Studies on Arsenic Release and its Mitigation from Tailings Dam Using Nanomagnetite Particles*

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Abstract

Knowledge of the geochemistry of As in tailings material after beneficiation of gold-bearing sulphidic ores is necessary to comprehend the nature, stability and mobilization of As into the geo-environment and its subsequent mitigation during storage. In this study, XRD combined with reflected light microscopy and SEM-EDX were employed to carry out studies on the mineralogical composition of As in a tailings material. Arsenic-rich solutions were generated from the tailings material using deionised water to ascertain As mobilisation. The remediation kinetics of the soluble As was carried out using nanomagnetite (Fe_3O_4). The XRD and SEM- EDX analyses showed that the major source of As in the tailings material is arsenopyrite (FeAsS). The study further confirmed that the residual As mineral in the tailings material is capable of decomposing during storage and can be subsequently mobilised into the geo-environment. It was established that nanomagnetite can efficiently remove As from tailings leachates; preferably at pH between 6 and 7 and Langmuir isotherm best described the sorption process while the Gibbs free energy of the sorption was found to be -12.1026 KJ/mol. Thus, nanomagnetite can be used to mitigate arsenic foot-prints from tailings dam.

1 Introduction

One very important anthropogenic source of arsenic is tailings material from mining and metallurgical operations which beneficiate arsenic (As) minerals. Arsenic and other heavy metals can be mobilized into the geo-environment when such tailings material undergo oxidation/weathering reactions (Ferreira da Silva *et al.*, 2004) which can pollute both surface and underground water since As is toxic.

Recent findings on the toxicity of arsenic in drinking water around the globe especially in countries such as Bangladesh (Smith *et al.*, 2002), Chile (Borgono and Greiber, 1971), Taiwan, the United States (U.S. EPA, 1997) and India prompted the drastic revision of the maximum contaminant level of arsenic in drinking water from 50 µg/L to 10 µg/L by the US EPA as well as other nations of the world. Consequently, interests in the area of arsenic and other heavy metal remediation have also increased appreciably in recent years.

High arsenic concentrations have been reported in soils (Amasa, 1975) and rivers (Smedley *et al.*, 1996) in the Obuasi vicinity. Work done by Kumi – Boateng (2007) also revealed that estimated average levels of arsenic in plants and soils in the Obuasi area is between 18 ppm and 27 ppm.

It is therefore important to remediate arsenic from secondary sources such as mine waste and other waste streams in order to prevent arsenic mobilization from these sources, from contaminating the geo-environment. The following As remediation methods have been proposed in the literature namely: electrochemical reduction, precipitation, reverse osmosis, ion exchange, solvent extraction, nano-filtration and adsorption (Hu *et al.*, 2004). Furthermore, a number of researchers have shown that iron oxides such as magnetite, goethite and hematite are good sorbents for arsenic remediation. For instance, Mayo *et al.*, (2007) reports that, magnetic properties of nanomagnetite allow relatively routine dispersal and recovery of the adsorbent into and from groundwater or industrial processing facilities using a magnetic field. Arsenic sorption onto nano-structured iron films is of high capacity (Yean and Cong *et al.*, 2005). In addition, nanomagnetite have strong and specific interactions with both As(III) and As(V) (Shipley, 2007) thus by carefully optimizing their particle sizes as well as surface properties, high metal removal from waste waters can be achieved.

This study hence focuses on the use of nanotechnology for remediation of arsenic from mine tailings materials.

2 Materials and Methods

2.1 Sampling

Tailings samples were collected from a "backfill unit" of bio-plant using automatic samplers. Samples were filtered and the residue, air dried in an oven at 25 ^{o}C overnight and a total of 8 kg of material was stored in a cold room at a temperature of 4 ^{o}C for laboratory analysis:

2.2 Mineralogical Investigations

The mineralogical investigation of the tailings material was carried out by using X-ray diffraction

(XRD) supplemented by reflected-light microscopy (RLM) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX).

