



Review

Arsenic in contaminated waters: Biogeochemical cycle, microbial metabolism and biotreatment processes

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ABSTRACT

Arsenic is responsible for the contamination of water supplies in various parts of the world and poses a major risk to human health. Its toxicity and bioavailability depend on its speciation, which in turn, depends on microbial transformations, including reduction, oxidation and methylation. This review describes the development of bioprocesses for the treatment of arsenic-contaminated waters based on bacterial metabolism and biogeochemical cycling of arsenic.

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1. Introduction

Arsenic is a natural element which occurs in many environmental compartments. Whatever its natural or industrial origin, it is often responsible for the contamination of water supplies. Depending on the physico-chemical condition of the environment, some arsenic compounds can be highly soluble, resulting in a high level of bioavailability. The presence of these compounds has therefore been declared as a major risk to human health in various parts of the world. The most dramatic effects have been observed in India and Bangladesh, where it has been estimated that the drinking water supplies of more than 50 million inhabitants are contaminated with arsenic (<http://www.who.int/inf-fs/fr>). Arsenic toxicity depends on its speciation—inorganic species of arsenic i.e. arsenite (As(III)) and arsenate (As(V)) are the most toxic, and also the most abundant in water, which in turn, depend on processes in which micro-organisms play a key role [1]. Bacterial transformations include reduction (including dissimilatory reduction), oxidation and methylation of compounds among the four oxidation states, and have been shown to occur in both aquatic and terrestrial systems [2,3]. Several studies suggest that the reduction of arsenate to arsenite is involved in the solubilisation of the element resulting in the contamination of important water supplies [4,5]. On the other hand, the oxidation mechanism converts highly toxic and highly soluble As(III) into less toxic and less soluble As(V). The biogeochemical cycle of this metalloid is described in the present

review, focusing on the contribution of micro-organisms to its speciation. The properties of arsenic accounting for its presence, bioavailability and toxicity in aqueous media are also presented. Recent studies on the development of bioprocesses, based on bacterial direct or indirect immobilization of arsenic, possibly providing alternatives to the chemical methods used at present to treat arsenic-contaminated waters are also presented.

2. The biogeochemical cycle

Arsenic is a ubiquitous element of both natural and anthropogenic origin. It is present in the atmosphere, the pedosphere, the hydrosphere and the biosphere. A very exhaustive review on these aspects has been presented by Mandal and Suzuki [6]. The biogeochemical cycle involves several physico-chemical processes (such as oxido-reduction, precipitation/solubilisation, and adsorption/desorption processes) as well as biological mechanisms, in which microbiological processes play a key role. These various mechanisms will be described in detail in Sections 2.2 and 2.3.

2.1. The origins of arsenic

2.1.1. Natural origins

Arsenic is the 20th most abundant element in the earth's crust, where it reaches levels between 1 and 2 mg/kg [7]. From a geochemical point of view, this element is associated with sulphurous minerals of sulphur, iron and various other metals (such as Au, Ag, Cu, Sb, Ni and Co in particular). Although it has been detected in more than 200 different minerals, the most common are

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arsenopyrite (FeAsS), orpiment (As₂S₃) and realgar (AsS) [8]. Its presence in hydrothermal environments is due to either recent or ancient volcanic activity [9]. The arsenic levels present in the atmosphere are due to wind erosion processes, volcanic emissions, sea spray, forest fires and the process of volatilization occurring in cold climates, mainly as the result of biological processes such as biomethylation [10]. Since arsenic is such a widespread element, it is hardly surprising that it is found in high levels in living organisms. In plants, for example, where the arsenic content relates directly with soil concentrations, the levels range from 0.001 to 5 µg of arsenic per gram of dry matter, depending on the species and the type of soil involved [11,12].

2.1.2. Anthropogenic origins

Arsenic is one of the components of a large number of compounds generated by human activities (precious metals mining, pharmaceutical manufacturing, wood processing, glassmaking industry, electronics industry, chemical weapons etc.) [13,14]. Arsenic has been widely used in agriculture: sodium arsenite, which is the only known fungicide available for protecting grapevines from excoresis, was indeed used until 2001 [15]. The main anthropogenic sources of atmospheric arsenic contamination are As-rich fossil fuels producing arsenic oxide (As₂O₃), which is highly toxic. It has been calculated that arsenic is retained in the atmosphere for less than 10 days before being released in the form of dust or precipitated by rainfall [10]. The atmospheric As levels have been found to be highest near industrial sites: higher levels therefore occur in the northern hemisphere, where there are many industrial sites, compared to the southern hemisphere [10].

