Immobilization of magnetite nanoparticles for the removal of arsenic and antimony from contaminated water

G. Sun & M. Khiadani

School of Engineering, Edith Cowan University, Joondalup, WA, Australia

ABSTRACT: Magnetite (Fe₃O₄) nanoparticles were synthesized and immobilized in a synthetic resin poly-methyl methacrylate (PMMA). The Fe₃O₄ nanoparticle-PMMA composites were studied for their efficiencies of removing dissolved arsenic (As) and antimony (Sb). The effects of major environmental and operating parameters on the removal of As and Sb were investigated in batch experiments. Singular and competitive adsorption of As and Sb onto the composites were studied. The results demonstrated the capability of the Fe₃O₄-PMMA composites for removing dissolved metalloids.

1 INTRODUCTION

Dissolved metalloids, including As and Sb, can be present in contaminated surface waters or groundwater. The health risk posed by arsenic, in particular when it is in inorganic dissolved form, has been widely recognized. Antimony is considered an emerging contaminant that is linked to skin, lung, and eye diseases (Cooper & Harrison, 2009). The removal of these metalloids from contaminated waters is essential for protecting human health and the environment.

A variety of methods have been studied for the removal of the two metalloids, including adsorption, membrane, coagulation/flocculation, oxidation/precipitation, etc. Among these methods, adsorption is considered a low cost conventional technique. Various high-tech or low-tech adsorbents, such as synthetic resins, activated carbon, agro-wastes, and mineral clays, etc., have been studied in lab experiments (Ungureanu *et al.*, 2015). Currently, many researchers are focusing their efforts on discovering innovative adsorbents, to further enhance adsorption efficiency and reduce cost.

Magnetite (Fe₃O₄) nanoparticles have the potential to be used as an adsorbent or electron donor for the removal of water contaminants, due to their high surface areas, reactivity and well-established synthesis methods. Another advantage of the magnetite-based adsorbents is that they can be recovered through magnetic field. Their disadvantages include mobility in water, agglomeration, and oxidation by non-target compounds in water; these have limited the application of iron-based nanoparticles to treat contaminated waters. Appropriate methods of applying the particles, such as entrapment in porous media or carriers, need to be investigated. In this study, comparative experiments

were carried out to study the efficiency of magnetite nanoparticles immobilized in a synthetic PMMA resin for the adsorption of As and Sb.

2 MATERIALS AND METHODS

2.1 Synthesis of magnetite nanoparticles

AR grade ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), 2-(4-chlorosulfonylphenyl) ethyl-trichlorosilane (CTCS), methyl methacrylate (MMA), and 30% ammonium hydroxide (NH₄OH) were purchased from Sigma Aldrich. Milli-q water was produced by a Merck Millipore instrument. Magnetic iron oxide nanoparticles were synthesized by co-precipitation of Fe²⁺ and Fe³⁺ ions to form Fe₃O₄ precipitates via the following reaction.

4.31 g of ferrous chloride tetrahydrate and 11.68 g of ferric chloride hexahydrate were added into a reaction chamber (500 mL triple neck round bottomed flask) pre-filled with 200 mL water (deoxygenated by purging with N₂ gas). The chamber was connected to a condenser and a mechanical mixer and placed in an oil bath. Ammonium hydroxide solution was gradually (dropwise) added to the solution. The color of the solution gradually changed from orange to dark brown and finally black. This was continued until the pH reached 8.0. A magnet was used to separate solid precipitates of Fe₃O₄ from the solution. The Fe₃O₄ precipitates were rinsed repeatedly with milli-q water and saline (0.1 M NaCl) water, vacuum-dried and stored.

