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Chapter 1

Introductory Chapter: Arsenic

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.78399

1. Arsenic occurrence

Arsenic (As) is a chemical element the abundance of which in the continental crust of the Earth is given as 1.5–2 ppm. Most often arsenic appears in nature in the form of Fe, Co and Ni arsenides, arsenic sulfide, and native arsenic. It belongs to the metalloids, in spite that it shows intermediate properties between metals and non-metals.

In general, arsenic forms soluble oxyanions with the predominant oxidation states +3 and +5, while the minor oxidation states are 0 and −3. The main form of As(III) is arsenite existing in solutions with pH between 5 and 9. H_3AsO_3 and the anions resulting from its dissociation occurring according to Eq. 1 are $H_2AsO_3^-$, $H_2AsO_3^{2-}$, and AsO_3^{3-}:

$$H_3AsO_3 \xrightarrow{pK_a=9.2} H_2AsO_3^- + H^+ \xrightarrow{pK_a=14.22} HAsO_3^{2-} + H^+ \xrightarrow{pK_a=19.22} AsO_3^{3-} + H^+ \quad (1)$$

The main form of As(V) is H_3AsO_4. The anions resulting from its dissociation are $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. The arsenates have high-ionization capacity due to the presence of the double bond. The H_3AsO_4 molecule easily loses hydrogen ions by dissociation remaining with a negative charge, forming successively several anions according to Eq. 2:

$$H_3AsO_4 \xrightarrow{pK_a=2.2} H_2AsO_4^- + H^+ \xrightarrow{pK_a=6.94} HAsO_4^{2-} + H^+ \xrightarrow{pK_a=11.3} AsO_4^{3-} + H^+ \quad (2)$$

2. Arsenic and its compound application and removal

Elemental arsenic has a limited application mainly as lead and brass alloy's ingredient, but its compounds are widely used in the industry. The gallium arsenide (GaAs) is extensively used in the electronic industry for high-frequency integrated circuits, laser diodes, and Light Emission Diodes (LEDs); the arsenic oxide is used in glass production industry; the arsenic sulfides

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are used as pigments in textile. There is a revival of the interest in arsenic as medicine for the treatment of acute promyelocytic leukemia, multiple myeloma, myelodysplastic syndrome, and various resistant solid tumors. Other applications of the arsenic compounds include the paper industry, the pyrotechnic industry, and so on. Arsenic compounds were used as pesticides in the past.

The conventional methods most applied for arsenic removal are:

- Coagulation and flocculation (the most commonly employed), which include two distinct processes: colloids destabilization neutralizing the electric charges allowing particles aggregation, followed by flocculation by a polymer building giant aggregates [1, 2].
- Precipitation including one of the following methods: alum coagulation [3], iron coagulation [4], lime softening [5], and combination of iron (and manganese) removal [6–8].
- Membrane filtration: a pressure driven process, which can include one of the following: microfiltration, ultrafiltration, nanofiltration, and hyperfiltration or reverse osmosis [9–12].
- Adsorption and ion exchange are employing solids to accumulate on their surface substances contained in liquid phase [12–16].
- Bioremediation, ozone oxidation, and electrochemical treatments are also applied.

3. Arsenic and its compounds toxicity

Arsenic is extremely poisonous for multicellular life, although several types of bacteria are capable of using arsenic compounds as respiratory metabolites. Pollution of groundwater with arsenic is a problem that affects millions of people around the world. Worldwide, up to 100 million people are at risk of exposure to arsenic from excess arsenic in drinking water in countries such as Argentina, Bangladesh, Chile, China, India, Mexico, and the USA. The US Environmental Protection Agency classifies arsenic as a carcinogen of group A due to the evidence of its adverse effects on health [17]. Exposure to 0.05 mg L^{-1} can cause 31.33 cases of skin cancer per 1000 inhabitants. For this reason, the maximum acceptance limit of 0.050 mg L^{-1} of arsenic was lowered to 0.010–0.020 mg L^{-1}. However, it was found that a daily intake of 12–15 μg arsenic as a microelement from meat, fish, vegetables, and cereals maintains the immune system activity. The WHO warns that the maximum safe arsenic concentration for health is as low as 10 ppb, but limit values for arsenic species are not established [17, 18].

Arsenic can be found as a pollutant in water or food, especially in shells and other seafood, and often polluting fruits and vegetables, especially rice. Today arsenic poisoning occurs through industrial exposure, from contaminated wine or smuggled spirits, or due to intentional use. The possibility of arsenic contamination of herbal preparations and food supplements should also be taken into account.

Inorganic forms of arsenic are more toxic than the organic ones. Arsenic oxides are the most common threat because arsenite and arsenate salts are the most toxic. These forms are components of geological formations and are extracted into groundwater.

The two forms of inorganic arsenic reduced (trivalent arsenic) and oxidized (five valent arsenic) can be absorbed and accumulated in tissues and body fluids. The trivalent form is more toxic and reacts with thiol groups. Very few organs and systems are not affected by the toxic effects of arsenic. The arsenic compound toxicity decays in the following order: As(III) > monomethylarsine oxide > dimethylarson > monomethylarsenate > As(V). The toxicity of As(III) is 10 times greater than that of As(V) and the lethal dose for adults is 1–4 mg kg^{-1}.

4. Analytical methods for arsenic quantification

The "total arsenic" determined in a sample most often do not represent a valuable information, because of the different properties and different toxicity of its species [19, 20]. The main problem is the easy conversion of the arsenic species to another caused by the pH changes, the presence of reducing agents, oxidizers, and certain bacterial strains able to produce a lot of organic As-species [21, 22]. That is why the As speciation is the only important way to characterize the origin of the As-related problems such as its toxicity and biogeochemical cycling and to find the best procedure for drinking water treatment. Unfortunately, As speciation remains challenging, because of the interference between the arsenic species possessing different toxicity [23], which is typical for the organic As-species [24, 25].

The best analytical methods for As speciation are considered those, including chromatographic separations [26, 27] such as IC [28] and HPLC [29], coupled with a sensitive detection system, such as ICP–MS, AFS–HG, and AAS–HG [30]. Specific sorbents and exchange resins have been developed and applied recently for this purpose [31–35]. Apart from the chromatographic and non-chromatographic methods for the arsenic species separation, simple and cost-effective electrochemical methods were developed recently based on the distinct As-species electrochemical properties [36, 37].

5. Conclusion

In spite of the arsenic and its compounds important industrial application, the greatest attention is paid to their influence on the human health, especially in case of long temp action by contaminated drinking water and food. That is why detailed studies on arsenic toxicity and cancer provoking mechanisms were realized. The toxicity of the arsenic species may differ 10 and more times from one to another, so their transformation caused by condition changes (as pH, dissolved oxygen, and bacterial activity) during the sample transportation and conservation prior the laboratory analysis may cause false results. For this reason, simple analytical techniques and sensors for arsenic speciation have been developed able to realize *in-situ* speciation to evaluate the real toxicity of contaminated water, food, or soil samples. To prevent

the negative arsenic influence on the human health, the most important is the decontamination of the affected waters and soils. Many methods based on different principles were developed ad successfully applied for this purpose.

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