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Arsenic speciation analysis and remediation techniques in drinking water

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ABSTRACT

Arsenic is present in environment in trace amounts in rocks, soil, water and air but its toxicity effects are highly dependent on its chemical forms; inorganic and organic. There is a direct association between elevated arsenic exposure through drinking water and prevalence of different types of cancers. Present review describes the brief account of arsenic chemistry with reference to water and environment which is relevant to its toxicity arising out of different arsenic species and finally its remediation technologies. The quantification of arsenic species is difficult owing to the low concentration of arsenic in drinking water which is relatively lower than detection limits of modern analytical methods. New hyphenated techniques with more advanced tools have therefore, been discussed in the present paper which are being used in arsenic speciation analysis. The present review also highlights the importance to identify and quantify each chemical species of arsenic as more than 20 arsenic compounds are present in natural environment and in biological systems. Below microgram per liter detection limits are required to quantify arsenic species from these systems and a combination of chromatographic separation with atomic spectroscopy and mass spectroscopic detection is therefore, the most suitable speciation choice. The second important criteria viz. arsenic remediation from contaminated water for supply of safer drinking water is discussed and various remediation technologies are reviewed.

Keywords: Arsenic; Drinking water; Toxicity; Remediation technologies; Speciation analysis; Hyphenated methods

1. Introduction

Several inorganic heavy metal contaminants in drinking water are toxic. Through different water sources, the toxic metals are reaching the underground aquifers in increasing quantities and that too in different chemical forms like inorganic or organic as well as in different oxidation states. Therefore, metal ion speciation analysis and ultimately its elimination from wastewater are important to protect public health.

Metal ion speciation analysis in drinking water is the identification and determination of an individual physical–chemical form of an element along with oxidation states present in drinking water sample. The toxicity, mobility, bioavailability and bioaccumulation of a particular metal depend on the chemical species [1]. The term chemical speciation was described by Ure et al. [2,3] as the determination of concentration of the various

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individual chemical species of an element which covers the total concentration of that element in a given sample. On the basis of this principle, there are two approaches viz. organometallic and inorganic speciation. In organometallic speciation, the inorganic and organic forms are specified by their different toxicities and mobilities while in inorganic speciation different oxidation states of a metal are specified by their different toxicities and mobilities. A few among several publications on metal speciation of environmental samples are available and helpful in this area [4–8].

Scientists have defined the elemental speciation as an analytical activity to identify the actual chemical species of an element and also their quantification [9–11]. Metal ion speciation analysis is necessary and has been the need of the day in order to know the extremely low concentration of a particular metal species, which inturn has adverse effects on human health.

Different speciation forms are available and generally found in drinking water for various metals. For example, lead, arsenic, antimony, mercury, chromium, selenium etc., are constituent trace elements of potable water. These metals in nature as well as in aqueous form exist in different oxidation states, out of which certain forms are toxic; whereas other forms are less toxic or have no toxicity. In certain cases, this toxicity in aqueous medium increases with increase in oxidation states, whereas decreases in case of some other metals. Thus, the precise knowledge of oxidation states along with the quantitative assessment is required in order to have accurate information about cause of toxicity. Metal ion speciation analysis has been established as an important analytical tool due to the development in advanced instrumentation and it has now been possible to detect trace metals and their species upto much lower detection limits. Earlier, the analytical instrumentation for metal ion analysis was a combination of off-line sample preparation unit with a suitable detector such as Atomic Absorption Spectrometry (AAS), Atomic Emission Spectrometry (AES), Atomic Fluorescence Spectrometry (AFS) and Inductively Coupled Plasma-Mass spectrometry (ICP-MS).

Nowadays, hyphenated techniques have become method of choice for scientists and researchers for metal speciation analysis due to the reproducibility of results, short analysis time and advanced instrumentation. Due to requirement of lower detection of metals in water for variety of advanced applications, combination of techniques, that is hyphenated techniques along with highly sensitive detectors resulting into reproducibility of results, short time analysis, reduced recurring cost of analysis, have come up which are capable of analyses upto nano level and even below [8,12,13]. Once the arsenic contamination is identified and the various species analyzed, the next immediate step is to reduce arsenic levels in drinking water as much as possible and as quickly as possible. Many technologies have been developed for the removal of arsenic and have been reviewed at length in the proceeding paragraphs. In a nutshell, technologies must meet several basic technical criteria like desired water quality wrt both chemical and bacteriological, technologies must be robust, user friendly and finally, technologies should be environmentally friendly and economically feasible.

