

## THE USE OF Al-BASED ADSORBENTS FOR MITIGATION OF ARSENIC CONTAMINATION

A.C.Q. Ladeira<sup>1</sup>, V.S.T. Ciminelli<sup>2</sup>, E.B. Paniago<sup>1</sup>

<sup>1</sup>Dept. of Chemistry, Universidade Federal de Ouro Preto -UFOP  
e-mail: eucler@iceb.ufop.br

<sup>2</sup>Dept. of Metallurgical and Materials Engng. Universidade Federal de Minas Gerais -UFMG  
Rua Espírito Santo 35, Belo Horizonte, CEP 30160-030, Minas Gerais, Brazil.  
e-mail: [ciminelli@demet.ufmg.br](mailto:ciminelli@demet.ufmg.br)

### ABSTRACT

This work aims at the evaluation of Al-based adsorbents (gibbsite and calcined gibbsite) for arsenic removal in water treatment. The thermal treatment consisted in the calcination in temperatures from 70 and 400°C. Both the specific surface area and the adsorption capacity were found to increase up to 20 and 10 times, respectively, as a result of the treatment. Leaching and elution procedures for arsenic-loaded substrates were performed in order to evaluate arsenic remobilization and elution. Among the leaching solutions tested, distilled water, acetic acid and sulfate solutions, the latter was the one that most favored both As(III) and As(V) remobilization. The leaching data also showed a high tendency for As(III) remobilization. Up to 10% of As(III) was released from the loaded solid, the solid was classified as toxic to the environment. In addition to, the treated gibbsite retained arsenic much more strongly than the raw sample. Elution with 3% and 0.5% NaOH solutions showed up to 80% of arsenic removal.

### INTRODUCTION

The change in groundwater and surface water quality, by the presence of an increasing number/concentrations of contaminants, is a relevant problem which affects mainly domestic water requirements. During the last thirty years surface water quality has changed significantly, and water supplies considered of excellent or good quality in the past are now classified as of medium or of poor quality ([www.feam.br](http://www.feam.br)). In the state of Minas Gerais (Brazil) the main contaminants of surface waters in levels higher than those permitted by the legislation are: cadmium, lead, nickel, manganese, phosphate, phenols and arsenic. Among these, arsenic contamination was detected in levels up to 35 times the permitted one. The permitted level for arsenic is 0.05mg/L in potable water, according

to the Brazilian legislation. The high arsenic levels in rivers, most of them responsible for public water supply, combined with the high arsenic background in some soils is a potential risk for local populations (Feam, 1994; Matschullat et al., 1998). Long term exposure to low concentrations of arsenic in drinking water can lead to cancer and other severe health problems, including cardiovascular diseases and diabetes, as well as developmental and neurological effects (NRC, 2000).

The capability of some soils constituents (hydrated iron and aluminum oxides) to adsorb arsenic, in a relative immobile form, is a well-known phenomenon (Foster et al 1996; Isaacson et al, 1994; Fendorf et al, 1997). Our group (Ladeira et al., 1998, 2000a, 2000b) previously studied the adsorption of arsenic on different soil samples. This adsorption capacity allows the use of these soils as liners in tailings dams and landfills, thus providing protection of the surroundings.

The remobilization of the arsenic adsorbed on soil liners during a long-term exposure is a matter of concern. A large number of leaching tests are generally used to predict this remobilization (Sullivan and Yelton, 1988; Tessler et al., 1979). The laboratory tests employed do not take into account the natural complex chemical, physical and biological factors found in the environment but they are helpful in the assessment of arsenic remobilization. Among all the leaching tests proposed, the American Environmental Protection Agency (EPA) adopted the TCLP extraction method (Toxicity Characteristic Leaching Procedure) to classify a potential toxic solid as toxic or non-toxic.

Another possible application of these soils is related to the use of these materials as adsorbents in households and water treatment filters. This utilization may require the elution of the arsenic adsorbed on the substrate in view of its posterior reutilization.

This study aims at the development of a gibbsite-based adsorbent for arsenic. A thermal treatment was selected to improve the adsorption capacity of the natural sample. A gibbsite sample and the product

obtained by calcination of this mineral were tested. The work investigated the possible utilization of both materials as soil liners or filter adsorbents. In the first case, the adsorption should be irreversible to avoid the remobilization of the element to the environment. The remobilization of arsenic adsorbed on the samples was determined using three different leaching solutions, including the TCLP test. In the second case, the adsorption should be reversible to allow the elution of arsenic and reutilization of the substrate. NaOH solution was tested as a possible eluant. The results have been discussed with a view of these two applications.

