

Need of Arsenic Monitoring: A Review

Dr. Monika Swami*, Dr. Bhavna Soni, Prof. H. R. Shah

Chemical Engineering Department, Sal college of Engineering

Abstract— The groundwater contaminated with arsenic is often associated with unwanted natural organic matters and microorganisms. It is therefore important to develop multi functional technologies for the treatment of groundwater. The toxicology and health hazard also has been reported for many years. Because of the recognition that arsenic at low concentrations in drinking water causes severe health effects, the technologies of arsenic removal that have become increasing important. High arsenic concentrations have been reported recently from the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India. The health hazard of arsenic is an important issue therefore this paper aims to review briefly arsenic toxicology and hazards and also the previous and current available technologies that have been reported in arsenic removal.

Key words: Arsenic removal, Health hazard, , Technology, Toxicology

I. INTRODUCTION

The word arsenic is derived from Latin, *arsenicum*, and Greek, *arsenikon*, meaning “yellow orpiment”, identified with *arsenikos*, meaning “male”, from the Greek belief that metals were of different sexes. The Arabic derivation was from *Az-zernikh*, meaning “the orpiment”, which came from Persian, *Zeni-zar*, meaning “gold”. It is believed that Albertus Magnus obtained the element in 1250 AD. In 1649 Schroeder published two methods of preparing the element. In 1733 Brandt showed that white arsenic is the oxide of the metal. Records showed that arsenic was extensively used by the poison brewers of the middle ages. In the Renaissance it was Paracelsus who pioneered the use of arsenic compounds in medicine. Arsenic acid and arsine, the hydride, were discovered by Scheele in 1775. Arsenic trioxide has been produced in China for some 500 years.

Arsenic (atomic number 33) is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust, 14th in the seawater, and 12th in the human body [1]. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions [2,3] as well as through a range of anthropogenic activities such as gold mining, non-ferrous smelting, petroleum-refining, combustion of fossil fuel in power plants and the use of arsenical pesticides and herbicides [2-6] Arsenic found in soil either naturally occurring or from anthropogenic releases forms insoluble complexes with iron, aluminum, and magnesium oxides found in soil surfaces, and in this form, arsenic is relatively immobile. Arsenic can

liberate from these complexes under some circumstances. Since arsenic in soils is highly mobile, once it is liberated, it results in possible groundwater contamination [7–11].

II. USES OF ARSENIC AND ITS EFFECT

(1) *In Agriculture:* Lead arsenate, copperacetoarsenite, sodium arsenite, calcium arsenate and organic arsenic compounds are used as pesticides. Methyl arsonic acid and dimethyl arsinic acid are used as selective herbicides.

Problem with As in Agriculture:

Rice grown in the United States contains an average of 1.4 to 5 times more arsenic than rice from Europe, India and Bangladesh, according to a survey of grains from around the world. Rice is the agricultural product most likely to contain high levels of arsenic because it's grown in flooded paddies. The watery, oxygen-free environment causes naturally occurring arsenic in the soil to be freed and thus more readily taken up by the plant.

(2) *In Forestry:* Chromated copper arsenite (CCA) used as fungicide, sodium arsenate and zinc arsenate are used as wood preservatives.

When CCA is used the copper in the treatment acts as a fungicide while the arsenic acts as an insecticide. The arsenic in this treatment makes this potentially hazardous to humans and the environment.

Problems with arsenic in forestry:

Issues arising from CCA treated timber are as follows:

- (i) Accumulation of arsenic on the treated timber's surface, directly exposing humans to arsenic.
- (ii) Accumulation of arsenic in surrounding soils, thus contaminating soils and increasing the risk of arsenic — uptake by plants.
- (iii) Arsenic leaching into ground water and downstream waterways, which can lead to plants and animal-uptake of arsenic.

(3) *In Industry:* Arsenic is used in the preparation of dyes, poisonous gas, transistor, as a component of semiconductor, as a preservative in tanning and in the industry of textile, paper etc.

(4) *In Pharmaceutical:* Small amount of arsenic continue to be used as drugs in some countries. Medicine arsenic has been used since the 5th century BC when Hippocrates recommended the use of an arsenic sulfide for the treatment of abscess. Arsenic preparations have been used for the treatment

of skin disorder, tuberculosis, leukemia, asthma, leprosy, syphilis, amoebic dysentery etc.. Homeopaths are also using arsenic as drug.

III. HEALTH EFFECT DUE TO ARSENIC

Health effects caused by arsenic depend on a variety of things. These include the type and amount of arsenic that has entered the body, how long you have been exposed to arsenic, and how the body responds to arsenic. Unborn babies, young children, people with long-term illnesses and elderly people are at greatest risk due to arsenic exposure.