Polished mounts (< 45 μm) with average diameters and thickness of 3 cm and 1 cm respectively were prepared with the tailings material using conducting graphite doped epoxy. This was then carbon coated for the SEM-EDX analysis in order to prevent electron build up on the sample surface during analysis.

The samples for the XRD analysis were prepared by hand grinding to <45 μm and processed by placing on a powder plate and compacting with a glass slide. The XRD powder patterns were obtained using a Rigaku D/MAX 2500 rotating anode powder diffractometer with monochromatic CuKα radiation. Phase identification was achieved using the JADE version 9.0 coupled with the ICSD and ICDD diffraction data bases.

2.3 Release of As from the Tailings material

Various slurries containing approximately 17 wt % solid at an average pH of 7.90 were prepared with de-ionised water and then leached on New Brunswick Orbital shaker, between 24 and 192 hrs. The pH was monitored during the leaching period. After the leaching, the slurry was centrifuged at 5000 rpm for 30 min using the Sorvall RC-5B Refrigerated Super speed Centrifuge. Supernatant solutions were then collected and filtered. The filtrates were acidified with a drop of 5 M hydrochloric acid to a pH of 4 and then analyzed for As, using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

2.4 Adsorption Test

Sorption experiments for As removal were performed using 20 nm nanomagnetite (Fe_3O_4), obtained from Reade Advanced materials (Rhode Island, U. S.A) as the adsorbent. About 30 ml of As solution (of 0.42 mg/L from Section 2.3) was contacted with 0.25 g/L nanomagnetite (20 nm) and then dispersed using a sonication bath (Model: 75 HT) for 20 min. The adsorptions were carried out at pH between 4.0 and 10 and at temperature of 23 ^{o}C. Residual arsenic in solution was then analysed using ICP-OES.

3 Results and Discussion

3.1 Mineralogical Investigations

Microscopic examinations of polished sections and the XRD, SEM-EDX analyses of the tailings material showed that it contained arsenopyrite and pyrite as major sulphides. The following were also present: quartz, dolomite, mica, albite, clinnochlore and gypsum in order of decreasing abundance.

The size of the arsenopyrite in the tailings material was between 50 and 500 μm while pyrites in the tailings was found to be finely grained with sizes usually up to 75 μm. The pyrite grains appeared to

contain less surface coatings than arsenopyrite coatings. Some fractures were also observed in some pyrite grains in the tailings material. Fig. 1 shows a backscattered electron micrograph of an arsenopyrite grain in the tailings surrounded by gangue material while Fig. 2 shows a backscattered electron micrograph of a pyrite grain with its corresponding EDX spectra.

Chemical analysis of some selected arsenopyrite grains in the tailings showed arsenic content of between 40 and 42 wt %. Minor amounts of silicon (Si) were observed in some arsenopyrite grains examined.
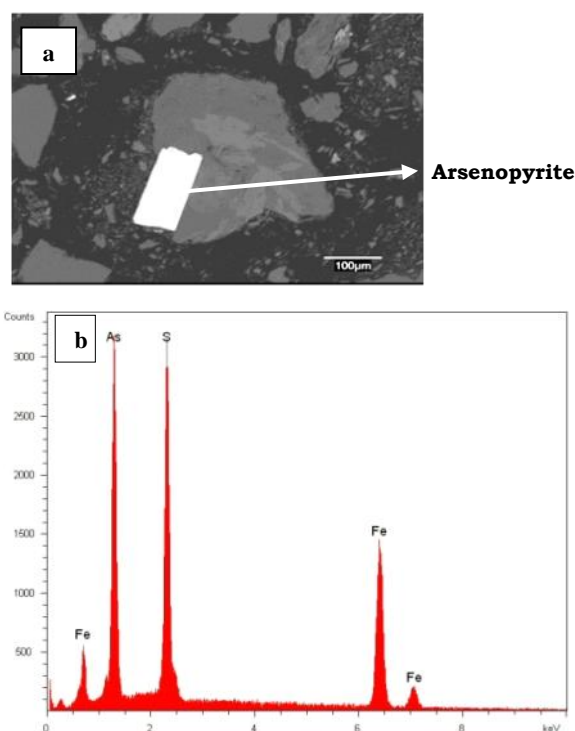

Fig. 1 SEM Backscattered Electron Micrograph (Tailings) showing a) Arsenopyrite Grain Surrounded by Gangue Material b) EDX Spectra Indicating Fe-As-S Composition of the Arsenopyrite grain.