2. Effect of different arsenic species on health

Natural arsenic occurs in minerals. In natural water arsenic comes from these minerals and other insecticides and herbicides. Arsenic, a highly poisonous and widely distributed metal in nature, occurs in the form of inorganic and organic compounds. Bangladesh ranked first all over the world for arsenic contamination in drinking water followed by India and China. Mandal and Suzuki [14] reported arsenic as 20th most abundant element in the earth's crust and 14th in the sea water.

High-arsenic contamination in ground water of South and East Asian countries has been reported (Volume II, Technical Report No. 31303 of WSP South and East Asia) and depicted in Fig. 1. United States Environment Protection Agency [15] has formulated the 10 ppb standard value for arsenic in drinking water. The development of on-line speciation using hyphenated techniques is urgent need of analytical chemistry due to the demand of faster analysis and requirement of lower detection limit.

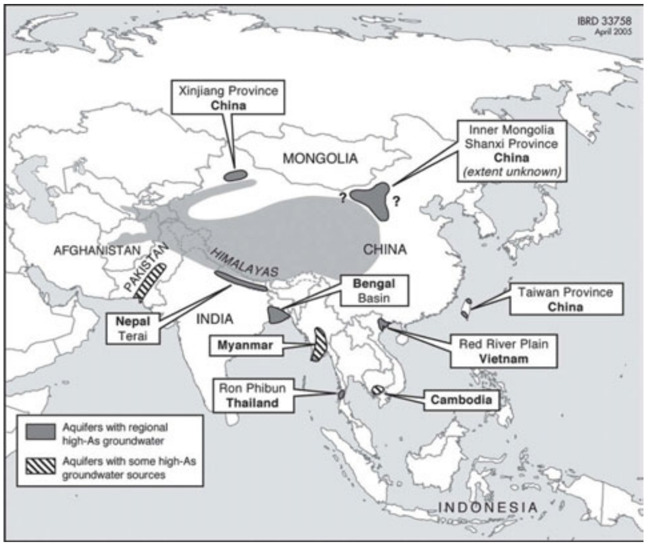

Fig. 1. High-Arsenic contamination in ground water of South and East Asian countries (Volume II, Technical Report No. 31303 of WSP South and East Asia).

The occurrence of arsenic metal in environment is due to weathering of the arsenic containing minerals and human activities. Different forms of arsenic show different chemical and toxic properties. The arsenic species enter the environment mainly in water through pesticides, industrial effluents, wood preservative agents and mining [16,17]. In pesticides, arsenic remains in the form of monosodium methane arsenate (MSMA), disodium methane arsenate (DSMA), arsenic acid and dimethylarsinic acid.

The speciation analysis of arsenic in environment mainly in water samples is interesting and necessary as its different species exhibits different level of toxicity. In environmental samples arsenic occurs in the form of mainly arsenite [As(III)] and arsenate [As(V)]. Arsenite compounds exhibit 10 times more toxicity than arsenate [18]. Inorganic arsenic compounds are found to be more toxic [19] and arsenite, that is As (III) compounds represent more toxicity than arsenate, that is As(V) compounds [20,21]. Kumaresan and Riyazuddin [18] reported that organic forms of arsenic, that is Monomethylarsonic acid [MMA(V)] and Dimethylarsinic acid [DMA(V)] have lower degree of toxicity. Mandal and Suzuki [14] confirmed that trivalent arsenic compounds are more toxic than pentavalent forms. Few important arsenic compounds and their toxic nature have been given in Table 1.

Samanta et al. [25] reported the following descending order toxicity of various arsenic species—AsH_3 > Arsenite > Arsenate > MMA > DMA.

Sambu and Wilson [26] summarized the presence of arsenic in water with its effects on human health and focused its occurrence in ground water of Bangladesh. Arsenic concentration in ground water of Bangladesh has been reported as 2.0 mg l^{-1} [27], against the guide lines of WHO as 0.01 mg l^{-1} [28]. The United States Environment Protection Agency has recommended the new arsenic standard value 10 μg l^{-1} to reduce the public health risks [15]. Welch et al. [29] reported the occurrence of arsenic in ground water of United States as arsenopyrite, a iron-arsenic compound. The toxic status of arsenic in ground water may be due to the natural local geochemistry. According to a report of Csalagovits [30], the higher level of arsenic in drinking was a consequence of natural biogeochemical processes instead of anthropogenic activities.

