

Microbial Transformations of Arsenic

Abhinandana, K. R. and Lohith Kumar, N.

Department of Agricultural Microbiology, GKVK, Bengaluru, Karnataka -560 065

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Biotransformation of toxic metals is an approach adopted by microbes to get rid of such toxic heavy metals. It is an important component of biogeochemical cycles of metals and is exploited for bioremediation of metal contaminated soils. Microbes transform metals by two ways: a) redox conversion of inorganic forms (e.g., oxidation and reduction), b) conversion of inorganic form to organic form and *vice versa* (e.g., methylation and demethylation) (Di *et al.*, 2019).

Arsenic (As) is one of the toxic metalloids found in nature. Natural processes as well as anthropogenic activities are responsible for the continuous release of arsenic into the environment. This increased arsenic contamination in soil and groundwater has become a serious health and environmental concern, because globally around 150 million people are estimated to be at risk from drinking water contaminated with arsenic above $50 \mu\text{g L}^{-1}$ (Majumder and Banik, 2019).

The toxicity of arsenic mainly depends upon its concentration, speciation and bioavailability. Arsenic has different speciation in different environments; they exist in both inorganic and organic forms. Among these, inorganic forms of arsenic are more toxic for plants and humans than organic forms. Further, inorganic arsenic forms are known to be present in four oxidation states *viz.*, -3, 0, +3, +5 [arsine (As^{-3}), elemental arsenic (As^0), arsenite (As^{+3}), and arsenate (As^{+5})], of which pentavalent As (V) and trivalent As (III) forms are more toxic.

Inorganic arsenic forms *viz.*, As (III) and As (V) mainly undergo microbially-mediated oxidation and reduction process respectively. As (III) oxidation is generally considered as the main transformation mechanism that converts more toxic As (III) into less toxic As (V). Currently, physiologically diverse As (III) oxidizers are found in various groups of bacteria and archaea, which includes both heterotrophic As (III) oxidizers (HAOs) and chemolithoautotrophic As (III) oxidizers (CAOs) (Cavalca *et al.*, 2013). Yamamura and Amachi (2014) reported that heterotrophic As (III) oxidation is a detoxification mechanism that converts more toxic As (III) into less toxic As (V), while CAOs As (III) oxidation is a

respiratory mechanism. These CAOs use As (III) as an electron donor. In this, arsenite itself can serve as an electron (e^-) donor for microbial respiration processes and oxidized to As (V) with e^- being passed to suitable e^- acceptors, such as oxygen (O_2) or nitrate (NO_3^-) under aerobic condition.

In contrast, a wide array of microorganisms have evolved the energy requiring detoxification process called arsenate reduction catalyzed by the *ars* operon, linked to the intracellular reduction of As (V) to As (III) by the ArsC protein under aerobic condition (Biswas *et al.*, 2019). In addition to the detoxifying As (V) reduction, certain bacteria can reduce As (V) as the terminal electron acceptor for anaerobic respiration. Such bacteria are defined as dissimilatory As (V) reducing prokaryotes (DARPs).

Methylation process is another important mechanism that confers arsenic biotransformation *i.e.*, conversion of inorganic form to organic form. This process produces volatile trimethylarsenites (TMAs), which will be rapidly oxidized into trimethylarsenates in the atmosphere, thus decreasing arsenic toxicity. Challenger (1945) proposed a scheme in which As (V) was eventually transformed to TMAs. In this scheme, As (V) is first reduced to As (III) then methylated and each methylation step results in the re-oxidation of the As, thus requiring a reductive step to As (III) prior to further methylation (Di *et al.*, 2019).

Therefore, microbial transformations of arsenic (oxidation, reduction, methylation and demethylation) play an important role in deciding environmental fate and toxicity of arsenic. Such microbial processes have the potential to promote As removal from contaminated soils/waters when used as intended.

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