



## Increasing arsenic sorption on red mud by phosphogypsum addition

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### HIGHLIGHTS

- ▶ This study investigates As sorption on by-products from Brazil.
- ▶ Red mud has been studied as a good adsorbent for arsenic.
- ▶ Phosphogypsum mixed with red mud increases arsenic retention capacity.
- ▶ The mixture provides S and Ca for plant growth during revegetation.
- ▶ The mixture constitutes an amendment to be tested in arsenic-contaminated soil.

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### ABSTRACT

Mining by-products have been tested as adsorbents for arsenic in order to reduce As bioavailability. This study evaluated a red mud (RM) treated with or without phosphogypsum (G) in order to improve its As retention. Red mud and G samples and their mixtures were chemically and mineralogically characterized to gather information concerning their composition, which is key for a better understanding of the adsorbent properties. Phosphogypsum was added to RM in the following proportions: 0, 1, 2, 5, 10, and 25% by weight. These mixtures were subjected to As adsorption and desorption and tested for their maximum adsorption capacity of As ( $As_{MAC}$ ). Arsenic adsorption increased upon increasing the proportion of G added to RM. The  $As_{MAC}$  at pure RM reached  $909 \text{ mg kg}^{-1}$ , whereas the 75%-RM + 25%-G mixture sorbed up to  $3333 \text{ mg kg}^{-1}$  of As, i.e., a 3.5-fold increase in  $As_{MAC}$ . Using G in mixtures with RM increases the efficiency of As adsorption due to the presence of  $Ca^{2+}$ , which alters the charge balance of the adsorbent, leading to the formation of ternary complexes. Addition of G to RM is thus a promising technique to improve As retention, while providing additional value to both by-products, G and RM.

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### 1. Introduction

Arsenic (As) was ranked first in the priority list of harmful substances to human health by the Agency for Toxic Substances and Disease Registry [1]. Exposure to this trace element can cause damage to human health at different levels, ranging from skin diseases (pigmentation, hyperkeratosis and ulceration) to mutagenic and carcinogenic effects [2].

The main As sources to the environment are weathering of rocks and mine tailings, industrial waste discharges, fertilizers, agricultural pesticides, smelting of metals and burning of fossil fuels [3]. According to Baird [4], leaching from abandoned gold mines is also a source of high relevance to pollution of As in aquatic systems.

Arsenic is moderately to highly toxic to plants and highly toxic to mammals [5]. This high toxicity to humans and animals leads to successively increasing concerns about environmental

contamination by As [6]. In this context, the remediation of As-contaminated soils and water bodies has become of great relevance.

There are several traditional methods used for As removal. However, in recent years, several studies have been conducted testing solid wastes and by-products as arsenic adsorbents. In this context, red mud (RM), an aluminum mining by-product, has been extensively studied [3,7].

Red mud is an alkaline residue generated in large amounts by the extraction of aluminum from bauxite through the Bayer process [8]. It is estimated that the production of 1 ton of alumina generates approximately 1–1.5 tons of RM [9]. An advantageous characteristic of this by-product for use in As retention is its oxide-rich constitution, especially iron and aluminum oxides.

Several modifications can be employed to the raw RM in order to improve its sorption capacity, such as heat and acid (HCl) treatments [10]. In addition, in order to reduce the alkalinity of RM, López et al. [11] did laboratory testing by adding different proportions of  $CaSO_4$  to RM. These authors noted that, besides reducing the pH of RM, its mixture with 8%  $CaSO_4$  (by weight) resulted in a stronger affinity for phosphorus and trace elements (Cu, Zn, Cd and

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Ni), which increased adsorption. Taking into account the chemical similarity between phosphorus and arsenic, the addition of phosphogypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to red mud in order to improve its As adsorption capacity appears promising.

Phosphogypsum (G), sometimes called only gypsum for the sake of simplicity, is a by-product of the phosphoric acid industry. It is estimated that gypsum production worldwide is around 100–280 million tons per year [12,13]. The annual production of phosphogypsum in Brazil is estimated at 4.5 million tons. From this total, 1.7 million tons per year are used as a soil conditioner in agriculture and 0.7 million tons per year are used in the cement industry, while the remainder 2.1 million tons are stored in gypsum stack piles, generating an environmental liability [14].

Due to the heterogeneous nature of individual by-products, as well as their mixtures, a detailed characterization of such materials before their use as adsorbents is necessary. Therefore, this study aimed to: (i) characterize, in their pure form or as mixtures, red mud and phosphogypsum collected from two mining sites in Brazil; and, (ii) evaluate the effect of the addition of G to RM in order to improve its As retention capacity.

## 2. Materials and methods

Three RM samples were randomly collected at the 0–20 cm depth in a reservoir located in Poços de Caldas and were supplied by ALCOA Brazil. These three samples were mixed and homogenized generating only one representative sample of RM for further analyses. The phosphogypsum sample came from Uberaba and was supplied by FOSFÉRTIL. Both municipalities, Poços de Caldas and Uberaba, are located in Minas Gerais State, Brazil (Fig. 1).