Inorganic arsenic compounds of water soluble arsenite As(III) are the most toxic species than arsenate As(V). These compounds are responsible for many types of health problems such as keratosis, skin lesions, bladder cancer and lung cancer [15,17]. A few researchers however, have established the applicability of arsenic for the treatment of leukemia, that is blood cancer [31,32]. Mabuchi and co-workers [33] reported that the spray of arsenic based aerosols was the reason for lung cancer in French Wine Yards. The skin problems in West Bengal have been ascribed due to arsenic [34]. According to Sambu and Wilson [26] 60 million people in Bangladesh have been found to drink the arsenic contaminated water beyond the standard limit of USEPA. In a study Suzuki et al. [35] reported that the effects of inorganic arsenic species was greater on the bladder of rats and mice after drinking of arsenic affected water. Kenyon and co-workers [36] explained that MMA(III) and MMA(V) were the predominant metabolite in kidney but DMA(III) and DMA(V) were reported as predominant metabolite in lung.

3. Arsenic speciation reactions in environment

Due to toxic and carcinogenic characteristic of inorganic and organic arsenic species in natural and drinking water, it is necessary to study their speciation [37]. Callahan and Michael [38] reported that the mobility of arsenic in aquatic environment increases with

Table 1
Arsenic compounds in speciation analysis and their toxic nature

S. N.	Compound name	Abbreviation with oxidation state	Chemical formula	Toxic nature	References
A. Inorganic species					
1	Arsenite (Arsenous acid)	As(III)	$As(OH)_3$	Very toxic	[20,21]
2	Arsenate (Arsenic acid)	As(V)	$AsO(OH)_3$	Less toxic	[20,21]
B. Organic species					
1	Monomethylarsonous acid	MMA(III)	$CH_3As(OH)_2$	Very toxic	[22,23,24]
2	Monomethylarsonic acid	MMA(V)	$CH_3AsO(OH)_2$	Less toxic	[18]
3	Dimethylarsinuous acid	DMA(III)	$(CH_3)_2AsOH$	Very toxic	[22,23,24]
4	Dimethylarsinic acid	DMA(V)	$(CH_3)_2AsO(OH)$	Less toxic	[18]

decrease in sorption and co-precipitation processes due to the complexation of trivalent and pentavalent arsenic with organic matter. Ridley et al. [39] showed the accumulation of arsenic and oxidation of arsenite to arsenate and also the formation of methylarsines through biomethylation reactions by aquatic organisms. McBride and Wolfe [40] established that methogenic bacteria were responsible for the production of methylarsines under aerobic conditions and also explained the formation of DMA and MMA as intermediate during the reductive methylation of inorganic arsenic to dimethylarsine. Saxena and Howard [41] showed the reductive methylation of arsenite to dimethylarsine. The sewage fungi *Candida humicola* converts arsenate to trimethylarsine under acidic conditions. According to Cullen and Reimer [42] arsenic shows much complicated chemistry in aquatic environment. Arsenic occurs in its (III) and (V) oxidation state in ground water [43]. The salinity, pH, pKa and redox potential play an important role in arsenic species distribution in water [44,45]. Organo-arsenicals normally occur in fresh water systems only due to bacterial biotransformation of inorganic arsenic forms [46,47]. The biological cycle of arsenic in environment, that is in air, water and sediment is given in Fig. 2.

The detection limit (D_L) of an analytical method may be calculated by using the formula (Vandecasteele and Block) as given below:

$$D_L = \frac{3\sigma_B}{b}$$

where b is the slope (sensitivity) of calibration curve; σ_B is the standard deviation of background.