3.2 Arsenic Release

The results of the arsenic release rate (and its corresponding pH variation) from the tailings samples are presented in Fig. 3. It can be observed that there was a gradual arsenic release from the tailings' material into solution with time in a synosoidal manner. The variation in pH is also synosoidal. The maximum As release was 0.27 mg/L after 60 hrs beyond which As relrease declined to 0.23 mg/L and then equilibrated there. Thus, the tailings material can release arsenic into the geo-environment.

3.3 Adsorption Test

The kinetics and efficiency involved in using nanomagnetite (20 nm) for the sorption of arsenic

from leachate was studied. The results of the asorbtion experiment are presented in Fig 4. It can be inferred that As sorbance onto Fe_3O_4 is pH dependent; As adsorption increases with decreasing pH. Arsenic sorption onto nanomagnetite is thus more effective in acidic medium than in alkaline medium. At pH 4.02 for instance, a nanomagnetite amount of 0.5 g/L was able to sorb a maximum of about 98 % of As within 24 h with an initial metal concentration of 0.4766 mg/L. At a pH of 9.02 and 6.94 with same initial As concentration and nanomagnetite dosage however, only 82 % and 94 % of As respectively were recovered in the same time period. This confirmed that the sorption of arsenic onto the nanomagnetite material is pH dependent.

This can be explained as follows: Yean *et al.* (2005) using potentiometric titrimetry showed that the surfaces of nanomagnetite particles are positively charged at pH below 6.8 due to the point of zero charge (pzc) of magnetite and that stronger As(V) adsorption to magnetite nanoparticles was observed at lower pH. The reduction in As(V) adsorption at high pH (i.e., pH 8) was attributed to the electrostatic repulsion of the negatively charged As(V) species by the negatively charged surface sites. Comparing the trend in Yean *et al.*'s work to this research, it could be inferred that the decline at pH 9 could be attributed to the predominance of As (V) species in the leachate from the mine tailings as arsenic sorption here decreased with increasing pH.
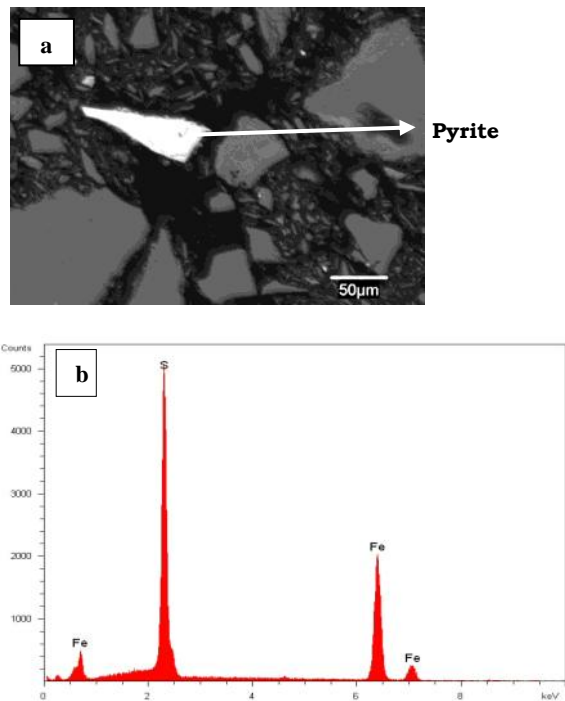

