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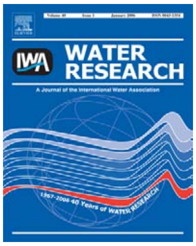

Mobilisation of arsenic from a mining soil in batch slurry experiments under bio-oxidative conditions

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ABSTRACT

Laboratory investigations were performed to estimate the potential mobility of arsenic (As) from a highly contaminated gold-mining soil under bio-oxidative aerobic conditions as a potential remediation process. The selected soil was sampled from a gold-mining site in the South of France. It contained 27700 $\mathrm{mg\,kg^{-1}}$ total As, with only 0.01% present under water-soluble forms. The nature of the immobilization mechanisms was identified by using complementary physical and chemical techniques. As was found to be strongly associated to iron (oxy)hydroxide solid phase by adsorption and/or co-precipitation. Determination of iron (Fe) and As mobility as a function of pH showed that the release of As was related with the dissolution of Fe (oxy)hydroxide at very low pH values. Bioleaching experiments were conducted with the objective to enhance the mobilization of As from the source material via biological oxidation of elemental sulfur (S°) into sulfuric acid by autotrophic exogenous or indigenous bacteria naturally located in the soil (i.e. *Acidithiobacillus* species). Tests conducted at 30 °C in shaker flasks supplemented with S° resulted in very acidic ($pH<1$) and oxidative conditions (oxidation/reduction potential (ORP) around +800 mV vs. NHE) and induced the extraction of up to 35% of As over 84 days of incubation. Under the experimental conditions of the study (batch experiments), As mobilization was strongly correlated to the dissolution of Fe solid phases. As mobilization was probably limited by the saturation of the liquid phase. Chimiolithotrophic exogenous population appeared to have a minor effect on As bioleaching. Endogenous populations were shown to rapidly develop their capacity to oxidize S° and mobilize As from the mining soil in the form of arsenate when elemental S° was supplemented. The use of microbial population adapted to high As concentrations reduced significantly the lag period to reach optimal pH/ORP conditions, and increased As extraction rate to a maximum of 41% within 70 days of incubation. However, As reprecipitation was subsequently observed, suggesting that the solution should be periodically replaced in order to optimize the process.

1. Introduction

According to the European regulation on contaminated soils, feasibility studies are requested to evaluate the potential benefits of treatment processes. Unlike organic contaminants, inorganic pollutants cannot be decomposed chemically or biologically. Treatment of metal-contaminated soils therefore involves, either reducing the water mobility of metals and metalloids (immobilization) or increasing it in order to extract them and thereby reduce their concentration

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in the soil. Classical techniques used for the extraction of heavy metals from polluted soils or sediments are based on the use of acidic, chelating or oxidizing aqueous solutions (Alloway, 1995). Biological leaching is currently an available technology for the recovery of valuable metals from low-grade ores (Kelly et al., 1979; Couillard and Chartier, 1993; Boseker, 2001). Biological leaching may be potentially used for remediation of contaminated soils and sediments. Microbial-based technologies for metal extraction have become attractive because they are cost effective as compared to chemical methods and may be applicable for a large number of inorganic pollutants (Hutchins et al., 1986).

The mechanisms involved in biological leaching may be direct or undirect (Hutchins et al., 1986). Direct biological leaching mechanisms are related to biochemical changes in the oxidation states of metal species. Undirect biological leaching may occur through the production of ferric sulfate ($Fe_2(SO_4)_3$) by Fe-chemolithotrophic bacteria such as *Acidithiobacillus ferrooxidans*. Ferric sulfate is a strong oxidant capable of dissolving a wide variety of metal sulfide minerals. Elemental sulfur (S°) or sulfide ions can also be converted to sulfuric acid (H_2SO_4) by sulfur-oxidizing bacteria such as thiobacilli (Funtowicz, 1995; Gourdon and Funtowicz, 1995, 1998; Gomez and Bosecker, 1999; Tsai et al., 2003). Acidic and oxidative conditions thus established create favorable conditions for metals mobilization by dissolving the solid-bearing phase and or increasing the solubility of metals in the liquid phase.