The available methods for the speciation study should be cheap, reliable and rapid [48]. A single run analysis for the separation and speciation of arsenic compounds is difficult due to different physical and chemical behavior of arsenic compound. To solve this problem the coupling of various separation and detection techniques, that is hyphenation methods are being used. Hydride generation-atomic absorption spectrophotometer (HG-AAS), electrothermal-AAS (ET-AAS), ICP-AES, ICP-AFS, ICP-MS are some hyphenated techniques which increase the DL 100 times more than commonly used nebulization methods for liquid samples [49]. Sun et al. [50] reported the hyphenation of liquid chromatography with ICP-MS, a most widely used method for arsenic speciation in environmental samples. Some authors have worked on electrochemical detection techniques [51,52] and optical emission spectroscopic methods with ICP-MS detector for arsenic speciation [53,54]. ICP-MS has become a versatile detection technique for the arsenic speciation analysis. Nürnberg [55] has reported electrochemical methods as an important tool for elemental speciation analysis.

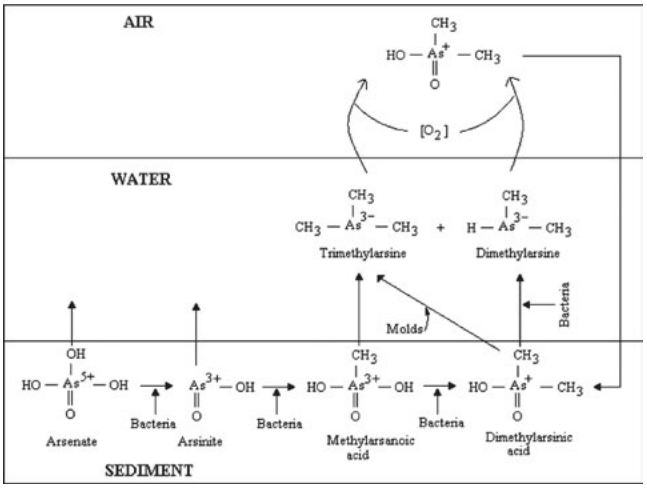

Fig. 2. Biological cycle of arsenic in environment.

4. Analytical techniques for elemental speciation of arsenic in drinking water

The increasing interest of scientists and academicians is towards the development of new analytical techniques for the determination of different forms of a metal present in matrix. Kot and Namiesńik [56] proposed the basic types of speciation analysis in the area of chemical science. The various analytical techniques useful for the metal species determinatation have also been summarized by Szpunar and Lobinski [57].

Chromatographic methods are important for metal speciation study as these methods are developed for the resolution of cations, anions and metal complexes by using different types of stationary phases including anion–cation resin, size-exclusion, reversed phase columns with different combinations of mobile phases [8,58]. The coupling, that is hyphenation of liquid chromatography (LC) with element specific detector such as with graphite furnace atomic absorption spectrometry (GFAAS), flame AAS (FAAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and hydride generation AAS (HGAAS) [13,59–64] is well documented. Among all these techniques, LC-ICP-MS possess a wide application range over other methods. Gas Chromatography (GC) can also be coupled for detection with FAAS, electrothermal AAS, ICP-AES and ICP-MS. Although, hyphenated LC-ICP-MS has wide application but GC-ICP-MS is reported as a better speciation method due to its about 100% efficiency and high resolving capacity. Super critical Fluid Chromatography (SFC) coupled with ICP-MS technique, has been reported as the best method considering its high resolving power and also 100% efficiency along with its application for volatile and non-volatile compounds [65–67]. Few published reports [8,66,68,69] are also important towards the use of hyphenated tool for metal speciation, that is capillary electrophoresis ICP-MS technique which works on the basis of charge and size of species and is also a fast and powerful technique. Besides this technique, some other significant techniques are also available for metal speciation study like flow injection analysis (FIA), differential pulse polarography (DPP), anodic stripping voltametry (ASV) and cathodic stripping voltametry (CSV) [70–74]. Komorowicz and Barałkiewicz [75] have reviewed the importance of HPLC–ICP-MS technique for arsenic speciation analysis in drinking water. A review on arsenic speciation analysis in drinking water and ground water has been published regarding ion chromatographic technique [76].

