²⁶. Hydrogels are three-dimensional porous structures capable of absorbing huge amounts of H₂O because of polar functionality²⁷. Due to polar functionality, metal ions can form stable complexes with the polar groups and hence can be removed from contaminated water. The high flexibility, elasticity and permeability of hydrogels can be attributed to their high

water-absorption ability. Hydrogels with preferred properties can be achieved by adjusting various synthesis factors like reaction temperature, amount of monomer, catalyst and crosslinker. Hydrogels can be prepared via copolymerization, grafting, semi-interpenetrating polymer network (semi-IPN) and IPN technologies²⁸.

Hydrogels are also termed as ‘smart gels’ because of their sensitivity towards various stimuli like pH, ionic strength, temperature, etc. These distinct features make hydrogels efficient in various fields like biomedical, agricultural, sensing and industrial applications. Hydrogels can be synthesized in various physical forms like beads, microgels, nanogels, cryogels or aerogels. Different kinds of biopolymer hydrogels are well reported in the literature for heavy metal removal. Extensive research has been conducted on natural polymer-based hydrogels for arsenic removal and most of the natural polymers used

Table 3. Advantages and disadvantages of various adsorbents used for arsenic removal³

Adsorbent	Arsenic species	Efficiency (%)	pH	Advantages	Disadvantages
Alumina manganese oxide	As(III)	94	Neutral pH	Also effective in removing other toxic metals	Requires long contact time
Aluminum alum	As(III) and As(V)	96	6.6	Low cost and simple operation	Toxic sludges, pre-oxidation is required for high removal efficiency
Ferric chloride	As(III) and As(V)	>90, often 95 or more	Wide range	Effective at a wide range of pH values, low cost, simple operation	Pre-oxidation is required, water should have low concentration of phosphate and silicate ions. In addition, for the removal of flocs, filtration may be required at the first step
Granular ferric hydroxide	As(III) and As(V)	More than 95	5.5–9	Low maintenance, toxic-free waste, safe technology and simple operation	Pretreatment with iron needed to avoid clogging of filter bed
Activated alumina	As(V)	98	Bangladesh water tested	–	–
Wood charcoal	As(V)	97--99		High removal efficiency	Very tedious
Anion exchangers	As(V)	99	Tap water	As(V) removal efficiency is very high	Sulphate and nitrate exchange before arsenic, TDS, selenium and fluoride can also decrease the life of resin
Mesoporous anion trap (Cu–EDA–Si)	As(V)	98.5	Between 5 and 6	High arsenic removal	High-tech operation

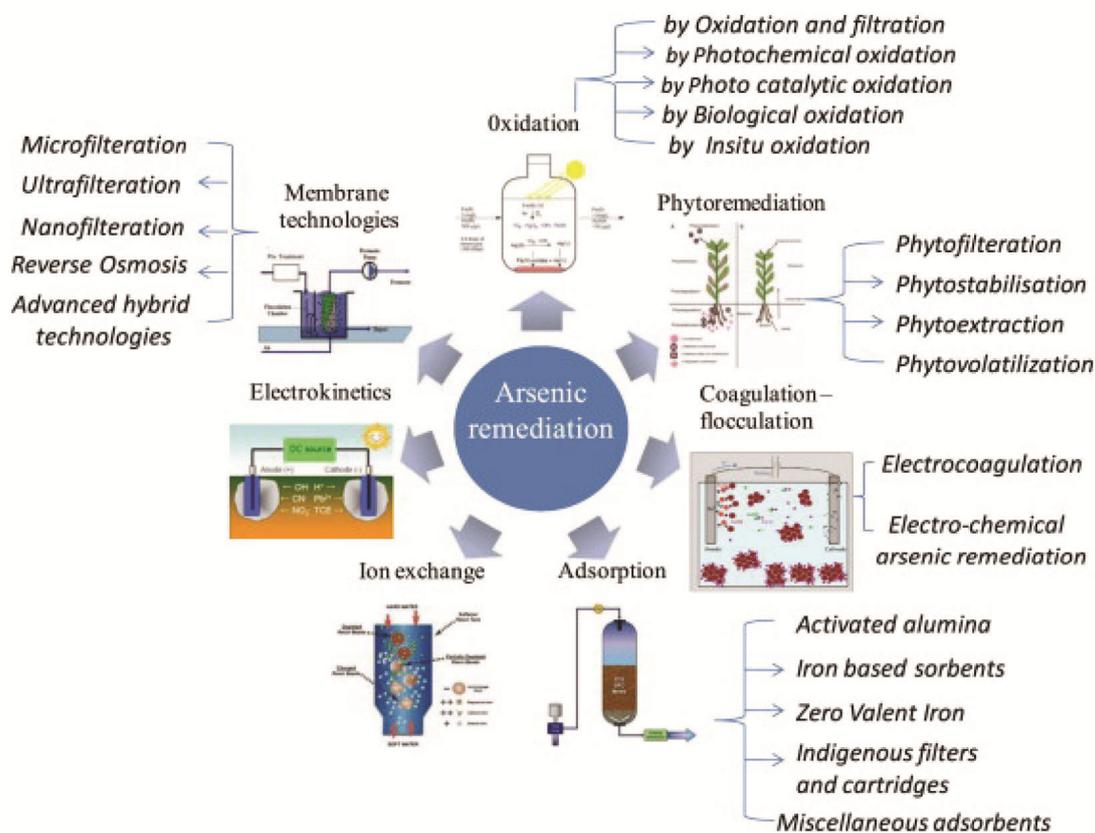


Figure 4. Various techniques used for removal of arsenic from soil and water. (Reprinted from Singh *et al.*⁷, © 2015, with permission from Elsevier.)

