

## ARSENATE ADSORPTION ONTO ALUMINIUM AND IRON (HYDR)OXIDES AS AN ALTERNATIVE FOR WATER TREATMENT

Juscimar Silva<sup>1</sup>, Jaime W.V. Mello<sup>1</sup>, Massimo Gasparon<sup>2</sup>, Walter A.P. Abrahão<sup>1</sup> and Tony Jong<sup>2</sup>

<sup>1</sup>Soil Department, Universidade Federal de Viçosa, Av. P. H. Rolfs s/n, 36570-000 Viçosa, MG, Brazil

<sup>2</sup>Earth Sciences, The University of Queensland, St Lucia, Qld 4072, Australia

### Abstract

The geochemical fates of iron and arsenic are so closely correlated that methods of arsenic removal from water are in general based on the high adsorptive affinity of this metalloid with iron (hydr)oxides. Under anoxic conditions, however, reductive dissolution of iron (hydr)oxides can take place, and arsenic may be released into the surrounding environment. The purpose of this study was to investigate the potential of Al-substituted goethites in adsorbing arsenic compared with other Fe and Al (hydr)oxides. Hematite (Hm), goethite (Gt), 2-line ferrihydrite (Fh), gibbsite (Gb), aluminium hydroxide, and three Al-substituted goethites (AlGt) were synthesized and characterized by X-ray powder diffraction (XRD), particle size analysis, and diffuse reflectance (DR) spectroscopy. Adsorption isotherms were obtained after shaking the samples with increasing concentrations of arsenate (40 - 1600 mg L<sup>-1</sup>) in a 10 mmol L<sup>-1</sup> CaCl<sub>2</sub> solution for 24 hours. The adsorption envelope was measured at pH ranging from 3 to 9. The As(V) adsorption maxima decreased in the following order: Al(OH)<sub>3</sub> > Fh > AlGt-15 > AlGt-25 > AlGt-35 > Hm > Gb > Gt. No relationship was observed between particle diameter and maximum adsorption, suggesting that re-aggregation could have taken place, or possibly that imperfections on the surface of the particles increased their surface net charge, resulting in high adsorption density. The behaviour of all samples was strongly dependent on pH, and the maximum adsorption was achieved in slightly acidic conditions. In general, Al-substituted goethites showed promising results for their potential use as an adsorbent to remove arsenic from water.

### Introduction

The presence of arsenic in soils, sediments, and water is attributed to natural sources, such as weathering of rocks and minerals with high As contents, and to human activity, such as use of arsenical fertilizers and pesticides, and industrial and mining activities as well. Anthropogenic sources have contributed to the increase of arsenic concentration in ground and surface water, often to values higher than the threshold of 10 µg L<sup>-1</sup> considered safe for drinking water by the World Health Organization (WHO). Some parts of Bangladesh, West Bengal, Vietnam, India, Mexico, Argentina, Chile and Brazil are well known for the anomalously high levels of As in drinking water (Smedley and Kinniburgh, 2002; Matschullat et al., 2000).

In Brazil, natural sources of As have been found in connection with gold deposits containing sulfide minerals. Contamination is particularly strong in three parts of the State of Minas Gerais, namely the "Iron Quadrangle", the "Morro do Ouro" in Paracatu county and the "Riacho dos Machados" county (Mello et al., 2006). As a result of mining activities in the Iron Quadrangle, an estimated 3.1 million metric tons of tailing materials with average As content of 14,500 mg kg<sup>-1</sup> have been deposited along valleys without adequate assessment of environmental impact (Deschamps et al., 2002). Moreover, previous studies in these areas revealed a naturally high As background, with average As concentrations above 100 mg kg<sup>-1</sup> in soils and 100 µg L<sup>-1</sup> in local water (Mello et al., 2006; Deschamps et al., 2002; Matschullat et al., 2000).

Many countries have reduced their regulatory limits of arsenic in drinking water due to its chronic toxicological effects. The WHO guideline recommended that As values in drinking water be reduced from 50 to 10 µg L<sup>-1</sup> in 1993, and several countries worldwide adopted this recommendation (Smedley and Kinniburgh, 2002). The European Commission also revised the maximum contaminant level (MCL), and all drinking water supply systems within the European Union must comply with the new limit of < 10 µg L<sup>-1</sup> (Zouboulis and Katsoyiannis, 2005). The US EPA also decided to implement the same limit for drinking water in USA (USEPA, 2000). In Australia, the drinking water guideline value for As is 7 µg L<sup>-1</sup> (NHMRC & NRMCC, 2004).