## EXPERIMENTAL

### Sample preparation and characterization

The gibbsite sample was supplied by Mineração Santa Lucrécia S.A. The solid sample was ground and screened in a 37 $\mu$ m sieve before calcination. The calcination was conducted in a laboratory furnace, during 8 hours temperatures varying from 70 to 400°C. The chemical composition of the untreated and calcined gibbsite was determined using X-ray fluorescence (*Philips PW2510*) and wet chemistry analyses. The specific surface area was calculated by the BET equation using a multiple point N<sub>2</sub> adsorption technique (NOVA 1000, *Quantachrome Corp*).

The solids adsorption capacity was determined based on adsorption isotherms, obtained by batch methods, through the stirring of 10g of soil with 100ml of arsenic solution. Arsenic concentration in solution varied from 100 to 1000mg/L. The pulps were shaken at pH 5.5 or 8.0 and temperature of 25 $\pm$ 0.2°C during 24 hours. The pH was adjusted with diluted HCl or NaOH during the initial four hours until complete stabilization. At the end of the experiment the solids were filtered, washed with deionized water and dried overnight at room temperature. Total As present in the filtrate was determined by atomic absorption spectroscopy (*Perkin Elmer 5000*). This procedure was repeated for distinct As(III) and As(V) solutions, prepared with di-sodium hydrogen arsenate heptahydrate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O PA; >98.5%, Fluka) and sodium (meta)arsenite (AsNaO<sub>2</sub> PA; >99.0%; Fluka). Additional information of the procedure described above is presented by Ladeira et al. (1998).

### Leaching and Elution procedures.

Samples containing 2g of dried arsenic-loaded solids were added to 40mL of the leaching solution to produce

a slurry with 20% solids. The erlenmeyers were shaken for 18 hours at constant temperature of 25  $\pm$  0.5°C. The slurry pH was not controlled during the experiments. After 18 hours, the pulp was filtered and the filtrate submitted to chemical analyses in order to determine the final As concentration. Duplicate samples were prepared for all experiments. The following leaching solutions have been evaluated: acetic acid (TCLP, standard USEPA procedure), 0.5M K<sub>2</sub>SO<sub>4</sub> and deionized Milli-Q water.

Similar procedure was applied to the elution tests. The experiments were carried out with sealed flasks containing 10g of loaded solid and 100ml of the eluant solution (0.5% and 3% NaOH). The flasks were continuously shaken for 24 hours at room temperature (25 $\pm$ 0.2°C). At the end of the experiments the pulp was filtered and the arsenic concentration in the filtrate was determined. Arsenic in solution was determined, in both procedures, by atomic absorption spectroscopy (*Perkin Elmer 5000*). Arsenic concentration in the solid samples varied from 0.06% to 2.02%, according to the sample (untreated or calcined) and to the arsenic species (trivalent or pentavalent).

## RESULTS

### Sample preparation and characterization.

Untreated gibbsite (Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O) was submitted to heat treatment in order to remove the hydration water present in the mineral structure. The purpose of this treatment was to increase the specific surface area and, therefore to increase the adsorption capacity of the solid sorbent. The results showing the specific surface area after calcination are presented in table I.

Table I - Gibbsite Calcination

| Temperature of Calcination (°C) | Specific surface area (m <sup>2</sup> /g) |
|---------------------------------|---|
| 25                              | 13.5                                      |
| 70                              | 13.7                                      |
| 200                             | 16.9                                      |
| 300                             | 287                                       |
| 400                             | 268                                       |

The specific surface area of the untreated gibbsite was 13.5m<sup>2</sup>/g. The calcination at temperatures above 300°C increases this area to values greater than 260m<sup>2</sup>/g. The highest specific surface areas obtained with this treatment are resembling those shown by materials like catalysts and activated carbons, employed

by petrochemical and mineral industries. The specific surface areas obtained at temperature of 300 and 400°C were considered to be very similar, and the latter was selected for the calcination procedures.