Arsenic(III) may oxidize rapidly to As(V) species, if collected water samples have not been preserved properly. For unpreserved water samples, it was found that As(III) species loses its 50% within first 2 d of sampling and overall loss of As(III) may take 6 d of sampling. Henze and co-workers [77] analysed fresh water samples for the speciation analysis of As(V) and As(III) in Cathodic stripping voltammetry (CSV) technique using mercury drop electrode and a double junction Ag/AgCl/3 M KCl reference electrode and a glassy-carbon auxiliary electrode. They found 0.52 μg l^{-1} DL for arsenic. Pretty and co-workers [78] reported ASV flow cell method followed by ICP-AES and ICP-MS for As(III) speciation. The determination of arsenite and arsenate has been done in ground water samples by a co-precipitation method by silver diethyldithiocarbamate (SDDS) spectrophotometric procedure [79].

The most commonly and widely used technique for the separation of arsenic species is high performance liquid chromatography (HPLC). After HPLC separation, the different species of arsenic can be detected by different types of on-line detectors like ultraviolet (UV), atomic absorption spectrophotometer (AAS), HG-AAS, ICP-AES, ICP-MS. Pantsar-Kallio and Manninen [80] separated and determined As(III) and As(V) species in water samples using ion-exchange-ICP-MS with the DL of 0.4–0.5 μg l^{-1} for both species. A research group [81] in India has evaluated and standardized a simple and rapid HG-AAS method for the speciation of As(III) and (V) species in ground water samples of West Bengal with the DL of 0.4 μg l^{-1}. Almost all water samples showed As(III) values in the range of 54–350 ppb except two samples.

For the speciation of arsenic in water samples, several techniques are being used like AES, AAS, graphite furnace and ICP-AES. Arsenic species form hydrides when treated with sodium boro hydride in acidic medium. The determination of inorganic As(III) and As(IV) can be done due to different oxidation and reduction conditions. Hydride generation, by varying pH and other pretreatment conditions, is generally used phenomenon for Arsenic speciation. Selective extraction methods like C_{18}, cation–anion exchange columns, 2-Mercepto-*N*-2-naphthylacetamide on silca gel or knotted reactors can be used for arsenic speciation. The complex formation of different species of arsenic is due to the selective retention properties of these species with various organic compounds like 2,3-dimercaptopropane-1-sulfonate on C_{18} [82], ammonium pyrrolidinedithiocarbamate (PDC) on anion exchanger column [83]. Various organic compounds like ammonium PDC [84], sodium diethyldithiocarbamate [85], ammonium *sec*-butyldithiophosphate [86] have also been employed for complexation of inorganic arsenic species followed by liquid–liquid extraction using many organic solvents like carbon tetrachloride, chloroform, 2,6-dimethyl-4-heptanone (DIBK) and methylisobutylketone (MIBK) in ETAAS, HG-AES, HG-AAS UV-Vis analytical techniques. Smichowski et al. [87] used *Saccharomyces cerevisiae* microorganism as substrate for the biosorption (quantitative determination) of Arsenic(III) species in the presence of Arsenic(V) species in aqueous solution using HG-ICP-AES technique. The accumulation of only As(III) was found in yeast cells while As(V) species were left in the solution.

Morita et al. [88] reported the simultaneous speciation analysis of multiple elements. They separated eight different arsenic species As(III), As(V), MMA, DMA, Arsenobetaine (AB), Arsenocholine (AC), Trimethylarsine oxide (TMAO) and Trimethylarsine (TMA) using a C_{30} RP-HPLC method hyphenated with ICP-MS for hot spring waters.

Akter et al. [66] performed a comparative study of capillary electrophoresis-ultraviolet detector (CE-UV), HG-AAS and liquid chromatography-inductively coupled plasma-mass spectrometry (LC-ICP-MS) for the speciation study of arsenic in ground water samples of Bangladesh. The comparison of various analytical parameters of these three methods is given in Table 2. After comparison of these three techniques, authors found LC-ICP-MS as the best method for the speciation of Arsenic species such as arsenite (As(III)), arsenate (As(V)) and one organoarsenic species, DMA in ground water samples.

The elemental speciation by various types of chromatographic separation techniques coupled with inductively coupled plasma mass spectrometry (ICP-MS) was reviewed [89]. ICP-MS has become a versatile and reliable technique as it detects at ≤ ppt levels. The specific applications of different types of chromatographic techniques coupled with ICP-MS for arsenic speciation in drinking water are given in Table 3.