The toxicity of arsenic to humans is well known, and the ingestion of as little as 100 milligrams (mg) can result in severe poisoning. The effects of the poison, when ingested in small amounts, appear very slowly; in fact it may take several years for the poisoning to become apparent. Chronic arsenosis can, in its most extreme form, cause death. Inorganic arsenic is absorbed readily from the gastrointestinal tract and becomes distributed throughout the body tissues and fluids. Studies link inorganic arsenic ingestion to a number of health effects. These health effects include:

Cancerous Effects: skin, bladder, lung, kidney, nasal passages, liver and prostate cancer; and

Non-cancerous effects: cardiovascular, pulmonary, immunological, neurological and endocrine (e.g., diabetes) effects.

In general, there are four recognized stages of arsenicosis, or chronic arsenic poisoning:

(a)Preclinical: the patient shows no symptoms, but arsenic can be detected in urine or body tissue samples.

(b)Clinical: various effects can be seen on the skin at this stage. Darkening of the skin (melanosis) is the most common symptom, often observed on the palms. Dark spots on the chest, back, limbs or gums have also been reported. Oedema (swelling of hands and feet) is often seen. A more serious symptom is keratosis, or hardening of skin into nodules, often on palms and soles. WHO estimates that this stage requires 5–10 years of exposure to arsenic.

(c)Complications: clinical symptoms become more pronounced and internal organ are affected. Enlargement of liver, kidneys and spleen have been reported. Some research indicates that conjunctivitis (pinkeye), bronchitis and diabetes may be linked to arsenic exposure at this stage.

(d)Malignancy: tumors or cancers (carcinoma) affect skin or other organs. The affected person may develop gangrene or skin, lung or bladder cancer.

IV. TOXIC LIMITS OF ARSENIC

The elevated concentrations of arsenic in the environment occur from both natural and anthropogenic sources [6]. Many industries such as mining, petroleum refining, wood preservation, and the production of pesticide, herbicide, and ceramic also contribute to arsenic contamination in water

sources. Arsenic high contents in groundwater destined to human consume constitute one of the most important problems related to population health in many countries in the world. Among affected countries, are Argentina, Bangladesh, Canada, Chile, China, Hungary, India (West Bengal), Mexico, Pakistan, Romania, Taiwan, Vietnam and USA.

World Health Organization (WHO) and the Environment Protection Association (EPA) have classified arsenic as cancerous, and established a maximum guide value [12- 21].

V. EPA LIMITS FOR

(a)Water: EPA has set a limit of 0.001 ppm (10 ppb) of arsenic in drinking water.

(b)Soil: It has been reported that EPA has set a limits of 10 ppm (10 mg per kg) of arsenic in soil. Arsenic levels over this limit empower EPA to order an owner-funded cleanup of a commercial site.

(c)Air: The Occupational Safety and Health Administration, OSHA, established a maximum permissible exposure limit for workplace airborne inorganic arsenic of 10 micrograms per cubic meter averaged over an eight-hour day.

VI. DETECTION - DOSAGE MECHANISM

Warning Signs: Both inorganic and organic Arsenic give no warning of its presence. arsenic compounds are white or colorless powders that have no specific taste or odor. Given the minute amount required to produce a lethal effect, the lack of a warning sign makes these very deadly substances.

Presence: Inorganic arsenic is found in many kinds of rock, especially in ores that contain copper or lead. When these ores are smelted to extract the copper or lead, most of the arsenic is collected for pesticide. Like radiation, everyone is exposed to low levels of arsenic (especially inorganic arsenic) because very low levels of it are always present in soil, water, food and air. The average person ingests about 8 micrograms (about 8/1000 of a gram) in food every day. Arsenic is also present in cigarette smoke where it originates from insecticides on tobacco.

Uptake Mechanisms: Arsenic can be taken in by ingestion, aspiration by breathing dust, and, to a much lesser degree, by absorption through the skin. Accidental poisoning has been reported to occur from wearing inadequate clothing when applying arsenic-based products.

A lethal dose of Arsenic can also be achieved by a cumulative process over two months. Multiple sub-lethal doses received over a period of several weeks can accumulate in the body to achieve a lethal dose. And at very small doses, arsenic is carcinogenic.

VII. CHEMISTRY OF ANTIMONY

Arsenic has a unique chemistry which allows it to exist as an oxo-anion in natural waters regardless of whether it exists in

arsenite (+3) or arsenate (+5) form, the two most dominant forms of arsenic in water.[46]

In general, the trivalent form, arsenic (III) species [As (III)], is the dominant species under reducing conditions and the pentavalent form, arsenic (V) species [As (V)], is the dominant species under oxidizing conditions.

