



Review Article

Methods of arsenic wastes recycling: Focus on flotation



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ABSTRACT

Arsenic in water poses today a serious threat to the health of people in many countries. Also, oxidative weathering and dissolution of As-containing minerals (such as arsenopyrite and other gangue minerals), among other, of dissolved inorganic arsenic oxyanions that are transported in surface or groundwater, can subsequently become adsorbed on soil and sediment particles. The removal of arsenic, i.e. from mine tailings, could meanwhile render them suitable for recycling and hence, sustainability. For centuries, water has been a manufacturing tool that industry has taken for granted, because it was inexpensive and plentiful. Flotation, being a unique separation technique, initially originated from mineral beneficiation. In line with flotation, specific investigations are usually required: such as measurements of the particles' electrokinetic behavior, contact angle with the gas bubbles, aqueous speciation of the studied system and in general, chemistry; as the presence of the appropriate surfactants, frothers, depressants and modifiers help the efficient separation process. Another focus of the present work constitutes the economic aspect may be of the recovery of useful valuable minerals (i.e., gold), contributing to recycling meanwhile with environmental technology and wastewater treatment. For instance, arsenic-rich auriferous pyrite concentrates, often stockpiled in the mine area, could be further enriched in arsenic to assist also Au beneficiation, in case gold is associated with arsenopyrite (as it is the case studied in the present). Such arsenic removal is accomplished by sorption, including biosorption, flotation etc. and perhaps, a combined process with membranes separation downstream, too.

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1. Introduction

For centuries, water has been a manufacturing tool that industry has taken for granted, because it was inexpensive and plentiful. But

population growth, globalization, and climate change are shepherding in a new water-constrained era. Good, clean water just cannot be replaced and it is becoming harder to come by. Sustainability in the field of water separation processes and its significance for the chemical and process industry has been recently commented [1]. There is now a burgeoning literature that examines sustainable development in the context of minerals and mining, most of which is concerned with

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sustainability at global and national scales. Sustainable development in the corporate mining context was reported [2]. It is becoming increasingly important that mines, for the benefit of ecology, surrounding communities, governments, and its employees, continue to tackle pressing socio-economic and environmental issues with improved strategy, and help put sustainable development into practice in the industry [3].

Arsenic in drinking water poses today a serious threat to the health of people in many countries – notably, Bangladesh [4]. It is known from the aqueous chemistry of arsenic that As(III) is more toxic and mobile than As(V). The distribution between dissolved trivalent and pentavalent arsenic is dependent on redox potential; it exists under different hydrolysis species, varying with the solution pH. Oxidative weathering and dissolution of As-containing minerals (such as arsenopyrite, arsenic pyrite and other gangue minerals), of dissolved inorganic arsenic that are transported in surface or groundwater, can subsequently become adsorbed on soil and sediment particles. Arsenic-rich pyrite concentrates are generally stockpiled in the mine area, as a deposit for possible future processing with economic interest, technologically capable. This is because gold, silver, etc. are often present, even in trace amounts.

The microbial biosorption of metals has attracted the interest of scientists as a treatment method, especially during the last decades [5]; for example, arsenates were removed by fungal biomass appropriately modified [6]. Metal accumulation by appropriate biological substrates can counteract metal mobilization into the environment. Microorganisms provide a large contact area that can interact with metals in the surrounding environment. The ability of several microorganisms, isolated from metal-polluted soils to biosorb and remove toxic metals from aqueous solutions were shown [7].

The ability of the carbonaceous matter-deactivating fungus, *Phanerochaete chrysosporium*, to also solubilize/oxidize sulfides found in refractory gold ores, so as to assess the potential of a single-stage process for the pretreatment of double refractory gold ores was elsewhere examined [8]. Mesophilic bacteria, isolated from acid mine drainage, were used for the oxidation of an arsenopyrite concentrate, selected due to its higher gold content [9].

Thiourea, applied in acidic media for gold recovery, was said to present an important alternative lixiviant to the commonly used cyanide (especially for cyanide refractory ores) but also mainly due to the severe environmental constraints on cyanide, related to tailings disposal, water quality and environmental impact [10]. In sulfidic refractory gold ores, tiny gold particles (typically <1 μm) may be highly disseminated and locked up within the grain boundaries or fractures of sulfide minerals, such as pyrite and arsenopyrite. Thus, decomposition of the sulfides is required to liberate the gold.