Mine wastewaters are the fluids with the highest arsenic contents [16]. Sulphurous mineral outcrops are naturally subject to oxidation, since they come in contact with both air and water, leading to the gradual development of sulphuric acid and the solubilisation of the metals present. Acid mine drainage (AMD) waters result from water percolating through excavated ores containing sulphites and/or collecting in galleries as a result of seepage or underground water movements. These effluents, which often contain extremely high levels of toxic metals, constitute one of the main environmental problems with which the world's mining industries are faced [17].

The production of AMD is favoured and amplified by both chemical and biological catalytic reactions. Acidic waters affect the structure of the communities of micro-organisms they harbour, and although some forms of life (mainly consisting of bacteria and archaea) are able to survive under these conditions [17], the number of species present (i.e., the biodiversity) usually decreases. In addition, the low pH levels generally existing in these environments inhibit the growth of many bacteria contributing to the decomposition of the organic matter present in the water, and thus reduce the amount of nutrients available for other species. In extreme cases, the higher organisms inhabiting running waters receiving AMD effluents disappear completely over long stretches [17,18].

2.2. Speciation and mobility

Arsenic is a metalloid which is present in the environment in four oxidation states, which are denoted -3, 0, +3 and +5. Arsenite (As(III)) and arsenate (As(V)) species are the main forms occurring in aquatic environments. The relative proportions of these oxidation states in a given environment depend on the biological processes involved (see Section 2.3) as well as on the local physico-chemical conditions, including the redox potential (Eh) and the hydrogen potential (pH), which are important factors. Since the pKa contents of arsenate (H₃AsO₄) are pKa1 = 2.19, pKa2 = 6.94 and pKa3 = 11.5, the H₂AsO₄⁻ form predominates in oxidative media with pH levels below 6.9, whereas the HAsO₄²⁻ form predominates at higher pH

levels. In the case of arsenite, the lowest pKa levels recorded are equal to 9.22. In most natural waters with pH levels below 9.2 as well as in slightly reductive environments, As(OH)₃ is the main form present [19]. The solubility of arsenic and the resulting bioavailability of this element, are closely related to its speciation. Several studies have shown that the reduction of arsenate into arsenite results in the solubilisation of this element [4,5]. However, arsenate may be sequestered after being co-precipitated with ferric iron [20] or sulphur [21] or adsorbed by clay, calcite, organic matter or hydroxides, in particular ferric oxyhydroxides [22]. The remediation procedures used at present are based on the chemical oxidation of arsenite into arsenate, followed by the immobilization of the latter substance using the methods described above.

2.3. Microbial processes and the sequestration of arsenic

The relative proportions of the various arsenic oxidation states in a given environment also depend on the bioprocesses involved in the metabolism by micro-organisms [23], especially those involving bacteria, such as As(V) reduction, As(III) oxidation and the various methylation reactions. These reactions protect bacteria from the toxic effects of arsenic (by enhancing the resistance mechanisms), and in the case of some species, contribute to energy metabolism processes.

2.3.1. Reduction

Many studies have been carried out on the mechanisms underlying the reduction of arsenate into arsenite. Since they have been extensively presented in various reviews [24] even very recently [25] we will not go in too many details. Briefly, two mechanisms of reduction have been described.

The first one is related to the detoxification of the cells and is based on the expression of the *ars* operon [24], composed at minimum of 3 genes (*arsRBC*) encoding respectively a transcriptional repressor, a transmembrane efflux pump and an arsenate reductase. In some bacteria an enlarged version composed of 5 genes (*arsRDABC*) was described, in which the product of *arsA* was identified as an ATPase providing the energy to the ArsB efflux pump, while *arsD* was found to enhance the efficiency of the ArsAB efflux pump. Arsenate ions enter the cells via phosphate transporters, due to structural homologies with phosphate ions. After reaching the cytoplasm, As(V) is reduced into As(III) by the arsenate-reductase enzyme ArsC before being excreted from the cell by transmembrane protein ArsB (which is also known as Acr3 in the context of some eukaryotic micro-organisms) or the ArsAB complex. This transformation process followed by the excretion of arsenic is a common occurrence in the living world and is widespread in bacteria [25,26].

A second reduction process, known as dissimilatory reduction, has been described in bacteria belonging to various phylogenetic groups including obligate or facultative anaerobic micro-organisms (for review see [25]). In this case, bacterial cells gain metabolic energy by "breathing" arsenic, since they utilize As(V) as an electron acceptor [27]. Respiratory arsenate reductase (consisting of 2 subunits, ArrA and ArrB), has been identified as a membrane-bound heterodimer protein [28].

It has been established in several studies that these two systems play a non-negligible role in the solubilisation of arsenic leading to major contaminations of aquatic environments [1,29].

2.3.2. Oxidation

A wide range of bacteria isolated from various contaminated environments were described for their ability to synthesize arsenite oxidases and thus to oxidize As(III) enzymatically. Since the first report, almost one century ago by Green, of a bacterium

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