Depending on the redox condition, pH range, presence of complexing ions and the microbial activity of the environment, As (V) species may exist as arsenic acid (HAsO_4) and arsenate ions ($\text{H}_2\text{AsO}_4^{-1}$, HAsO_4^{2-} , AsO_4^{3-}). Similarly, As (III) species may be present as arsenious acid (H_3AsO_3) and arsenite ions ($\text{H}_2\text{AsO}_3^{-1}$, HAsO_3^{2-} , and AsO_3^{3-}).

The pH of community water supplies is found to be between 6 and 9. In this pH range, deep ground waters contain As (III) in the form of HAsO_3 . As (III) species oxidizes to As (V) species in the presence of oxygen (pumping ground water to surface), chlorine (disinfections of water), hydrogen peroxide or potassium permanganate. In shallow groundwater and surface water sources, As (V) in the form of $\text{H}_2\text{AsO}_4^{-1}$ and HAsO_4^{2-} are the dominant species. Because of its ionic charge, As (V) is easier to remove from source waters than As (III). At pH 8 (the pH of interest for this study), As (V) species exist in water as di-anionic form (HAsO_4^{2-}) and the Eh values of water are between -150 mV and 758 mV

The oxo-anion configuration allows arsenic to interact with metal (hydr)oxide surfaces by forming monodentate and bidentate inner-sphere complexes. This interaction makes many of the metal (hydr)oxide materials suitable media for removal of arsenic from water by adsorption

Efficiency of treatment methods depends on the aqueous chemistry of arsenic. Arsenic exists in a variety of inorganic forms and oxidation states in water. The speciations of arsenic are dependent on the type and amounts of sorbents, pH, redox potential, and microbial activity. The predominant As(III) compound is neutral in charge, while the As(V) species are negatively charged in the pH range of 4–10. Therefore As(III) is less efficiently removed than As(V) from aqueous solutions by almost all of the arsenic removal technologies and preoxidation of As(III) to As(V) using some oxidizing chemical agents are necessary for better removal [22-45].

VIII. TECHNIQUES FOR REMOVAL OF ARSENIC FROM WATER SAMPLE

The stricter regulation on arsenic in drinking water leads to a great challenge to conventional water treatment technologies. The conventional technologies for arsenic removal from aqueous solution include coagulation, electrocoagulation, coprecipitation, ion-exchange, adsorption, and membrane filtration through nanofiltration (NF) membrane. Most of them however have one or more drawbacks and limitations. Membrane filtration can be used for arsenic decontamination when it is operated with the NF mode [1]. It normally requires high working pressure and costly membrane. Microfiltration

(MF) and ultrafiltration (UF) need much lower pressure in the operation; however, they normally cannot remove the dissolved arsenic with an acceptable efficiency. Few UF membranes can achieve slightly better performance for removal of arsenic. However, the operation is often sensitive to the water chemistry [2,3]. Recently, affinity membranes are thus developed with an inclusion of adsorptive materials during their fabrication. The membrane filtration operated under MF and UF modes may be effective in removal of dissolved inorganic contaminants [4]. Adsorption is an efficient method for removal of trace toxic pollutants present in water. Various adsorbents have been developed and used for the decontamination of arsenic containing water. Iron oxide based sorbents are commonly studied and reported in the literatures for treatment of arsenic contaminated water [5,6]. Zirconium based sorbents have recently been reported for their high efficiency in removing arsenic. Balaji et al. studied the removal of As(V) and As(III) by Zr-loaded lysine diacetic acid chelating resin [7]. The maximum sorption capacities were 0.656 and 1.184 mmol/g for As(V) and As(III), respectively. Zirconium was loaded on a phosphoric chelate adsorbent through the polymerization technology [8]. Removal efficiencies for As(III) are poor compared to removal As(V) by any of the technologies evaluated due to the negative charge.

Coagulation/Filtration (C/F), is an effective treatment process for removal of As(V) according to laboratory and pilot-plant tests. The type of coagulant and dosage used affects the efficiency of the process. Within either high or low pH ranges, the efficiency of C/F is significantly reduced. Alum performance is slightly lower than ferric sulfate. Other coagulants were also less effective than ferric sulfate. Disposal of the arsenic-contaminated coagulation sludge may be a concern especially if nearby landfills are unwilling to accept such a sludge.

Lime Softening (LS) operated within the optimum pH range of greater than 10.5 is likely to provide a high percentage of As removal for influent concentrations of 50 $\mu\text{g/L}$. However, it may be difficult to reduce consistently to 1 $\mu\text{g/L}$ by LS alone. Systems using LS may require secondary treatment to meet that goal.