Table 2
Comparison of three analytical techniques [66] for arsenic speciation analyses in drinking water

S. N.	Analytical characteristic	HG-AAS	CE-UV	LC-ICP-MS
1	Sample preparation	Complex formation of sample is required	Only filtration is required	Only filtration is required
2	Separation capacity	Separates only single species	Separates three species [As(III), As(V), DMA]	Separates four species [As(III), As(V), MMA, DMA]
3	Range	0.13–40 μg l^{-1}	0.1–4 mg l^{-1}	2–100 μg l^{-1}
4	Detection limit	0.1 μg l^{-1} As(III), 0.19 μg l^{-1} (DMA)	100 μg l^{-1} of As(III) and DMA, 500 μg l^{-1} As(V)	0.2 μg l^{-1} As(III) and As(V); 0.1 μg l^{-1} (MMA and DMA)
5	Analysis cost	Low	Low	High

Table 3
Various types of chromatographic techniques coupled with ICP-MS

S. N.	Matrix	Metal species	Technique	Detector	Detection limit	References
1	Spring water, bottled mineral water	Arsenite, Arsenate, MMA, DMA, Arsenobetaine, Arsenocholine	Reversed phase ion-pair LC, RP-column (250 mm × 4.6 mm)	ICP-MS having VG elemental plasma quadrupole with concentric nebulizer	1.0–3.0 μg l^{-1}	[90]
2	Fresh water	As(III), As(V), MMA, DMA	Anion-exchange LC	Hewlett-Packard 4500, Babington nebulizer	0.06 μg l^{-1}	[91]

5. Remediation techniques of arsenic contamination in drinking water

Arsenic is a constituent present ubiquitously in many industrial raw materials, products, and wastes, and is a contaminant of concern in groundwater at many remediation sites. Because arsenic readily changes valence state and reacts to form species with varying toxicity and mobility, effective treatment of arsenic can be challenging [92,93]. Treatment can result in residuals that, under some environmental conditions, have unstable toxicity and mobility. The technologies frequently used at full scale for arsenic removal from drinking water, ground water, industrial wastewater, surface water, mine drainage, and leachate are precipitation/co-precipitation, adsorption, ion-exchange and membrane filtration [94,95]. Each of these technologies include more than one type of treatment system [96]. For example, nanofiltration and reverse osmosis treatment systems are used to treat arsenic, yet both techniques are discussed under a single membrane filtration technology because of their similarity in design, operation and application to arsenic treatment.

Oxidation of As(III) to As(V) can improve the performance of these technologies. Chlorine, potassium permanganate, aeration, peroxide, ozone, and photocatalytic oxidation or the addition of oxidizing chemicals such as potassium permanganate, sodium hypochlorite, or hydrogen peroxide have been used to convert As(III) to As(V) [94,97]. Many studies have been published on the oxidation of As(III) by chemical oxidants like chlorine, chlorine dioxide (ClO_2) [98], chloramines (NH_2Cl) [99], ozone [100], hydrogen peroxide [101,102], permanganate (MnO_4^-) [103], peroxydisulfate ion [104], ferrate (FeO_4^{2-}) [105,106], photocatalytic oxidation [107–116]. Many arsenic treatment systems use oxidation as a pretreatment step to improve performance while some of them include oxidation as an intrinsic part of their application. Whether oxidation is used as a pretreatment step or an intrinsic part of another technology, it is not typically used alone for arsenic treatment.

The main arsenic removal technologies are presented herewith along with a brief description of the various factors affecting the removal efficiency viz. arsenic concentration and speciation, pH, and the presence of other dissolved constituents.

6. Precipitation/co-precipitation technique

Precipitation uses chemicals to transform dissolved contaminants into an insoluble solid [117]. In co-precipitation, the target contaminant may be in a dissolved or in a colloidal or suspended form. Dissolved contaminants do not precipitate, but are adsorbed onto other species which inturn gets precipitated. Colloidal or suspended contaminants become enmeshed with other precipitated species, or are removed through processes such as coagulation and flocculation [105]. Arsenic removal from drinking water involves processes which is a combination of precipitation and co-precipitation [92]. The precipitated/co-precipitated solid is then removed from the liquid phase by clarification or filtration. The technology involves pH adjustment.