2.2 Synthesis and characterization of Fe_3O_4 -PMMA composite

Three grams of the Fe_3O_4 precipitates were mixed in 40 mL of dehydrated toluene. 1.3 mmol CTCS was added to the solution, and kept in room temperature for 24 h, to produce Fe_3O_4 particles immobilized with CTCS. The particles were separated from the solution, washed, dried and weighted. For polymerization, 1.6 g of these particles were added to 80 mL toluene and mixed with 50 g MMA in the reaction chamber in N_2 environment. The reactor was submerged in the oil bath at 80°C , and the solution was stirred by a mechanical impeller for 4 h. By the end of the polymerization period, magnetic composites in the liquid were separated by the magnet, collected, washed, centrifuged, and dried. Surface characteristics of the Fe_3O_4 nanoparticles and Fe_3O_4 -PMMA composites were analyzed by a scanning electron microscope (JCM-6000, JOEL). An X-ray powder diffraction apparatus (PANAnalytical) was used to analyze the chemical compositions of the Fe_3O_4 nanoparticles.

2.3 Batch testing of As and Sb removal by the nanoparticles

An arsenic stock solution was prepared by diluting 1000 mg L^{-1} As(III) standard solution (Agilent) to 100 mg L^{-1} . An 274 mg L^{-1} antimony (III) stock solution by dissolving measured amount of antimony potassium tartrate $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6) \cdot 2.3\text{H}_2\text{O}$ in milli-q water. A series of batch adsorption tests were then carried out to study As and Pb removal by the Fe_3O_4 nanoparticles, in mobile (bare particles) and PMMA immobilized forms. The batch adsorption studies were carried out using 100 mL flasks, each filled with 50 mL of As, Sb, or mixed As and Sb solutions, which were placed on an orbital shaker rotated at 180 rpm for 90 minutes. As and Pb concentrations of the solutions, at the beginning and end each batch test, were analyzed by a MP-AES instrument (Agilent).

3 RESULTS AND DISCUSSION

3.1 Characteristics of the synthesized nanoparticles and Fe_3O_4 -PMMA Composites

Figure 1 shows the surface of the synthesized nanoparticles and Fe_3O_4 -PMMA composites. It appears that the sizes of the particles were indeed in nm range. The Fe_3O_4 impregnated PMMA composites were observed to have more rugged surfaces, compared with the surfaces of blank (without particle impregnation) MMA polymer.

XRD analyses of the synthesized nanoparticles and a commercial Fe_3O_4 sample produced similar profiles. Both synthesized and commercial samples had six significant diffraction peaks observed in both samples (at 2θ of 511, 442, 440, 400, 311 and 220), confirming the presence of hematite in the synthesized nanoparticles.

Figure 1. The SEM images of the Fe_3O_4 nanoparticles (left) and Fe_3O_4 -PMMA composites (right).

Figure 2. Percentage removal of As and Sb by the Fe_3O_4 -PMMA composites at different pH.

3.2 Batch testing results of As and Sb removal

Figure 2 shows the percentage removal of As and Sb at different pH, when As and Sb were present as single contaminants in separate solutions. Efficiencies of commercial and synthesized nanoparticles, dosage, and co-existence (competitive removal) of these metalloids were also investigated.

4 CONCLUSION

Magnetite nanoparticle-PMMA composites were synthesized and tested for the removal of As and Sb. The results demonstrated their potential as an effective, recoverable adsorbent for *in situ* remediation of metalloid contaminated water.

ACKNOWLEDGEMENTS

The authors acknowledge Mr. Seyed Seyedi and Mr. Willie Tan, who contributed to the experiments.

REFERENCES

- Cooper, R.G. & Harrison, A.P. 2009. The exposure to and health effects of antimony. *Indian J. Occup. Environ. Med.* 13(1): 3–10.
- Ungureanu, G., Santos, S., Boaventura, R. & Botelho, C. 2015. Arsenic and antimony in water and wastewater: overview of removal techniques with special reference to latest advances in adsorption. *J. Environ. Manag.* 151: 326–342.