Activated Alumina(AA) is effective in treating water with high total dissolved solids (TDS). However, selenium, fluoride, chloride, and sulfate, if present at high levels, may compete for adsorption sites. AA is highly selective towards As(V); and this strong attraction results in regeneration problems, possibly resulting in 5 to 10 percent loss of adsorptive capacity for each run. Application of point-of-use treatment devices would need to consider regeneration and replacement.

Ion Exchange (IE) can effectively remove arsenic. However, sulfate, TDS, selenium, fluoride, and nitrate compete with arsenic and can affect run length. Passage through a series of columns could improve removal and decrease regeneration

frequency. Suspended solids and precipitated iron can cause clogging of the IE bed. Systems containing high levels of these constituents may require pretreatment.

Reverse Osmosis (RO) provided removal efficiencies of greater than 95 percent when operating pressure is at ideal psi. If RO is used by small systems in the western U. S., 60% water recovery will lead to an increased need for raw water. The water recovery is the volume of water produced by the process divided by the influent stream (product water/influent stream). Discharge of reject water or brine may also be a concern. If RO is used by small systems in the western U. S., water recovery will likely need to be optimized due to the scarcity of water resources. The increased water recovery can lead to increased costs for arsenic removal.

Electrodialysis Reversal (EDR) is expected to achieve removal efficiencies of 80 percent. One study demonstrated arsenic removal to 3 µg/L from an influent concentration of 21 µg/L.

Nanofiltration (NF) was capable of arsenic removals of over 90%. The recoveries ranged between 15 to 20%. A recent study showed that the removal efficiency dropped significantly during pilot-scale tests where the process was operated at more realistic recoveries. If nanofiltration is used by small systems in the western U. S., water recovery will likely need to be optimized due to the scarcity of water resources. The increased water recovery can lead to increased costs for arsenic removal.

Point of Use/Point of Entry (POU/POE) The 1996 SDWA amendments specifically identify Point-of-Use (POU) and Point-of-Entry (POE) devices as options that can be used for compliance with NPDWRs. POU and POE devices can be effective and affordable compliance options for small systems in meeting a new arsenic MCL. A Federal Register notice is being prepared by EPA to delete the prohibition {§141.101} on the use of POU devices as compliance technologies. Because of this prohibition, few field studies exist on the application of POU and POE devices. One such case study was performed by EPA, in conjunction with the Village of San Ysidro, in New Mexico (Rogers 1990). The study was performed to determine if POU Reverse Osmosis (RO) units could satisfactorily function in lieu of central treatment to remove arsenic and fluoride from the drinking water supply of a small rural community of approximately 200 people. A RO unit, a common type of POU device, is a membrane system that rejects compounds based on their molecular properties and characteristics of the reverse osmosis membrane. The RO units removed 86% of the total arsenic.

Prospective Technologies

Ion Exchange with Brine Recycle. Research recently completed by the University of Houston (Clifford) at McFarland, CA and Albuquerque, NM has shown that ion exchange treatment can reduce arsenic (V) levels to below 2

µg/L even with sulfate levels as high as 200 mg/L. Sulfate does impact run length, however; the higher the sulfate concentration, the shorter the run length to arsenic breakthrough. The research also showed the brine regeneration solution could be reused as many as 20 times with no impact on arsenic removal provided that some salt was added to the solution to provide adequate chloride levels for regeneration. Brine recycle reduces the amount of waste for disposal and the cost of operation.

Iron (Addition) Coagulation with Direct Filtration. The University of Houston (Clifford) recently completed pilot studies at Albuquerque, NM on iron addition (coagulation) followed by direct filtration (microfiltration system) resulting in arsenic (V) being consistently removed to below 2 µg/L. Critical operating parameters are iron dose, mixing energy, detention time, and pH.

Conventional Iron/Manganese (Fe/Mn) Removal Processes. Iron coagulation/filtration and iron addition with direct filtration methods are effective for arsenic (V) removal. Source waters containing naturally occurring iron and/or manganese and arsenic can be treated for arsenic removal by using conventional Fe/Mn removal processes. These processes can significantly reduce the arsenic by removing the iron and manganese from the source water based upon the same mechanisms that occur with the iron addition methods. The addition of iron may be required if the concentration of naturally occurring iron/manganese is not sufficient to achieved the required arsenic removal level.