Table 4. Various mechanisms for arsenic removal by renewable hydrogels

Biopolymer hydrogels	Mechanism	Reference
Zerovalent/chitosan foam	Adsorption-coupled reduction mechanism of ICCFs on As(III) and As(V)	34
As(V) sorption on molybdate-impregnated chitosan beads	Complex formation between arsenates and molybdate ions	35
Cellulose/Fe ₃ O ₄ ·NH ₃	Electrostatic interaction	36
Hydrogel–biochar composite	Electrostatic interaction	37
Chitosan beads immobilized with iron	Inner sphere complex formation for As(III) at pH less than 9 and electrostatic interaction at high pH	38
Iron oxyhydroxide–chitosan nanostructure	Complex formation	39

are of polysaccharide origin. Besides, biopolymeric hydrogels are used in different sectors like hygiene products, agriculture, biomedical materials, heavy metal ions, dyes, biosensors, etc.^{29–33}.

Several mechanisms of arsenic adsorption have been reported in the literature like electrostatic interactions, complex formation and physical adsorption (Table 4)^{34–39}. As evident from the literature, the key mechanisms for arsenic adsorption are electrostatic interactions and complex formation of heavy metal ions with the polar groups. Besides, the ion exchange mechanism has also been reported by some researchers. The complex mechanism of arsenic remediation by hydrogels has been reported using FTIR-spectroscopic technique. The pH also influences hydrogel performance.

Biopolymers like sodium alginate, chitosan, chitin, pectin, cellulose and hemicellulose are widely used for arsenic removal. For instance, radiation-grafted polyvinyl alcohol and polyvinyl alcohol/polysaccharide blend hydrogels have been synthesized by Chowdhury *et al.*⁴⁰ The prepared materials showed good adsorption efficiencies for both As³⁺ and other heavy metals (Mn²⁺, Cr²⁺, Fe³⁺, Ni²⁺, Cu²⁺ and Pb²⁺). The TiO₂ nanoparticles reinforced chitin hydrogel was synthesized for As(V) removal⁴¹ and the study revealed that inclusion of TiO₂ enhanced the adsorption capacity of As(V). In another study, hydrogel-rice husk-derived biochar composite was used for As(V) adsorption⁴². Polyethylenimine and ferric ion-coated coffee powder (coffee-PEI-Fe) hydrogel was synthesized for As(V), Cu(II) and P(V) ions removal⁴³. Hybrid materials prepared by immobilizing oxides of Fe and Mn into a konjac glucomannan have been used for the removal of As(III) from contaminated water. The effect of varying pH and of coexisting anions on arsenite elimination was also studied in detail⁴⁴. Cellulose-g-poly(*N,N*-dimethyl aminoethyl methacrylate) hydrogel for arsenic and *F-* was reported by Meng *et al.*⁴⁵. The adsorption characteristic of modified hydrogel was also studied at various pH values. The modified cellulose hydrogel showed high adsorption capacity compared to other reported adsorbents (AsO₄³⁻ is 88.99 mg g⁻¹). Calcareous soil-alginate composites for Fe³⁺, Mn²⁺ and As⁵⁺ adsorption were synthesized by El-Sherbiny *et al.*⁴⁶. The study revealed that the synthesized soil-alginate

composites exhibited maximum adsorption efficiency for iron followed by manganese and arsenic metal ions.

As evident from the literature, different hydrogels have shown prominent arsenic adsorption; however, comparing the adsorption efficiencies of different hydrogels against As(III) and As(V) ions is challenging as the adsorption efficiency of any adsorbent depends upon various factors like pH, temperature, arsenic concentration, interfering ions, adsorbent dosage as As(III) and As(V) ratios. Furthermore, comparison of different hydrogel adsorption efficiencies is tedious as some of the experiments are either documented in batches or columns. Moreover, the presence of interfering ions affects the adsorption efficiency of the targeted pollutant. Hence, in order to avoid the competitive mechanism, research should be focused on determining the water quality and adsorbent-selective adsorption mechanism towards a particular metal ion. Moreover, the difficulties of developing a biopolymer hydrogel for real-world applications are ingrained in the various complicated factors like presence of organic matter, ligands, variation in pH and temperature in different water samples.

Conclusion and future perspective

This article discusses the adsorption of arsenic metal ion using biopolymer-based hydrogels. Among the available techniques for arsenic removal, adsorption technique using biopolymer hydrogels is considered to be the most effective. Various natural polymers like chitin, cellulose, pectin, sodium alginate, etc. have been widely used for arsenic removal because of low cost, non-toxicity, biodegradability and biocompatibility properties. Here we have summarized the different types of biopolymer-based adsorbents, their advantages and disadvantages, and the mechanisms involved in arsenic removal. Though biopolymer-based hydrogels are effective in reducing arsenic level below the WHO limit, arsenic waste disposal is a challenging task in different parts of the world. Further, reusability, recovery of hydrogels, removal of selective metal ions and stability of the biopolymer-based hydrogels in harsh conditions should be considered in future

research in order to make the overall process more sustainable and economic. We believe that natural polymer-based hydrogels have a bright future; however, some collaborative efforts are needed among the scientific community in order to commercialize the hydrogels for water remediation application.

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