Arsenic can occur in the environment in several oxidation states (-3, 0, +3, +5), but in natural waters it can be found mainly as inorganic arsenite [As(III)] and arsenate [As(V)] oxyanions deriving from deprotonation of the acids H<sub>3</sub>AsO<sub>3</sub> and H<sub>3</sub>AsO<sub>4</sub>. The distribution of arsenic species in the environment depends primarily on redox potential (Eh) and pH (e.g. H<sub>3</sub>AsO<sub>4</sub>/H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> pK<sub>a1</sub> = 2.2; H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>/HASO<sub>4</sub><sup>2-</sup> pK<sub>a2</sub> = 6.9; HASO<sub>4</sub><sup>2-</sup>/AsO<sub>4</sub><sup>3-</sup> pK<sub>a3</sub> = 11.4).

Sorption processes play an important role on As mobility, solubility and toxicity in the soil-water system. Arsenate is the primary anion in aerobic surface water, and arsenite is the primary species in groundwater. The reduced state, As(III), is much more toxic, soluble, and mobile than the As(V) oxidized form (Schnoor, 1996).

The biogeochemical cycles of iron and arsenic are closely related in the environment, and the mechanism of arsenate adsorption onto Fe (hydr)oxides is considered to be ligand exchange with surface hydroxyls and/or surface water groups (Goldberg, 1986). Spectroscopy studies indicate that arsenate forms inner-sphere binuclear complexes with Fe (hydr)oxides surfaces. This phenomenon was also observed for Al hydroxides (Ladeira et al., 2001).

Several technologies have been considered for arsenic removal from contaminated waters, such as coagulation with ferric or aluminium salt followed by filtration (Jekel, 1994) and adsorption using natural and/or synthetic Fe and Al (hydr)oxides (Deschamps et al., 2003; Garcia-Sanchez et al., 2002; Ladeira et al., 2001; Driehaus et al., 1998; Pierce and Moore, 1982). General experience indicates that the methods using Fe (salt or solid material) are more effective than Al in removing As from water. Nevertheless, Fe materials used to adsorb As appear to be unstable in low Eh environments. Thus, under reducing conditions, the mechanism of arsenic sorption may also depend on Fe reduction (Cummings et al., 1999).

The disposal of Fe-As-rich waste generated during the sorption process is an environmentally very sensitive issue, and requires the development of methods to improve the stability of these compounds under anaerobic conditions. Previous investigations have shown a positive correlation between goethite stability under reducing conditions and structural Al content (Schwertmann, 1991; Maurice et al., 2000; Gonzales et al., 2002). In this study we assess the potential of Al-substituted goethites in adsorbing arsenate in comparison to other Al and Fe (hydr)oxides.

## Material and Methods

### 1. Synthesis of iron and aluminium (hydr)oxides

Hematite (Hm), 2-line ferrihydrite (Fh) and goethite (Gt) were synthesized following the procedures described in Schwertmann and Cornell (2000). A series of three Al-substituted goethites, labelled as AlGt-15, -25 and -35 according to Al:Fe ratio, were also synthesized following the same method. Different amounts of 1 mol L<sup>-1</sup> AlCl<sub>3</sub> solution were added to 1 mol L<sup>-1</sup> FeCl<sub>2</sub> · 4H<sub>2</sub>O solution (15:50, 25:50 and 35:50, v/v) to obtain isomorphic substitution of iron by aluminium. The pH was adjusted at 11.7 ± 0.2 with 1 mol L<sup>-1</sup> KOH solution under constant stirring. The solution was then left to oxidize (by air) for three months, and after this procedure a dense yellow product was formed.