"Arsenic Removal Using Bottom Ash" or ARUBA is based on coating the surfaces of particles of bottom ash (a finely powdered and sterile waste material from coal-fired power plants) with ferric (hydr)oxide. The manufacturing process is conducted at room-temperature and atmospheric pressure. Thus, the material can be produced with relatively simple equipment at low cost.

Removing arsenic from contaminated drinking water is simple. ARUBA is mixed into the water, where it reacts with and immobilizes arsenic by adsorption and/or co-precipitation.

The resulting complex can be filtered or settled out of the water, and is safe enough for disposal in municipal landfills, per EPA standards.

Bottom ash is much less expensive than solid ferric oxide particles, which are often used as a filter media to bond arsenic species. Moreover, it has a high surface to volume ratio meaning that less material is required for water treatment, and hence less waste is produced.

The cost of raw materials needed for ARUBA production is expected to be low- less than 0.5 cents (\$0.005) per kg ARUBA. Based on field results over three trips to Bangladesh in 2007 and 2008, treating 1 liter of Bangladesh

groundwater at an initial arsenic concentration of 400 ppb requires approximately 4-5 grams of ARUBA.

Besides the methods mentioned above, several new methods have been studied recently. Some interesting methods are shortly described below [49-56]:

- (a) Fe-Mn-Oxidation
- (b) Green sand filtration
- (c) Coagulation assisted Microfiltration
- (d) In situ (sub-surface) arsenic immobilization
- (e) Enhanced coagulation (aka electrocoagulation, electroflotation)
- (f) Biological arsenic removal
- (g) Phytoremediation
- (h) Electrokinetic treatment
- (i) IOCS (iron oxide coated sand (see also chapter 3.1)
- (j) Memstill®
- (k) Water Pyramid
- (l) Solar Dew Collector
- (m) Conventional iron and manganese removal can

IX. ANALYTICAL TOOLS FOR MONITORING ARSENIC IN THE ENVIRONMENT

Various analytical techniques are available for the determination of arsenic species. Lab-based instrumentation such as ICP-MS, atomic fluorescence spectrometry, inductively coupled plasma (ICP), ICP/mass spectrometry (MS), and LC/MS/MS. and graphite furnace AAS applications provide accurate and reproducible results. The development of newer technology such as AFM and SERS is still in its infancy and they might suffer from high throughput potential and cost issues. X-ray fluorescence can be used for measuring arsenic in biological materials and environmental samples. This method has the advantage that no sample digestion or separation steps are required. However, the sample must be pre-concentrated on a suitable solid substrate such as resin to give a detection limit of 20-50 ppb. Hydride generation combined with atomic fluorescence spectroscopy is a relatively new technique that provides sensitivity better than 20 parts per trillion and linearity up to 10 ppm.

ICP: The plasma atomizes and ionizes all forms of arsenic so that the response does not vary with species as in the more traditional AAS methods. ICP is often used together with MS or AES (Atomic Emission Spectroscopy). The ICPMS technique provides higher precision and lower detection limits. Sample introduction *via* electrothermal vaporization should be used to overcome plausible interference from high levels of chloride due to the formation of argon chloride in the plasma (the same mass as arsenic, 75As). However, it is still problematical for the determination of low concentrations of arsenic in “real-world” samples due to the poor ionization efficiency in ICP. [48]

Surface Enhanced Raman Spectroscopy (SERS): Raman spectroscopy identifies and quantitates the concentration of molecules by measuring the wavelength and intensity of the laser light scattering. A molecule is adsorbed onto a metal surface (usually silver), and laser light is reflected off the adsorbed molecule. The change in wavelength of the scattered light is dependent on the vibrational spectrum of a target molecule. Raman spectra of arsenite and arsenate in solution are known, although minimum detection limits have not been determined. However, a sensor that uses cationic coated silver particles as substrates to detect perchlorate, chromate, dichromate, and cyanide anions has been developed. The coating attracts the anions to the SERS substrate where they are identified and quantified by their characteristic Raman scattering. The technique is able to detect chromate anions to levels of 60 ppb [30]. This technology can be miniaturized with recent advances in laser and microfabrication, therefore, SERS technology can be a serious contender

Atomic Force Microscopy (AFM): AFM uses a microcantilever, coated with a “detector film” that interacts with the desired species. The adsorption of a target analyte onto the film causes one of several changes: surface stress, a temperature change, or increased mass. These surface changes all result in the microcantilever deforming (bending). This technology has been applied for the detection of chromate and cesium. These sensors all demonstrated excellent sensitivity, capable of ppb detection limits, and high selectivity. It may be possible to design a coating capable of selectively binding arsenic. Microcantilevers have been fabricated in array for multiple sensing applications.