The chemical composition of the untreated and calcined sample showed that the main constituents were silica (6.7% and 8.9%) and aluminum oxide (59.0% and 75.6%), respectively. The presence of minor elements like iron (1.3% and 1.9%) and titanium (0.9% and 1.1%), respectively, was also detected. The major difference showed by the samples was related to the weight loss: 30.49% for untreated gibbsite and 11.50% for the calcined one. This difference is due to the loss of hydration water during the calcination process. The calcination at 400°C removes around 60% of hydrated water, so not all the water was extracted by the thermal treatment.

### Adsorption Isotherms.

Figures 1 and 2 show the isotherms obtained with the As(III) and As(V) species. The results have been adjusted (solid lines in figure 1) to a Langmuir type equation:

$$Q = Q_{\max} \cdot [KC / (1 + KC)] \quad (1)$$

where  $Q$  = the amount of arsenic adsorbed by the clay (mg/g),  $Q_{\max}$  = maximum arsenic uptake (mg/g),  $C$  = equilibrium concentration of arsenic in aqueous phase (mg/L) and  $K$  = constant.

For the untreated gibbsite the  $Q_{\max}$  values for the pentavalent species adsorbed were 1.7mg/g at pH 8.0 and 3.0mg/g at pH 5.5. Maximum As(V) adsorption occurs at pH 5.5; pH values lower than 5.5 were not investigated due to possible dissolution of gibbsite. For the trivalent arsenic the  $Q_{\max}$  were determined as 4.3mg/g at pH 8.0 and 3.4mg/g at pH 5.5. The adsorption of the trivalent species was favored by the increase of pH.

The  $Q_{\max}$  determined for As(III) adsorbed on calcined gibbsite were 23.4mg/g at pH 8.0 and 25.4mg/g at pH 5.5. For As(V)  $Q_{\max}$  increased from 23.6mg/g at pH 8.0 to 45.7mg/g at pH 5.5. The  $Q_{\max}$  values for arsenic uptake by the calcined gibbsite were much higher than the uptake presented by the untreated sample. Figure 2 shows that at pH 5.5 the loading capacity of the calcined samples was substantially greater than the others. This represents a very significant result, in a context of possible applications, considering that As(V) species are the preponderant species in the aquatic environment. In addition to, pH values around 5.5 are a common condition of natural systems. For both As(III) and As(V), the increase in the adsorption

capacity is certainly associated with the much higher surface area shown by the calcined sample. Thus, the thermal treatment represents a very efficient process to improve the adsorption capacity of the raw sample.

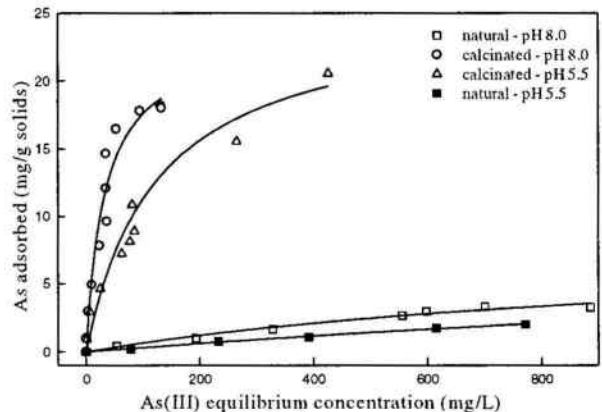


Figure 1: Equilibrium As(III) adsorption isotherms for untreated and calcined gibbsite;  $I=0.15M$ , temperature  $25\pm 0.2^\circ C$ . Solid lines represent the fit to the Langmuir equation.

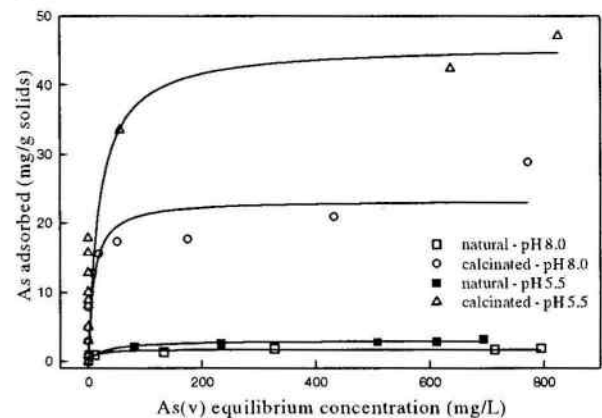


Figure 2: Equilibrium As(V) adsorption isotherms for untreated and calcined gibbsite;  $I=0.15M$ , temperature  $25\pm 0.2^\circ C$ . Solid lines represent the fit to the Langmuir equation.