### 2.1. Characterization

Arsenic semi-total concentrations (excludes the fraction bound to silicates) in samples of phosphogypsum and red mud were determined by microwave furnace-digestion according to the 3051A method of the United States Environmental Protection Agency [15]. The samples were grounded in an agate mortar and passed through a 0.15-mm sieve. Then, 1 g of the materials was weighted and 10 mL of concentrated nitric acid were added for digestion. The quality control was performed using reference soil samples from the North American Proficiency Test Program of the Soil Science Society of America and the certified reference material NIST SRM 2709a San Joaquin Soil to check for the accuracy of As determinations, which were found to be satisfactory, i.e., having less than 20% of variation from certified values [16].

For characterization of oxides of Si, Al, Fe, Ti, and P, the samples were digested in sulfuric acid, according to Embrapa [17]. These determinations can be considered to produce reliable indices of the total element concentrations, because they digest mostly the fine particles. The analytical methods used to measure the concentrations of the elements in the obtained solutions after digestion were colorimetry for Si, P, and Ti, and titration for Fe and Al [17].

For evaluation of the effect of G addition to RM on As adsorption, the G was mixed with RM in the following proportions: 0, 1, 2, 5, 10, and 25% by weight of G. After 20 days of incubation at room temperature ( $24 \pm 3^\circ\text{C}$ ) and water content near 20–25% (by weight), these adsorbent mixtures as well as the pure G were characterized by X-ray diffraction (XRD), according to the methodology recommended by Jackson [18]. The scanning interval used was  $10\text{--}60^\circ 2\theta$  in a Philips PW 1830/40 equipment, using cobalt  $K\alpha$  radiation with a nickel filter.

### 2.2. Arsenic adsorption and desorption

The adsorbents were air-dried, grounded in an agate mortar, passed through a 2-mm sieve and submitted to As adsorption/desorption at room temperature ( $24 \pm 3^\circ\text{C}$ ). For adsorption, 0.3 g of adsorbents were weighted in triplicate and suspended in 30 mL of  $15\text{ mmol L}^{-1}$  NaCl prepared with growing As concentrations (0, 100, 185, 380, 840, and  $1300\text{ }\mu\text{mol L}^{-1}$ ) added as disodium acid arsenate heptahydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ). These concentrations were chosen according to Campos et al. [19].

Arsenic-containing solutions had their initial pH value adjusted to  $5.5 (\pm 0.2)$  using  $10\text{ mmol L}^{-1}$  HCl or NaOH. However, after the contact of these solutions with RM and with its mixtures with G, the pH value obtained in suspension was higher than 5.5, because of the high alkalinity of RM. Considering this fact, the suspension pH value was determined approximately 10 min after the contact of the adsorbents with As-containing solutions. All samples were analyzed in triplicate and the adsorbent:solution ratio was 1:100.

Ionic speciation calculation was performed using the Visual Minteq program, version 2.53 [20], aiming to check for the occurrence of precipitation of arsenate salts (e.g., calcium arsenate). This speciation was performed for three arsenic concentrations (100, 380, and  $1300\text{ }\mu\text{mol L}^{-1}$ ), using their respective suspension pH values, i.e., the suspension pH determined 10 min after the contact of the adsorbents with As-containing solutions. The different percentages of phosphogypsum tested were included in this speciation by the addition of this material as a “finite solid”, as described in the Visual Minteq program.

The total adsorption reaction time was 72 h, which comprised three alternate cycles of 12 h of shaking and 12 h of rest. Then, the samples were centrifuged for 20 min at 3000 rpm and the supernatant was collected for As analyses in order to calculate As adsorption. This batch configuration (methodology) used in this work has been documented in several studies involving metal adsorption and desorption [21–26]. The reaction time of 72 h was selected based on kinetic studies conducted on Oxisols (oxide-rich soils, as is the red mud), which showed that the reaction time used in this study (72 h) was sufficient to reach the equilibrium of the reaction between the solid and liquid phases [27].

Arsenic adsorbed per unit weight of adsorbent was calculated using Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{M} \quad (1)$$

where,  $q_e$  is the As adsorbed ( $\text{mg kg}^{-1}$ ),  $C_i$  and  $C_e$  are the initial and the equilibrium As concentrations in the solution ( $\text{mg L}^{-1}$ ), respectively,  $V$  is the volume of the solution (mL), and  $M$  is the mass of the adsorbent (g).

Adsorption data were fitted to the Langmuir isotherm in order to estimate the maximum adsorption capacity of As ( $A_{S\text{MAC}}$ ). The Langmuir isotherm (Eq. (2)) has been used in studies concerning arsenate adsorption on RM [7,10], and its linearized form is presented in Eq. (3), as follows:

$$q_e = \frac{A_{S\text{MAC}} \times b \times C_e}{(1 + b) \times C_e} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{A_{S\text{MAC}} \times b} + \frac{C_e}{A_{S\text{MAC}}} \quad (3)$$

where,  $q_e$  is the As adsorbed ( $\text{mg kg}^{-1}$ ),  $b$  is the adsorption constant ( $\text{L mg}^{-1}$ ),  $A_{S\text{MAC}}$  is the maximum adsorption capacity ( $\text{mg kg}^{-1}$ ), and  $C_e$  is the equilibrium solution concentration ( $\text{mg L}^{-1}$ ).

Desorption experiments were performed immediately after the removal of the supernatant solutions from the previous adsorption. For that, to the residue of the adsorption experiment, we added 30 mL of  $15\text{ mmol L}^{-1}$  NaCl to promote the desorption of the

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