TABLE I

Arsenic Method	Comments	Limit of Detection (LOD) /gL-1 (ppb)
ICP-AES	High sensitivity, however equipment is expensive and requiring trained personnel	0.7
ICP-MS	Higher precision and lower detection limits compared to ICP-AES	0.002-0.06
N AA	High sensitivity, possible spectral interferences	0.001-0.02
Capillary Electrophoresis	Good sensitivity but requires indirect measurement methods	2-5
Surface Enhanced Raman (SERS)	Selectivity and sensitivity have been shown for chromate could be promising for arsenic	-
Colorimetric Assays	Simple, but generates arsine gas and is prone to false positive and	1-30

	falsenegative readings	
Polarography (LSP, DPP, SQP)	Poor detection limits, use of toxic mercury and better electrochemistry techniques now available	10
Cathodic Stripping Voltammetry (CSV)	Sensitive, however copper interference a problem and use of mercury a concern	0.5
Anodic Stripping Voltammetry (ASV)	Highly sensitive, however interference from other metals (copper) a major concern, analysis time can be lengthy. Reusability of electrodes and reproducibility of signal a concern	0.05-0.5
Modified boron doped diamond (BDD) with Pt nanoparticles	Sensitive and elimination of interferences by copper and chloride. Reproducible signal and reusable	0.5
Electrode Arsenite Oxidase based Biosensor	Sensitive and very selective to As(III). No interference from copper and fast analysis time (10 s)	1.0
Biosensor (AcP and PPO)	Sensitive and selective to As(V), however enzymes can be inhibited by other metals and chemicals	1.5

Neutron Activation Analysis (NAA): The decay of target nuclides in the sample with a definite half-life, upon activation with formation of radioactive nuclides, emits beta particles and gamma rays which can be detected by a NAA high-resolution gamma-ray spectrometer. As one of the most sensitive analytical techniques, NAA is often used as a reference method. However, spectral interferences are encountered, possibly owing to a high salt level in sea water [47]. This problem might be overcome by using $Pb(NO)_3$ and $TiCl_3$ as the carrier and reducing agent.

Capillary Electrophoresis (CE): In combination with a sensitive detection technique, CE using a 50-75 μ m diameter fused silica capillary has potential as an analytical technique. Under an applied separation potential, charged analytes are provided good sensitivity and selectivity for arsenic compounds can be attained

Biosensor and Bioassay:

Many micro-organisms such as algae, fungi, yeast and bacteria have been used for biosorption of toxic elements. As an example, *Chlorella vulgaris* can transform inorganic arsenic compounds and oxidize As(III) to As(V). The arsenite oxidizing bacteria so far isolated either can gain energy from arsenite oxidation or have been proposed to do so as part of a detoxification process. Aerobic growth with arsenite as the electron donor is exergonic, generating a

substantial amount of free energy. Other microorganisms can reduce arsenate to arsenite or even arsine (AsH_3) whereas marine algae transform arsenate into non-volatile methylated As compounds such as methylarsionic acid and dimethylarsinic acid in seawater. However, this fact has not yet been exploited as a practical way toward the development of a biosensor for As(III) or an analytical system for arsenic speciation.