Various factors affecting the precipitation/co-precipitation performance are the valence state of arsenic, pH, specific arsenic compound and the presence of other chemicals with which arsenic might react. The presence of the more soluble trivalent state of arsenic might reduce the removal efficiency. Oxidation of trivalent arsenic to its less soluble pentavalent state could improve arsenic removal through precipitation/co-precipitation [118]. Arsenic removal is maximized at the pH at which the precipitated species is least soluble. The optimal pH range for precipitation/co-precipitation depends upon the waste treated and the specific treatment process. The presence of other metals or contaminants will impact the effectiveness of precipitation/co-precipitation. For example, sulfate decreases arsenic removal in processes using ferric chloride as a coagulant, while the presence of calcium or iron may increase the removal of arsenic in these processes.

Precipitation/co-precipitation technique suffers from the limitation of generation of sludge residual, which requires dewatering and subsequent disposal treatment. Some sludge from the precipitation/co-precipitation of arsenic can be a hazardous waste and require additional treatment such as solidification/stabilization prior to disposal. In the presence of other metals or contaminants, arsenic precipitation/co-precipitation processes might also cause other compounds to precipitate, which can render the resulting sludge hazardous [92]. The effluent may also require further treatment, such as pH adjustment, prior to discharge or reuse.

7. Adsorption treatment technique

Adsorption is a well known equilibrium separation and an effective technique for water decontamination applications [119]. In adsorption, the contaminants concentrate on the surface of an adsorbent, thereby reducing their concentration in the bulk liquid phase. For large scale arsenic treatment, the adsorption medium is usually packed into a column. As contaminated water is passed through the column, contaminants are adsorbed. When adsorption sites become filled, the column must be regenerated, or disposed of and replaced with new media.

Adsorption technique has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and exhibit resistance to fouling from toxic pollutants. Also, adsorption does not result in the formation of harmful substances. This technology has reduced arsenic concentrations to less than 0.050 mg l^{-1} and in some cases has reduced arsenic concentrations to below 0.010 mg l^{-1} [92,120]. Its effectiveness is sensitive to a variety of untreated water contaminants and characteristics.

A number of materials have been extensively investigated as adsorbents in arsenic remediation in drinking water. Some of the important ones include silica gel, activated alumina [121–123], clay [124–126], kaolinite [127,128], titanium dioxide [129–131], iron hydroxide [132], ferrihydrate [133,134], hematite [135] etc. A review article has extensively discussed on the various adsorbents used for arsenic remediation with their advantages and disadvantages have recently been published [136]. Arsenic adsorption by activated carbon has also been studied in detail [137].

The potential limitations of this technology lie in the high cost of commercial activated carbon, problem of regeneration of spent adsorbent and competition from other contaminants in the adsorptive media. Competition for adsorption sites could reduce the effectiveness of adsorption because other constituents might be preferentially adsorbed, resulting in a need for more frequent bed regeneration or replacement.

The wider applications of activated carbon as adsorbent is often restricted due to its higher cost [138]. The use of carbons based on relatively expensive starting materials is also unjustified for arsenic remediation applications. These drawbacks attracted scientists to develop low-cost adsorbents by using a wide range of carbonaceous and other precursors [139,140]. The growing demand for efficient and low cost treatment methods and the importance of adsorption technology for arsenic remediation in drinking water has given rise to the development of low cost adsorbents [141,142]. The production of activated carbons from solid wastes is one of the most environment-friendly solutions by transforming negative-valued wastes to valuable materials. Activated carbon from waste products/by-products of industry and agriculture is a research field of increasing interest as it deals with the problem of the disposal of wastes, at the same time producing an added-value product that can be used in a number of environmental applications. A number of agricultural wastes/industrial by-products has been successfully investigated as adsorbents by a number of workers. Some of the adsorbents as reported in literature are iron oxide [143–147], clay [148,149], blast furnace slag [150–152], fly ash [153–156], carbon slurry [157,158], synthetic resin [159], zeolites synthesized from fly ash [160], hen feathers [151–161], determination of toxic ions by chemical sensors [162–167], agro based waste like bottom ash and deoiled soya [168–174], walnut shells [175], saw dust [176], spent mushroom [177], hazel nut shells [178], oat hull [179], timber industry waste [180] etc.

8. Ion exchange technique

Ion exchange is a physical/chemical process in which ions held electrostatically on the surface of a solid are exchanged for ions of similar charge in a solution. It removes ions from the aqueous phase by the exchange of cations or anions between the contaminants and the exchange medium [92,181,182]. A strong base anion exchange resin is used to treat arsenic. The medium used for ion exchange is typically a resin made from synthetic organic materials, inorganic materials, or natural polymeric materials that contain ionic functional groups to which exchangeable ions are attached.