Fig. 2 SEM Backscattered Electron Micrograph of Tailings Material showing a) Pyrite grain surrounded by Gangue Material b) EDX Spectra Indicating Fe-S Composition of the Pyrite Grain.
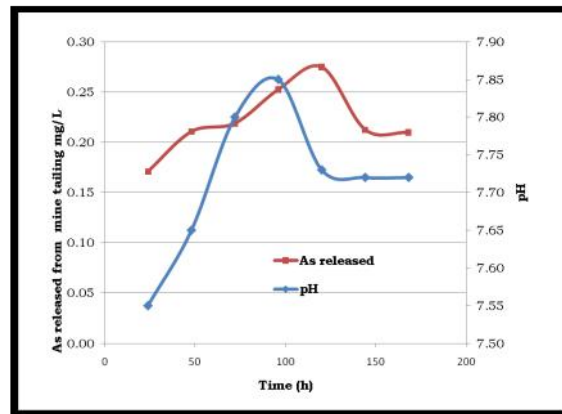

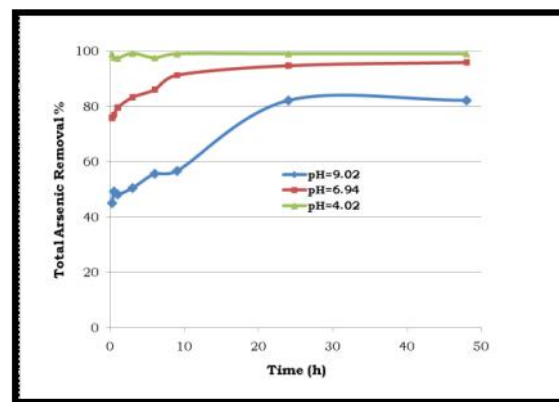**Fig. 3 As release During Leaching of Tailings Material with De-ionised Water.**

Fig. 4 Influence of pH on As Removal Using 0.5 g/L Fe_3O_4 (20 nm)
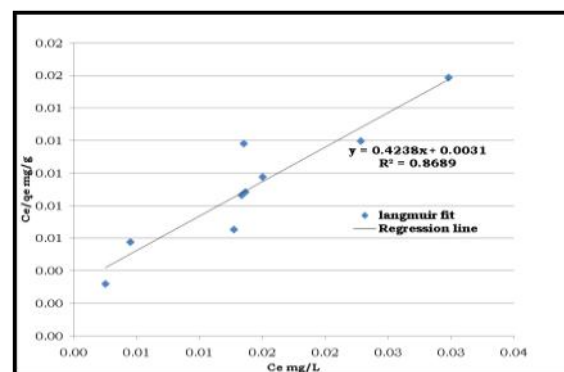

Fig. 5 Langmuir Isotherm Model for Arsenic Removal

The adsorption isotherm was found to obey Langmuir linearised equation as presented in Fig 5. Other researchers (Zhang *et al.*, 2003; Harper and Kingham, 1992) also have shown that the sorption nature of arsenic onto iron oxides and oxyhydroxides from contaminated solutions followed Langmuir model. Standard Gibbs free energy for the adsorption process was calculated using the following equation:

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^o}{RT}$$

Where:
b is the Langmuir canstant (L/mg)
R is the Ideal gas constant (8.314 J/K mol)
T is the temperature in K

A negative Gibbs free energy value (-12.1026 kJ/mol) was obtained. This indicates that the adsorption of As from the mine tailings leachate onto the nanomagnetite (20 nm Fe_3O_4) material is spontaneous and that the reaction is thermodynamically feasible.

4   Conclusions

From the results and discussions, it can be concluded that:

- The tailings material contain sulphides namely arsenopyrite (FeAsS) and pyrite (FeS_2).
- There are sulphides (FeAsS and FeS_2) in the tailings. Consequently, leaching the tailings with de-ionised water resulted in mobilising arsenic into the leachate. Thus, the tailings material is capable of decomposing during storage.
- Nanomagnetite can be used to remove arsenic from leachate solution preferably in a pH between 6 and 7 and for the 20 nm sample the q_{max} was found to be 2.40 mg/g.
- The sorption process using nanomagnetite is thermodynamically feasible.

Acknowledgements

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