REFERENCES

- [1] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, *Talanta* 58:201–235, 2002.
- [2] B.K. Biswas, J. Inoue, K. Inoue, K.N. Ghimire, H. Harada, K. Ohto, H. Kawakita, Adsorptive removal of As(V) and As(III) from water by a Zr(IV)-loaded orange waste gel, *J. Hazard. Mater.* 154: 1066–1074, 2008.
- [3] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.* 17: 517–569, 2002
- [4] M.J. Haron, W.M.Z.W. Yunus, N.L. Yong, S. Tokunaga, Sorption of arsenate and arsenite anions by iron(III)-poly (hydroxamic acid) complex, *Chemosphere* 39,2459–2466. 1999
- [5] C.P. Huang, P.L.K. Fu, Treatment of arsenic(V)-containing water by the activated carbon process, *J. Water Pollut. Control Fed.* 56, 233–242, 1984.
- [6] A. Violante, M. Ricciardella, S.D. Gaudio, M. Pigna, Coprecipitation of arsenate with metal oxides: nature, mineralogy, and reactivity of aluminum precipitates, *Environ. Sci. Technol.* 40, 4961–4967, 2006
- [7] M. Çolak, Ü. Gemici, G. Tarcan, The effects of colemanite deposits on the arsenic concentrations of soil and groundwater in Iğdeköy-Emet, Kutahya, Turkey, *Water Air Soil Pollut.* 149, 127–143, 2003
- [8] M. Çöl, C. Çöl, Arsenic concentrations in the surface, well and drinking waters of the Hisarcik, Turkey, area, *Hum. Ecol. Risk Assess.* 10, 461–465, 2004.
- [9] Ü. Gemici, G. Tarcan, Hydrogeological and hydrogeochemical features of the Heybeli spa, Afyon, Turkey: arsenic and the other contaminants in the thermal waters, *Bull. Environ. Contam. Toxicol.* 72, 1107–1114, 2004
- [10] M. Doğan, A.U. Doğan, Arsenic mineralization, source, distribution, and abundance in the Kutahya region of the western Anatolia, Turkey, *Environ. Geochem. Health* 29, 119–129, 2007
- [11] Ü. Gemici, G. Tarcan, C. Helvacı, A.M. Somay, High arsenic and boron concentrations in groundwaters related to mining activity in the Bigadiç borate deposits (Western Turkey), *Appl. Geochem.* 23, 2462–2476, 2008.
- [12] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.* 17, 517, 2002.
- [13] P. Mondal, C.B. Majumder, B. Mohanty, Laboratory based approaches for arsenic remediation from contaminated water: recent developments, *J. Haz. Mat.* B137, 464, 2006
- [14] National Research Council, Arsenic in Drinking Water, National Academy of Sciences, Washington, DC, USA, 2001.
- [15] WHO, Guidelines for drinking-water quality, addendum to vol.1 recommendations Geneva, 1998.
- [16] US Environmental Protection Agency, Panel 14: national primary drinking water regulations: arsenic and clarifications to compliance and new source contaminants monitoring, vol. 66, p. 194, Washington DC, USA., 2001
- [17] T.S.Y. Choong, T.G. Chuah, Y. Robiah, F.L. Gregory Koay, I. Azni, Arsenic toxicity, health hazards and removal techniques from water: an overview, *Desalination* 217, 139, 2007.