Arsenic retention on technosols prepared with nanoparticles for treatment of mine drainage water

D. Bolaños¹, V. Sánchez¹, J. Paz², M. Balseiro³ & L. Cumbal^{2,4}

¹*Department of Earth and Construction Science, Universidad de las Fuerzas Armadas ESPE, Sangolquí, Ecuador*

²*Department of Life Science and Agriculture, Universidad de las Fuerzas Armadas ESPE, Sangolquí, Ecuador*

³*Department of Chemical Engineering, Centre for Research in Environmental Technologies (CRETUS),
Universidade de Santiago de Compostela, Spain*

⁴*Center of Nanoscience and Nanotechnology (CENCINAT), Universidad de las Fuerzas Armadas ESPE,
Sangolquí, Ecuador*

ABSTRACT: Arsenic (As) concentrations of 4.8 to 27.5 $\mu\text{g L}^{-1}$ have been detected in wastewater of gold mines in southern Ecuador (Portovelo) thus there is a need of applying remediation techniques to avoid superficial and groundwater contamination. In this study we have prepared a technosol composed by a ferric soil collected in the mining area and multicomponent nanoparticles synthesized using sodium borohydride and orange peel extract as co-reductants. The sorption capacity of the technosol was experimentally characterized using sorption isotherms. Langmuir model fits the experimental results and its parameters such as maximum sorption capacity and adsorption bond energy are 71185 mg kg^{-1} 7.50 kg mg^{-1} , respectively. Based on these preliminary results, it seems that the as-prepared technosol will be a cheap cost solution for capturing arsenic from the mine drainage water.

1 INTRODUCTION

Mine drainage water usually contains high concentrations of heavy metals and other compounds. Due to poor handling, this contaminated water may leach and migrate to ground and spring water, becoming a potential contaminant of drinking water sources (Bolaños, 2015; Polizzotto *et al.*, 2006). There are many available technologies to cleanup As-contaminated water, whose efficiency and applicability will mainly depend on the chemical form of As in water (Cumbal, 2004). Adsorption of As in specific sorbents has been widely used due to its high versatility, easy operation and handling, and low costs. The application of specifically “tailored” technosols, composed of soil components and non-harmful residues with sorption capacities for specific contaminants, has shown successful results on the restoration of degraded mining areas contaminated with a wide variety of trace metals and metalloids (Macías, 2012). On the other hand, nanosorbents has emerged as a promising alternative for the cleanup of As-contaminated water (zero valent iron and iron oxide nanoparticles), because of their distinctive and advantageous properties, such as the small size, high surface area, and high reactivity due to the large number of sorption active sites (Pérez-Esteban *et al.*, 2016).

The objective of the present study was to find out the arsenic sorption capacity of a tailored technosol composed of a ferralsol, with 25,531 mg kg^{-1} of Fe (2% w/w, associated to Fe and Mn oxides) and multicomponent nanoparticles.

2 METHODS

Water samples were collected at three discharges of artesian gold-processing plants located in the border of the Amarillo River (Portovelo, Ecuador), the main collector of liquid wastes from the gold-processing artesian plants. pH, Eh, electric conductivity were measured on site and heavy metals and As were analyzed with an atomic absorption spectrometer using standardized methods. For the fabrication of multicomponent nanoparticles (MCPNs) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and Na_2SO_4 solutions were mixed and purged with nitrogen. Then, NaBH_4 and orange peel extract were added as co-reductants. The technosol was prepared mixing 12.5 mg of MCPNs and 4,987.5 mg of soil. Arsenic sorption was performed in batch tests mixing 5 g of technosol with 100 mL of arsenic contaminated water at neutral pH.

Mine drainage water was doped with six different concentrations of arsenic (25, 50, 100, 200, 400, 600 $\mu\text{g L}^{-1}$). The amount of arsenic sorbed on the technosol was determined by mass balance using the equation (Vanderborght & Van Grieken, 1977):

$$q = V/m (C_i - C_f) \quad \dots\dots\dots (1)$$

where q = concentration of As in the soil, V = volume of water contaminated with As, m = mass of soil and C_i and C_f initial and final As concentrations.