Gibbsite (Gb) was prepared following the procedures outlined in Kyle et al. (1975). An Al(NO<sub>3</sub>)<sub>3</sub> solution was titrated with NaOH to a pH of 4.5 ± 0.2. The gelatinous precipitate was heated for two hours at 40 °C, then washed twice, transferred to dialysis membranes, dialyzed with Milli-Q water for 36 days, and dried at 60 °C. Aluminium hydroxide Al(OH)<sub>3</sub> was prepared from an aluminium nitrate solution by precipitation with NaOH. The procedure was similar to that followed for the synthesis of gibbsite, but with the suppression of the heating step to preserve a low crystallinity.

To prevent the crystallization of the amorphous phase, the 2-line ferrihydrite and aluminium hydroxide were freeze dried. In addition, all samples were crushed to a grain size <53 µm and characterized by X-ray powder diffraction (XRD) and particle size analyses. Diffuse reflectance (DR) spectroscopy was also used for the characterization of the iron (hydr)oxides.

### 2. Adsorption studies

Batch experiments were carried out with As(V) solutions by dissolving analytical reagent grade di-sodium hydrogen arsenate heptahydrate (Na<sub>2</sub>AsO<sub>4</sub> · 7H<sub>2</sub>O; Ajax Finechem) in Milli-Q water. To obtain adsorption isotherms, the solid sample (0.1000 g) and 25 mL of As solution (concentration of 40 up to 1600 mg L<sup>-1</sup>) were equilibrated for 24 hours on a rotary shaker, at a constant temperature of 25 °C. The ionic strength was set at 10 mmol L<sup>-1</sup> using CaCl<sub>2</sub>. The samples were then centrifuged and syringe filtered using 0.22 µm membrane filters (Millipore Millex-GV, USA). Arsenic in the equilibrium solutions was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), using a Perkin Elmer Optima 3300 DV. Typical detection limits (3σ) of 7 µg L<sup>-1</sup> As were obtained. The adsorption envelope was obtained as for the adsorption isotherm step, but the pH was adjusted for each sample between 3 and 9 by adding HNO<sub>3</sub> or NaOH. In addition, blank experiments containing arsenic in solution but no adsorbent material were used to measure the amount of arsenic adsorbed by the walls of the reaction vessels.

## Results and Discussion

The XRD analyses revealed that the samples are homogenous and correspond to the desired mineral phases. The crystalline phases showed diffraction peaks of highest intensity at 0.269, 0.418 and 0.485 nm, corresponding to hematite (104), goethite (110) and gibbsite (002), respectively. The DR spectra also confirmed the identification of all iron (hydr)oxides synthesized. Particle size analysis was carried out after all samples had been passed through the < 53 µm sieve. The mean particle size decreased in the following order: Fh (23.47 ± 0.311 µm) > Gb

$(21.01 \pm 0.460 \mu\text{m}) > \text{Al}(\text{OH})_3 (12.60 \pm 1.313 \mu\text{m}) > \text{AlGt-15} (11.33 \pm 3.866 \mu\text{m}) > \text{AlGt-25} (3.248 \pm 0.466 \mu\text{m}) > \text{AlGt-35} (2.548 \pm 2.712 \mu\text{m}) > \text{Gt} (0.972 \pm 0.022 \mu\text{m}) > \text{Hematite} (0.201 \pm 0.001 \mu\text{m})$ .

### 1. Adsorption isotherm

To determine the maximum As uptake onto different mineral surfaces, adsorption isotherms were calculated for arsenate. The adsorption data were fitted to the Langmuir equation  $q = b \cdot K \cdot C / (1 + K \cdot C)$ , where  $q$  is the uptake of adsorbed arsenate by the sorbent ( $\text{mg g}^{-1}$ ),  $b$  is the maximum arsenic uptake ( $\text{mg g}^{-1}$ ),  $C$  is the equilibrium concentration of the solute remaining in the solution ( $\text{mg L}^{-1}$ ), and  $K$  ( $\text{L mg}^{-1}$ ) is the equilibrium constant related to the energy of adsorption. The experimental data had an excellent fit to the Langmuir equation, with a minimum correlation coefficient value of 0.94.