- [18] A. Kovski, EPA recalculation of cancer risk for arsenic could have costly impact on many industries, *Environ. Reporter – Bureau Natl. Affairs Inc.* 40 (36), 2138–2139, 2009
- [19] US Department of Health and Human Services (Ed.), *Toxicological Profile for Arsenic*, US Department of Health and Human Services, Washington DC, 2000.
- [20] C.P. Huang and P.L.K. Fu, Treatment of arsenic (V)- containing water by the activated carbon process, *J. Water Pollut. Control Fed.*, 56, 233, 1984.
- [21] E.S. Lomaquahu and A.H. Smith, Feasibility of new epidemiology studies on arsenic exposures at low levels, *AWWA Inorganic Contaminants Workshop*, San Antonio, TX, February 23-24, 1998.
- [22] US EPA, National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring; Final Rule, *Federal Register*, vol. 66, no. 14, January 22, pp. 6975-7066, 2001
- [23] Agency for Toxic Substances and Disease Registry (ATSDR), *Draft Toxicological Profile for Arsenic*, Prepared for the US Department of Health and Human Services, by the Research Triangle Institute, August 1998.
- [24] Agency for Toxic Substances and Disease Registry (ATSDR): *ToxFAQs TM for Arsenic*, July 2001.
- [25] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.* 17, 517–568, 2002
- [26] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry; A Comprehensive Text*, 3rd ed., Interscience Publishers, New York, 1972.
- [27] N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Reed Educational and Professional Publishing Ltd, Woburn, MA, USA, 1997.
- [28] S.R. Randall, D.M. Sherman, Surface complexation of arsenic(V) to iron(III) (hydr)oxides: structural mechanism from ab initio molecular geometries and EXAFS spectroscopy, *Geochim. Cosmochim. Acta* 67, 4223–4230, 2003.
- [29] D. Mohan, C.U. Pittman Jr., Arsenic removal from water/wastewater using adsorbents—a critical review, *J. Hazard. Mater.* 142, 1–53, 2007
- [30] C. Namasivayam and S. Senthilkumar, Removal of As (V) from aqueous solution using industrial solid waste: adsorption rates and equilibrium studies, *Ind. Eng. Chem. Res.*, 37(12), 4816, 1998.
- [31] S.A. Wasay, J. Haron, A. Uchiumi and S. Tokunaga, Removal of arsenite and arsenate ions from aqueous solution by basic yttrium carbonate, *War. Res.*, 30, 1143, 1996.
- [32] M.J. Haron, W.M.Z. Wan Yunus, N.L. Yong and S. Tokunaga, Sorption of arsenate and arsenite anions by iron (III)-poly (hydroxamic acid) complex, *Chemosphere*, 39, 2459, 1999
- [33] US EPA, National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring; Proposed Rule, *Federal Register*, vol. 65, no. 121, June 22, 2000, pp. 6975-7066.
- [34] US EPA Office of Emergency and Remedial Response, *Comprehensive Environmental Response Compensation and Liability Information System database (CERCLIS 3)*, October 2001.
- [35] National Research Council (NRC), *Arsenic in Drinking Water*. National Academy Press, Washington, D.C., p 310. 1999
- [36] K.J. Irgolic, Determination of total arsenic and arsenic compounds in drinking water, in W.R. Chappell, C.O. Abernathy, and C.R. Cothem, eds., *Arsenic: Exposure and Health*, Northwood, UK, 1994, pp.51–0.
- [37] D. Clifford and Z. Zhang, Arsenic chemistry and speciation. Paper presented at the American Water Works Association Annual Conference. New York, NY, June 19-23, 1994.
- [38] A.H. Welch, D.B. Westjohn, D.R. Helsel and R.B. Wanth, Arsenic in ground water of the United States: occurrence and geochemistry, *Ground Water*, 38(4) 589. 2000.
- [39] J. Fergusson, *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*, Pergamon Press, Oxford, 1990.
- [40] T.R. Harper and N.W. Kingham, Removal of arsenic from wastewater using chemical precipitation methods, *Water Environ. Res.*, 64, 200. 1992.
- [41] T. Viraghavan, K.S. Subramanian and J.A. Aruldo-s, Arsenic in drinking water-- problems and solutions, *Wat. Sci. Tech.*, 40, 69. 1999.
- [42] H.S. Altundogan, S. Altundogan, F. Tumen and M. Bildik, Arsenic removal from aqueous solutions by adsorption on red mud, *Waste Management*, 20, 761. 2000.
- [43] J. Pattanayak, K. Mondal, S. Mathew and S.B. Lalvani, A parametric evaluation of the removal of As (V) and As (III) by carbon-based adsorbents, *Carbon*, 38, 589. 2000
- [44] US EPA, *Proven Alternatives for Aboveground Treatment of Arsenic in Groundwater*, Washington, DC, EPA-542-S-02-002, 2002.
- [45] D.G. Brookins, *Eh-pH Diagrams for Geochemistry*. Springer-Verlag, Berlin, pp. 28-29. 1988
- [46] H. Gecol, E. Ergican and A. Fuchs, Molecular level separation of arsenic (V) from water using cationic surfactant micelles and ultrafiltration membrane, *J. Membr. Sci.*, 241, t05, 2004
- [47] S. Wang, C.N. Mulligan, Occurrence of arsenic contamination in Canada: sources, behaviour and distribution, *Sci. Total Environ.* 366, 701–721, 2006
- [48] Y. Xu, T. Nakajima, A. Ohki, Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded Shirasuzzeolite, *J. Hazard. Mater.* B92, 275–287, 2002
- [49] H. Sun, L. Wang, R. Zhang, J. Sui, G. Xu, Treatment of groundwater polluted by arsenic compounds by zero valent iron, *J. Hazard. Mater.* B129, 297–303. 2006
- [50] J.H.T. Luong*, E. Majid and K.B. Male, Analytical Tools for Monitoring Arsenic in the Environment, *The Open Analytical Chemistry Journal*, 1, 7-14, 2007
- [51] Rottschafer, J. M.; Boczkowski, R. J.; Mark, H. B. *Talanta*, 19, 163, 1972
- [52] Goossens, J.; Moens, L.; Dams, R. *J. Anal. At. Spectrom.*, 8, 921, 1993
- [53] J.I. Oh, S.H. Lee, K. Yamanot, Relationship between molar volume and rejection of arsenic species in groundwater by low-pressure nanofiltration process, *J. Membr. Sci.* 234 167–175, 2004
- [54] P. Brandhuber, G. Amy, Arsenic removal by a charged ultrafiltration membrane—influences of membrane operating conditions and water quality on arsenic rejection, *Desalination* 140, 1–14, 2001
- [55] P. Brandhuber, G. Amy, Alternative methods for membrane filtration of arsenic from drinking water, *Desalination* 117, 1–10, 1998.
- [56] E. Klein, Affinity membranes: a 10-year review, *J. Membr. Sci.* 179, 1–27, 2000.
- [57] M.L. Pierce, C.B. Moore, Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.* 16, 1247–1253, 1982
- [58] G.S. Zhang, J.H. Qu, H.J. Liu, R.P. Liu, G.T. Li, Removal mechanism of As(III) by a novel Fe–Mn binary oxide adsorbent: oxidation and sorption, *Environ. Sci. Technol.* 41, 4613–4619, 2007