Among the four types of ion exchange resins, strong base resins are typically used for arsenic treatment as dissolved arsenic is usually in an anionic form, and weak base resins tend to be effective over a smaller pH range [183].

The ion exchange technology has an inherent limitation that the spent regenerating solution might contain a high concentration of arsenic and other sorbed contaminants, and could be corrosive. The spent resin may thus require treatment prior to reuse or disposal. The performance of the technology is also sensitive to a variety of contaminants; various characteristics in the untreated water viz. organics, suspended solids, calcium, or iron can cause fouling. Therefore, it is typically applied to groundwater and drinking water, which are less likely to contain fouling contaminants. It may also be used as a polishing step for other water treatment technologies.

9. Membrane filtration technology

Membrane filtration technique separates contaminants from water by passing it through a semi permeable barrier. The membrane allows some constituents to pass through, while blocking others [184].

There are four types of membrane processes: reverse osmosis (RO), nanofiltration (NF), microfiltration (MF), and ultrafiltration (UF). All four are pressure-driven and are categorized by the size of the particles that can pass through the membranes or by the molecular weight limit (i.e., pore size) of the membrane [92]. The force required to drive fluids across the membranes depends on the pore size; NF and RO require a relatively high pressure (50–150 pounds per square inch [psi]), while MF and UF require a relatively low pressure (5–100 psi). The low-pressure processes primarily remove contaminants through physical sieving and the high pressure processes primarily remove contaminants through chemical diffusion across the permeable membrane [92].

Because arsenic species dissolved in water tend to have relatively low molecular weights, only NF and RO membrane processes are likely to effectively treat dissolved arsenic [92,185,186]. MF has been used in conjunction with precipitation/co-precipitation to remove solids containing arsenic. Membrane filtration processes generate two treatment residuals from the influent waste stream: a treated effluent (permeate) and a rejected waste stream of concentrated contaminants (reject).

RO is a high-pressure process that primarily removes smaller ions typically associated with total dissolved solids. The molecular weight cutoff for RO membranes ranges from 1 to 20,000, which is a significantly lower limit than for NF membranes [92]. The molecular weight cutoff for NF membranes ranges from approximately 150 to 20,000. NF is a high-pressure process that primarily removes larger divalent ions associated with hardness (e.g., calcium [Ca], and magnesium [Mg]) but not mono-valent salts (e.g., sodium [Na] and chlorine [Cl]). NF is slightly less efficient than RO in removing dissolved arsenic from water [92].

MF is a low-pressure process that primarily removes particles with a molecular weight above 50,000 or a particle size greater than 0.050 μm. The pore size of MF membranes is too large to effectively remove dissolved arsenic species, but MF can remove particulates containing arsenic and solids produced by precipitation/co-precipitation processes [92].

Membrane technologies are capable of removing a wide range of dissolved contaminants and suspended solids from water. RO and NF technologies require no chemical addition to ensure adequate separation. This type of treatment can be run in either batch or in continuous mode. This technology's effectiveness is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organics, colloids, and other contaminants can cause membrane fouling. Therefore, it is typically applied to groundwater and drinking water, which are less likely to contain fouling contaminants. It is also applied to remove solids from precipitation processes and as a polishing step for other water treatment technologies when lower concentrations must be achieved.

10. Conclusions

In spite of all progress made for quantitative determination of arsenic species from drinking water, a lot of factors still needs to be overcome in achieving required lower detection level. The mechanism of toxicities of different arsenic species is still not known. Selenium interacts with arsenic and affect metabolism. Simultaneously speciation analysis of arsenic and selenium is also a future challenge in identifying their co-binding efficiency with biomolecules. The new modifications in available methods are therefore, required in order to overcome insufficient sensitivity of arsenic speciation method. Although various technologies exist for arsenic remediation, yet, its removal efficiency will vary according to many site-specific chemical, geographic, and economic conditions. Hence, since various factors affect arsenic removal efficiency like arsenic concentration, speciation, pH and co-existing solutes, any technology needs to be tested on the contaminated drinking water, before implementation of arsenic remediation system on a large scale.

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