2. Technologies for arsenic removal from soils and wastewaters

Before analysis of the flotation process for the arsenic removal from water/wastewater, it is necessary to briefly report some main technologies applied both for soils/wastes and wastewaters [11–18]. In the case of soil detoxification from arsenic, the main technologies applied are listed in Table 1. Solidification and stabilization (S/S) is an established treatment technology often used to reduce the mobility of arsenic in soil and waste. The most frequently used binders for S/S of arsenic are pozzolanic materials such as cement and lime. S/S can generally produce a stabilized product that meets the regulatory threshold of 5 mg/L leachable arsenic as measured by toxicity characteristic leaching procedure (TCLP) tests. However, leachability tests may not always be accurate indicators of arsenic leachability for some wastes under certain disposal conditions. Another process is vitrification, which has been applied in a limited number of projects to treat arsenic-contaminated soil and waste. For soil treatment, the process can be applied either in-situ or ex-situ.

This technology typically requires large amounts of energy to achieve vitrification temperatures, and therefore can be expensive to operate. Off-gases may require further treatment to remove hazardous

constituents. Soil washing/acid extraction (soil washing) has been used to treat arsenic-contaminated soil in a limited number of applications. The process is limited to soils in which contaminants are preferentially adsorbed onto the fines fraction. The separated fines must be further treated to remove or immobilize arsenic. Furthermore, pyrometallurgical processes have been implemented to recover arsenic from soil and wastes in four full-scale applications. These technologies may have only limited application because of their cost and because the cost of importing arsenic is generally lower than reclaiming it using pyrometallurgical processes. Moreover, in-situ soil flushing has been used to treat arsenic-contaminated soils in some applications [19–21]. Some projects have been identified which are operating at full or pilot scale [22–25].

Focusing on the treatment of wastewaters, some main techniques are widely applied for arsenic removal. For this purpose, it is essential to collect all advantages and disadvantages for them before proceeding to flotation analysis. Technologies for removing arsenic from the environment should meet several basic technical criteria that include robustness, no other side effect on the environment, and the ability to sustain water supply systems for long terms and meet the quality requirement of physical chemical, and microbiological approaches.

The insolubility of certain inorganic As(V) compounds is the basis of many hydrometallurgical As-removal processes. The most common methods for removing As from process streams are by precipitation as As(III) sulfide, calcium arsenate or ferric arsenate. Unfortunately, all these materials are unstable under certain conditions and, therefore, not suitable for direct disposal to uncontained sites as they will produce arsenic-bearing leachates [26–28]. Calcium arsenate compounds are generated by adding CaO or Ca(OH)₂ to contaminated waters. Different precipitates can be generated. When operated at pH values 10.5, a high As-percentage can be precipitated from solutions bearing 50 mg As/L. However, it is difficult to achieve final concentrations below 1 mg/L [28]. As(V) can be removed through precipitation of ferric arsenate. One possibility is the addition of ferric salts to As-bearing water [27]:



Coagulation and filtration is one of the classical possibilities to remove As-species from water that has been studied in a large number of investigations [29]. Coagulants can be alum (Al₂(SO₄)₃), ferric chloride (FeCl₃), or ferrous sulfate (FeSO₄) [30]. The mechanism of As-elimination is that of a sorption onto the freshly precipitated Al(OH)₃ and Fe(OH)₃ particles or flocs. Iron salts provide generally better elimination than aluminum salts. Elimination is effective, when As was present as As(V). As(III) elimination is rather unsatisfactory and needs pre-oxidation by means of H₂O₂, NaOCl, or Cl₂ which converts As(III) to As(V) [30]. The disadvantage of the process lies in a relatively large volume of As-bearing sludge that needs to be discharged. A similar mechanism occurs during oxidation of Fe and Mn from reduced ground waters by aeration. As-elimination is fairly efficient during Fe-precipitation whereas it is less efficient during Mn-precipitation [30]. The same kind of As-elimination has been proposed and studied in field experiments for an underground As-elimination [31].

Membrane processes offer additional possibilities for As-removal. Elimination can be achieved by (i) filtration of As-bearing particles, (ii) exclusion because of size of hydrated ions, or (iii) electric repulsion by the membrane. Microfiltration and ultrafiltration do not allow any direct elimination because As-species are too small by far and can pass through the membrane. Nanofiltration, which usually shows a predominant removal of divalent species, can eliminate As(III) and As(V) species predominantly through size exclusion. As-removal rates in bench and pilot scale experiments ranged from 60 to 95%. Again, the results were less satisfactory for As(III). Reverse osmosis has been shown to be another reliable method for As-elimination. Both bench and pilot-scale experiments demonstrated As(V) elimination rates 95% and As(III) elimination rates of about 74%. A slight increase of performance was observed for high DOC raw waters. All above and some other advantages and disadvantages

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