The maximum As(V) adsorption decreased in the following order:  $\text{Al}(\text{OH})_3 > \text{Fh} > \text{AlGt-35} > \text{AlGt-25} > \text{AlGt-15} > \text{Gt} > \text{Hm} > \text{Gb}$ . The  $b$  value of the Langmuir isotherm allowed us to classify the adsorbents in three groups: 1) amorphous phases ( $>100 \text{ mg g}^{-1}$  of arsenate); 2) Al-substituted goethites ( $\sim 30 \text{ mg g}^{-1}$ ); 3) Hm, Gb and Gt ( $< 19 \text{ mg g}^{-1}$ ). Although the specific surface area analyses of these materials were not performed, the results seem to be strongly dependent on this property, considering the values reported in the literature for similar materials (Cornell and Schwertmann, 1996; Pierce and Moore, 1982).

The higher adsorption capacities of  $\text{Al}(\text{OH})_3$  and Fh could be due to their considerably larger specific surface area and lower degree of crystallinity. Moreover, the incorporation of Al in the goethite structure favoured the adsorption of As(V) compared to pure goethite, hematite and gibbsite. A decrease of As(V) uptake along with increase of Al:Fe ratio was also noted, suggesting higher arsenic adsorption onto iron compounds. The isomorphic substitution of Al for Fe in the structure of goethite has a marked effect on goethite properties, e.g. variations in crystal size, shape and surface area (Schulze and Schwertmann, 1987). Gonzales et al. (2002) found that the crystal size of goethite became smaller as Al substitution increases, but did not find a clear trend between Al content and surface area. On the other hand, the lower As(V) adsorption capacity observed for pure Hm, Gb, and Gt could be due to fewer reactive hydroxyls and/or surface water groups than other materials.

A relationship between the  $b$  parameter and particle size was not observed, and therefore we do not expect a correlation between specific surface area and particle diameter (see also Schulze and Schwertmann, 1987).

Changes in the solution pH greatly affect the sorption process. In all samples the adsorption of arsenate decreased with increasing pH. In general, maximum adsorption was achieved at pH between 3.2 and 5.3, with the highest value for hematite. The samples with low crystallinity showed adsorption maxima at more acidic condition ( $\text{pH} < 3.5$ ).

The adsorption behavior of As(V) as a function of pH has been widely reported in the literature (Pierce and Moore, 1982; Manning and Goldberg, 1997; Garcia-Sanchez et al., 2002; Deschamps et al., 2003). The decrease in arsenate adsorption with increasing pH could be due to two interacting factors: the increasing negative surface potential on the sorption surface and the increase of the negative charge of the As(V) species (due to deprotonation of  $\text{H}_3\text{AsO}_4$ ) in solution. At the pH values observed for adsorption maxima, the most likely arsenic species present is  $\text{H}_2\text{AsO}_4^-$ , since it is the predominant form within the pH range of 2.2 – 6.9. This suggests that the adsorption of As(V) may be described by surface complexation models involving ligand exchange of surface hydroxyl groups.

### Conclusions

The following preliminary conclusions can be drawn from this study:

1. the highest arsenate adsorption was observed in aluminium hydroxide and 2-line ferrihydrite, followed by Al-substituted goethites;
2. the expected relationship between particle diameters and maximum As(V) adsorption capacity was not observed, suggesting that phenomena of re-aggregation could have taken place during the analyses, and/or the possible presence of irregularities on the surface of the particles, mainly of the amorphous material, may have contributed to the increase of surface area;
3. arsenic adsorption onto all samples was strongly influenced by pH changes, and the maximum adsorption was achieved in slightly acidic conditions.

These preliminary results obtained for Al-substituted goethites are promising with respect to their use as an adsorbent to remove arsenic from water.

### Acknowledgements

This study was carried out while the first author was an Academic Visitor at The University of Queensland, with funding from CNPq (Brazil). A UQ SMI grant provided funding to cover the cost of particle size analyses and ICP-OES analyses. Laboratory work was carried out at UQ (Earth Sciences and CMLR) with the assistance of A. Seeber (Earth Sciences), and M. Edraki and C. Lokhart (CMLR).