The present study investigates As leaching from mine tailings of a gold-mining site under bio-oxidative conditions by adding S° which can be used as an energy source by *Acidithiobacillus* sp. commonly present in natural soils and numerous ores (Funtowicz, 1995). The selected mining soil is characterized by high concentrations of arsenic (As) (ca. 3 wt%). After a physical and chemical characterization of the matrix to identify the major inorganic pollutants and evaluate the mobility of As as a function of pH, bio-oxidative leaching was studied using batch tests where the soil was suspended in a liquid medium and supplemented with S° in order to produce H_2SO_4 Exogenous strains of *Acidithiobacillus* were used in an attempt to improve the conversion of sulfur into H_2SO_4 Other experiments were performed to estimate the As bio-oxidative leaching by the indigenous microbial population.

2. Material and methods

2.1. *Sample collection, preparation and initial characterization*

An As-contaminated soil collected from a gold-mining site in France, where mining activities and smelting processes of gold ores took place over several decades, was used for the study. The site is located in the district of the city of Salsigne, Aude, Languedoc-Roussillon, France. Under the supervision of the French Environmental Protection Agency (ADEME), an area was selected for primary sampling. The site was already known to present high concentrations of As (ADEME, 2003; Chatain, 2004; Chatain et al., 2003, 2005a, b). No vegetation was observed on the surface sampling area. Due to the variety of the past activities on the site, mixing of the natural soil with residues from ore-processing probably occurred repeatedly. A representative top-surface soil sample (depth: 5–35 cm) of about 50 kg was collected using a mechanical scoop. Prior to the physical–chemical characterization and leaching experiments, the primary sample was gently air-dried overnight at room temperature ($20 \pm 3\,^\circ C$), rolled to break up macro-aggregates and finally sieved through a 2 mm stainless steel sieve (No.10) to remove coarse debris and gravel. After a manual homogenization, the soil sample was stored at 4 °C in the dark.

Soil sample analysis included global parameters like moisture content (AFNOR, 1994), natural pH and oxidation/reduction potential (ORP) vs. normal hydrogen electrode (NHE), total carbon (TC), total inorganic carbon (TIC) and total organic carbon (TOC) contents, and cation exchange capacity (CEC). TC, TIC and TOC have been determined with a Shimadzu® 5000A TOC-meter with combustion and CO_2 IR-analyzer and Solid Samples Module SSM5000A according to the French standard procedure NF X31-409 (AFNOR, 1995). Sand (50–200 μm), silt (2–50 μm) and clay ($<2\,\mu m$) fractions have been determined using the French standard procedure NF X31-107 (AFNOR, 1983). CEC has been determined according to the French standard procedure NF X 31-130 (AFNOR, 1993) by using the ammonium acetate method.

Total content of major elements (Si, Al, total Fe, Mn, Mg, Ca, Na, K, P, total S and Ti) and trace elements (As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Ta, Tb, Th, Tm, U, V, W, Y, Yb, Zn, Zr) were determined after fusion ($T = 1080\,^\circ C$, $t = 2\,h$) of the solid sample previously dried and crushed at $<80\,\mu m$ with lithium metaborate ($LiBO_2$), followed by an acid digestion with nitric acid (HNO_3, 1 M) according to the French standard procedure NF X31-147 (AFNOR, 1996). Major elements in the liquor have been analyzed by CNRS Nancy by inductively coupled plasma atomic emission spectrometry (ICP-AES Jobin Yvon® 70T II) and trace elements by inductively coupled plasma mass spectrometry (ICP-MS Perkin Elmer® 5000). Global characteristics and the total content of trace and major elements of the soil are summarized in Table 1. The soil consisted of 63 wt% sand, 24.6 wt% silt, and 12.4 wt% clay and contained ca. 3 wt% As, ca. 2 wt% sulfur, ca. 9 wt% iron (Fe) , and ca. 1.3 wt% total carbon (TC) (Chatain, 2004; Chatain et al., 2003, 2005a, b).

As described in previous works (Chatain, 2004; Chatain et al., 2005b), X-ray diffraction (XRD, Siemens D500®) and scanning electron microscopy (SEM, JEOL 840A LGS®) equipped for energy dispersive spectrum (EDS) analyses were carried out in conjunction with a sequential chemical extraction procedure adapted from Matera et al. (2003) to identify the mineralogical phases present in the soil and the distribution of As.

2.2. *Leaching experiments*

The leachability of inorganic pollutants in water was determined according to the leaching standard procedure CEN by mixing the soil samples with distilled water at a liquid-to-solid ratio (L/S) of 10 (CEN TC 292 prEN 12457-2, 2002). The