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Arsenic-interacting plant proteins as templates for arsenic specific flotation collectors? A review

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A B S T R A C T

Arsenic-bearing minerals commonly occur within ore bodies that contain lead, nickel, gold and most notably copper. Due to similarities in the surface properties of base metal sulfide minerals and arsenic-bearing minerals, selective separations of arsenic from such ores by flotation remain challenging. Arsenic is also ubiquitous in the natural environment and extremely toxic to all forms of life. However, certain plant species have evolved mechanisms that allow them to thrive in arsenic rich soils, by hyper-accumulating arsenic within their root and leaf mass. This paper reviews the biological functions of arsenic hyper-accumulating plants and identifies the key biomolecules involved in the uptake, detoxification and sequestration of arsenic chemical species within these plants. The review then examines the possibility that these molecules hold the key to developing arsenic-specific flotation collectors.

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1. Introduction and background

Arsenic is ubiquitous in the natural environment and extremely toxic to all forms of life. Its occurrence in the environment predominantly results from the weathering of arsenic containing rocks and minerals or from anthropogenic activities, such as mining, pesticide-use and waste processing (Briat, 2010; Bruckard et al., 2010; Jedynak et al., 2012; Machado-Estrada et al., 2013; Niazi et al., 2012; Wang et al., 2011; Zhang et al., 2012).

In the environment, arsenic typically occurs in two valent states, As(III) and As(V), of which As(III) is the more toxic of the two (Francesconi et al., 2002; Ma et al., 2001b; Tripathi et al., 2007; Wang and Zhao, 2009). According to the World Health Organization (WHO), the median lethal dose of arsenic (LD_{50}) in human beings is 1–5 mg As/kg, and the safe concentration in drinking water is as low as 10 $\mu l/dm^3$. Yet contamination levels in excess of 1000 mg As/kg have been found in many agricultural and mining sites around Australia as well as Africa and the United States (Smith et al., 1998). Such high toxicity levels have a profound impact on the diversity of both plant and animal life in the areas, with several documented human deaths (Das et al., 1996).

In agricultural areas, the high levels of arsenic contamination are generally owed to the widespread use of pesticides. However in the mining areas, the contamination occurs as a result of waste production from treatment of arsenic-rich mineral ores. This contamination comes from two main sources: (1) the leaching of arsenic from waste dumps into both soil and ground water; and (2) the airborne release of arsenic during smelting (Smith et al., 1998). This is one of the reasons why modern smelting operations impose a strict penalty on the arsenic content of the concentrates sent for smelting, allowing for no more than 0.2% arsenic (Plackowski et al., 2012).

1.1. Arsenic in the minerals industry

Arsenic-bearing minerals commonly occur within ore bodies that contain lead, nickel, gold, silver and most notably copper. Common arsenic-bearing minerals include enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$). These minerals bear valuable copper as well as arsenic and commonly occur together with minerals such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4) and other copper sulfides. While enargite and tennantite could theoretically be recovered for their copper content, the high arsenic content makes it impractical from the environmental and economic perspective. In addition, the contamination of copper metal with the arsenic metalloid causes deterioration in properties such as conductivity, with detrimental consequences for the quality of the final copper metal product. Therefore, a selective separation of minerals such as enargite and tenantite from chalcopyrite and other copper sulfides is desirable.

Another arsenic mineral is arsenopyrite (FeAsS), which commonly occurs together with pyrite (FeS). While neither of these two minerals contain valuable metals, they both occur in close association with gold, whereby tiny gold grains are locked within the arsenopyrite and pyrite matrices (Morey et al., 2008). As with copper, the occurrence of arsenic within these minerals makes the selective recovery of gold even more challenging.

In mineral processing operations, the ore body is typically comminuted to a small particle size distribution. The comminution step is followed by a flotation step, where the minerals are separated based on their surface properties, namely their hydrophobicity. In order to improve the efficacy of the flotation step, reagents are typically added to the flotation pulp to enhance the hydrophobicity of the desired minerals. These reagents are called collectors. Other reagents are added to decrease the hydrophobicity of the unwanted gangue species, and these are called depressants (Gaudin, 1957). One of the key factors that are exploited to enhance the selectivity of reagent adsorption (and hence the selectivity of flotation) are the differences in the surface chemistry of the valuable and the gangue species. However, the surface characteristics of arsenic-bearing minerals such as enargite, tennantite and arsenopyrite very closely resemble those of the valuable mineral species such as chalcopyrite, bornite and pyrite. Previous attempts to find selective reagents for the depression of arsenic-bearing minerals have been met with limited success, as these reagents tend to adsorb onto the surfaces of both the arsenic-bearing and desired mineral species (Ásbjörnsson et al., 2004; Fullston et al., 1999; Plackowski et al., 2014, 2013; Richardson and Vaughan, 1989).

The modification of surface properties of arsenic minerals using Eh and pH manipulation has so far been the most successfully used technique for selective separation. The pH and Eh of the flotation pulp determine the degree of oxidation (as well as the speciation of the oxidised surface sites) of sulfide minerals. Careful manipulation of these two variables can lead to the generation of differences between the surface properties of arsenic-bearing and non-bearing sulfides (Bruckard et al., 2007; Plackowski et al., 2012; Smith and Bruckard, 2007; Smith et al., 2009, 2012). These differences can then be potentially exploited to achieve selective reagent adsorption and subsequent flotation. However, success has been partial and truly selective separations continue to elude both the research community and industrial practice.

There is therefore a strong need to consider more imaginative and unconventional avenues for locating a new type of arsenic-specific reagent. A potential opportunity exists in the natural world, in the form of arsenic hyper-accumulating ferns, which can be used as economic and environmentally friendly options of environmental remediation.

1.2. Arsenic hyper-accumulators in phytoremediation applications

The principle behind phytoremediation is that the plants are able to detoxify the environment by removing the contaminant from soils and/or groundwater, and then transform it into a stable and less toxic complex which remains stored within the plant biomass, which can then be harvested and stored/disposed appropriately.

A number of technologies for the remediation of arsenic-contaminated groundwater and soil, resulting from natural weathering of arsenic containing rocks, mining activities or pesticide use have been investigated. However, given the widespread nature of arsenic contamination (especially in low-socioeconomic and developing countries), phytoremediation is a logical choice because it is the most environmentally friendly and economically feasible option (Meharg and Hartley-Whitaker, 2002; Tripathi et al., 2007; Wang and Zhao, 2009).

A range of plants have been described to grow in soils containing higher than normal concentrations of arsenic (e.g. *Holcus lanatus* [Yorkshire fog grass] and *Cytisus striatus* [Portuguese broom shrub]). A good summary of plants exhibiting tolerance to arsenic is