## References

- Cornell R.M., Schwertmann U. (1996). The iron oxides. Structure, reactions, occurrences and use Weinheim: VCH, 573 p.
- Cummings D.E., Caccavo Jr. M., Fendorf S., Rosenzweig R.F. (1999). Arsenic mobilization by the dissimilatory Fe(III)-reducing bacterium *Shewanella alga* BrY. *Environmental Science and Technology* 33, 723-729.
- Deschamps E., Ciminelli V., Frank L.F.T., Matschullat J., Rue B., Schmidt H. (2002). Soil and sediment geochemistry of the Iron Quadrangle, Brazil: the case of arsenic. *Journal of Soil and Sediments* 2, 216-222.
- Deschamps E., Ciminelli V., Weidler P.G., Ramos A.Y. (2003). Arsenic sorption onto soils enriched in Mn and Fe minerals. *Clays and Clay Minerals* 51, 197-204.
- Driehaus W., Jekel M., Hildebrandt U. (1998). Granular ferric hydroxides – a new adsorbent for the removal of arsenic from natural water. *Journal Water SRT-Aqua* 47, 30–35.
- EPA (2000). National primary drinking water regulations; arsenic and clarifications to compliance and new source contaminants monitoring; proposed rule. *Federal register* 65, 38888-38983.
- Ganzales E., Ballesteros M.C., Rueda E.H. (2002). Reductive dissolution kinetics of Al-substituted goethites. *Clay and Clay Minerals* 50, 470-477.
- Garcia-Sanchez A., Alvarez-Ayuso E., Rodriguez-Martins F. (2002). Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soils. *Clay Minerals* 37, 187-194.
- Goldberg S. (1986). Chemical modeling of arsenate adsorption on aluminium and iron oxide minerals. *Soil Science Society of American Journal* 50, 1154-1157.
- Jekel M. (1994). Arsenic removal in water treatment. In: Nriagu J. (ed.), *Arsenic in the environment*, 433-446.
- Kyle J.H., Posner A.M., Quirk J.P. (1975). Kinetics of isotopic exchange of phosphate adsorbed on gibbsite. *Journal of Soil Science* 26, 34-43.
- Ladeira A.C.Q., Ciminelli V.S.T., Alves M.C.M., Duarte H.A., Ramos A.Y. (2001). Mechanism of anion retention from EXAFS and density functional calculations: Arsenic (V) adsorbed on gibbsite. *Geochimica et Cosmochimica Acta* 65, 1211-1217.
- Manning B.A., Goldberg S. (1997). Adsorption and stability of arsenic (III) at the clay mineral – water interface. *Environmental Science and Technology* 31, 171-177.
- Matschullat J., Borba R.P., Deschamps E., Figueiredo B.R., Gabrio T., Schwenk M. (2000). Human and environmental contamination in the Iron Quadrangle, Brazil. *Applied Geochemistry* 15, 181-190.
- Maurice P.A., Lee Y.J., Hersman L.E. (2000). Dissolution of Al-substituted goethites by an aerobic *Pseudomonas mendocina* var. bacteria. *Geochimica et Cosmochimica Acta* 64, 1363–1374.
- Mello J.W.V., Roy W.R., Talbott J.L., Stucki J.W. (2006). Mineralogy and arsenic mobility in arsenic-rich Brazilian soils and sediments. *Journal of Soils and Sediments*, 10.1065/jss2005.09.144.
- NHMRC & NRMCC (2004). Australian drinking water guidelines. National Water Quality Management Strategy Paper No 6, National Health and Medical Research Council and Natural Resource Management Ministerial Council, Australian Government Publishing Service, Canberra.
- Pierce M.L., Moore C.B. (1982). Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Research* 16, 1247–1253.
- Schnoor J.L. (1996). *Environmental modeling: fate and transport of pollutants in water, air, and soil*. A Wiley-interscience publication pp. 684.
- Schulze D.G., Schwertmann U. (1987). The influence of aluminium on iron oxides: XIII. Properties of goethites synthesized in 0.3 M KOH at 25°C. *Clay Minerals* 22, 83–92.
- Schwertmann U. (1991). Solubility and dissolution of iron oxides. *Plant and Soil* 130, 1–25.
- Schwertmann U., Cornell R.M. (2000). *Iron oxides in the laboratory*. Wiley-VCH, New York, 2<sup>nd</sup> ed. 188 p.
- Smedley P.L., Kinniburgh D.G. (2002). A review of source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry* 17, 517-568.
- Zouboulis A.I., Katsoyiannis I.A. (2005). Recent advances in the bioremediation of arsenic-contaminated groundwaters. *Environmental International* 31, 213-219.