### Leaching tests.

The use of soils containing ferric and aluminum oxyhydroxides as protective liners in tailing dams and landfills are increasing owing to the legislation requirements regarding wastes disposal. These soil liners may adsorb toxic substances generated by the residues and hence hinder their migration to the environment. The assessment of the soil retention is a valuable tool to estimate the risks of future contamination. The soil retention of the contaminants should be an irreversible process and the leaching tests

are used as an indicative of the liner behavior as regard as this irreversibility. The leaching solutions used in the tests were:  $K_2SO_4$  0.5M, acetic acid solution (TCLP, EPA) and deionized water. The leaching in the presence of  $SO_4^{2-}$  ion was selected owing to the production of this species during the oxidation of arsenopyrite (FeAsS) and pyrite ( $FeS_2$ ), two important constituents of mining wastes. Acetic acid solution was the main component of the TCLP standard procedure. This procedure classifies the solid as toxic if the concentration of the toxic elements in the final leaching solution exceeds 5mg/L. For concentrations lower than 5mg/L the residue is classified as non-toxic. This value of 5mg/L will be considered in the present study for all leaching conditions employed. The leaching results are shown on tables II and III.

Table II - Leaching Results for As(V)

| Sample                           | Leaching Solution | As(V) in the filtrate (mg/L) | As(V) leached (%) |
|----------------------------------|-------------------|------------------------------|-------------------|
| Untreated                        | TCLP              | 2.46                         | 2.05              |
| Gibbsite <sup>(1)</sup>          | $K_2SO_4$ 0.5M    | 7.62                         | 6.35              |
|                                  | H <sub>2</sub> O  | 0.9                          | 0.75              |
| Calcined Gibbsite <sup>(2)</sup> | TCLP              | <0.70                        | <0.07             |
|                                  | $K_2SO_4$ 0.5M    | 5.49                         | 0.54              |
|                                  | H <sub>2</sub> O  | 1.5                          | 0.15              |

(1) arsenic content 0.24%

(2) arsenic content 2.02%

Table III - Leaching Results for As(III)

| Sample                           | Leaching Solution | As(III) in the filtrate (mg/L) | As(III) leached (%) |
|----------------------------------|-------------------|--------------------------------|---------------------|
| Untreated                        | TCLP              | 11.73                          | 39.1                |
| Gibbsite <sup>(3)</sup>          | $K_2SO_4$ 0.5M    | 9.41                           | 31.4                |
|                                  | H <sub>2</sub> O  | 8.48                           | 28.3                |
| Calcined Gibbsite <sup>(4)</sup> | TCLP              | 36.52                          | 5.2                 |
|                                  | $K_2SO_4$ 0.5M    | 11.02                          | 1.6                 |
|                                  | H <sub>2</sub> O  | 7.56                           | 1.1                 |

(3) arsenic content 0.06%

(4) arsenic content 1.4%

It was observed that arsenic dissolution varied with the leaching solutions and with the nature of the samples. For the pentavalent arsenic (table II) the limit of 5mg/L was exceeded only in the presence of sulfate ions. In view of this fact, the disposal of wastes containing potential sulfate-producers (arsenopyrite and

pyrite) should involve some precautions such as the monitoring of the local soil and groundwater. These residues may generate the  $SO_4^{2-}$  ion and consequently dislocate the arsenic adsorbed on the substrate, thus promoting the migration of this element to the environment. In acetic acid solutions and deionised water, arsenic dissolution was lower than 2.5mg/g and the loaded samples were considered non-toxic. Table II also shows that the calcined gibbsite retains arsenic much more strongly than the untreated one. This fact was verified by the low arsenic content of the filtrates, which varied from <0.07 to 5.49mg/L. Similarly, the values of the % of As(V) leached from the calcined sample was significantly lower than those leached from the untreated gibbsite.

For the trivalent species the high arsenic content of the filtrates shown in table III, as well as the elevated % of As(III) leached, are consistent with the higher mobility of this species. All the experiments conducted with samples loaded with the trivalent species presented high As remobilization. These loaded solids were characterized as toxic and the limit of 5mg/L was exceeded in all the selected experimental conditions. It is also observed that the TCLP procedure is more effective in removing trivalent than the pentavalent arsenic. By observing table III, it was concluded that the calcined gibbsite retains trivalent arsenic much more strongly than the untreated one; the same behavior was presented for the adsorption of pentavalent arsenic. The superior performance of the calcined sample was demonstrated once more.

The mechanism proposed by Ladeira et al. (2000b) to elucidate the As(V) adsorption on gibbsite may explain in part the high retention of this element on soils. The authors used X-ray absorption fine structure spectroscopy (EXAFS) and Density functional calculations (DFT) to determine the structural model of arsenic surface complex on gibbsite mineral. The most stable structure predicted for As(V)-gibbsite system was the bidentate-binuclear complex. The observations reported in this study are consistent with the stability of adsorbed As(V) species on gibbsite in aqueous solutions, reported by Ladeira and Ciminelli (2000a).

### Elution Tests.

The utilization of the adsorbents in households or in water treatment filters may involve the elution procedure. The elution process is the subsequent step after the substrates have been loaded with arsenic. During elution arsenic will be removed from the adsorbent and this will in turn allow successive reutilization of the material. Tables IV and V show the elution yields for the untreated and the calcined



gibbsites loaded with As(V) and As(III). According to Gosh and Yuan (1987) arsenic is effectively eluted from alumina with NaOH solutions. In the present study, 0.5% NaOH solution was employed for the elution of As(V) and 3% NaOH solution for the elution of As(III) .

Arsenic adsorbed on untreated gibbsite was 100% eluted, which corroborates the leaching results regarding the weak retention of this element compared to the calcined sample. However, a high dissolution of aluminum (8.7% and 25%) occurred during the elution procedure while using 0.5% and 3% NaOH solutions. With respect to the calcined gibbsite the arsenic elution was 85% for As(V) and 65% for As(III). Once again, aluminum dissolution was notably high (8.0% and 11.4%); acceptable values are around 3% (Gosh and Yuan, 1987). Different eluants are under investigation in an attempt to minimizing aluminum dissolution.

Table IV - Elution of As(V) with 0.5% NaOH

| Sample                               | As(V) in the filtrate (mg/L) | As(V) eluted (%) | Aluminum leached (%) |
|--------------------------------------|------------------------------|------------------|----------------------|
| Untreated<br>Gibbsite <sup>(1)</sup> | 24.5                         | 100              | 8.7                  |
| Calcined<br>Gibbsite <sup>(2)</sup>  | 165.0                        | 81               | 8.0                  |

(5) arsenic content 0.24%

(6) arsenic content 2.02%

Table V - Elution of As(III) with 3% NaOH

| Sample                               | As(III) in the filtrate (mg/L) | As(III) eluted (%) | Aluminum leached (%) |
|--------------------------------------|--------------------------------|--------------------|----------------------|
| Untreated<br>Gibbsite <sup>(3)</sup> | 5.9                            | 100                | 25.0                 |
| Calcined<br>Gibbsite <sup>(4)</sup>  | 115.6                          | 65                 | 11.4                 |

(7) arsenic content 0.06%

(8) arsenic content 1.8%

## CONCLUSION

The calcination procedure promoted an increase of about 20 times in the specific surface area of the gibbsite. This fact improved considerably the adsorption capacity of the samples. For As(V) adsorbed on the untreated and calcined gibbsite the maximum uptake increased from 3.0mg/g to 45.7mg/g, respectively. The thermal treatment also increased the capacity of arsenic retention as demonstrated by the leaching tests. These tests showed that As(III) remobilization exceeded the value of 5mg/L for all conditions, which characterizes the loaded samples as toxic solid. This remobilization indicates a probability of arsenic migration and contamination of the environment. So, the presence of soluble trivalent arsenic in the environment is critical owing to its high mobility. However, calcined gibbsite may be used as liner protection of tailings and dam since the pentavalent species are the predominant species to be adsorbed. The elution tests of calcined gibbsite loaded with arsenic are promising despite of the considerable dissolution of aluminum. It is necessary to evaluate other eluants in order to minimize this dissolution.

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