

RE-USE OPTIONS OF VENEZUELAN BAUXITE RESIDUE: POTENTIAL APPLICATIONS IN ACID MINE DRAINAGE REMEDIATION

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Abstract

Several studies have shown successful results for bauxite residue application in environmental management and remediation purposes. A study of the adsorption capacity of acid neutralised (with HCl) bauxite residue was performed on solutions artificially contaminated with Zn, As (V) and Pb, following batch methods. The results show that the retention of the trace metals in this system was mainly due to surface phenomenon. Most of the trace metals were associated with Fe-Al hydroxides phases. The reversibility tests show a low leaching rate of the elements bound to the solid. The findings show the potential use of Venezuelan bauxite residue as a sorbent agent in the remediation of waters and soils polluted by these metals.

Introduction

The ultimate goal in the management of bauxite residue (BR) at global level is to reach zero waste. By using these residues as raw material in various application domains (engineering, metallurgy, environment, etc.) we could reduce the environmental problem and add a significant value to their use.

The BR has significant reactive surface for the adsorption of elements such as cadmium, lead, zinc, arsenic.¹⁻³ This material can be used for neutralising acidic soils and acid mine drainages (AMD). The excess of hydroxide (OH^-), carbonate (CO_3^{2-}) and aluminate ($\text{Al}(\text{OH})_4^-$) present in the residue, will act as a buffer to reduce acidity. In addition, the large number of Fe and Al oxyhydroxides incorporated in the residue, will act as the substrate on which the metal ion contaminants present in the AMD, can be sorbed.⁴⁻⁶

Given that Venezuela (CVG Bauxilum) is one of the most important south-american alumina producing countries, this article focuses on the study of the sorbent properties of the Venezuelan bauxite residue (solid residue) under acid conditions similar to those of acid mine drainage. For this, we study the adsorption properties of

acid neutralised BR using batch tests, and the partitioning of trace metals using sequential chemical extractions.

Materials and Methods

Sample description

Bauxite residue slurry was obtained from the CVG Bauxilum alumina refinery, Venezuela. The slurry was dried at 40 °C and neutralised with 0.5N HCl in a 1:20.⁷

Table 1: Chemical and mineralogical composition of acid neutralised bauxite residue

Chemical composition ¹		Mineralogical composition ²	
Constituent	(%w/w)	Mineral phases	(%w/w)
Fe ₂ O ₃	42.73	Quartz (SiO ₂)	9.7
SiO ₂	27.1	Calcite (CaCO ₃)	n.d.
Al ₂ O ₃	13.78	Hematite (Fe ₂ O ₃)	18.6
TiO ₂	3.81	Goethite (FeO(OH))	15.4
CaO	0.12	Gibbsite (Al(OH) ₃)	20.9
K ₂ O	0.04	Amorphous	35.4
Na ₂ O	0.01		
P ₂ O ₅	0.17		
MnO	0.08		
LOI	11.03		

1: Determined by fusion XRF; 2: Determined by XRD

All pH measurements were carried out in a suspension of BR diluted 1:5.⁸ The mineralogical phases were identified by X-ray diffraction using a Bruker-AXS spectrometer model D4, with a copper anticathode ($\lambda = 1,541\text{\AA}$). The chemical composition of the major elements was determined by X-ray fluorescence on a Panalytical Axios wavelength dispersive XRF Advance after digestion of the samples by fusion technique. The results on chemical and mineralogical composition are given in Table 1. The particle size distribution analysis was conducted using a Mastersizer 2000 particle size analyzer. The average particle size in the treated BR is 21 μm , we worked with the <40 μm fraction chosen after wet sieving. The surface area for the studied fraction (<40 μm) of neutralised BR was $27.6 \pm 0.2 \text{ m}^2.\text{g}^{-1}$. The analysis was performed using a Quantachrome Nova 2220 and analysed and interpreted by the BET model.⁹

Adsorption experiments

Batch tests are commonly applied in the study of sorption properties and characteristics of the adsorption phenomenon (e.g. kinetics) of various materials, including BR.^{1, 7, 10-12}

To study the adsorption of metal / metalloid As, Zn and Pb on the Venezuelan BR, the batch testing protocol (static study) was used. The concentration ranges for each component have been chosen while taking into account the reference values in the literature.¹³⁻¹⁵

The parameters pH (4.5 ± 0.1) and ionic strength (0.01 M) were selected based on results obtained in prior tests performed. The L/S ratio 1:20 (50 g L^{-1}) was used i.e. 1 g BR in 20 mL of solution (15 mL KNO_3 solution and 5 mL of metal solution). Working solutions were prepared from the salts PbNO_3 for Pb, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for Zn and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ for arsenic.

One gram of dry BR (neutralised and sieved $<40 \mu\text{m}$) was placed in polyethylene vials (chemically inert) with 15 mL of 0.01M KNO_3 electrolyte solution. The pH was adjusted to ± 4.5 with a few drops of HNO_3 solution or 0.1 M KOH. The temperature was set at ($22 \pm 1 \text{ }^\circ\text{C}$). The vials were stirred continuously for 24 hours.⁷ After this pre-equilibrium step, the metal solutions (with increasing concentration of Pb, Zn, or As) were added ($\pm 5 \text{ mL}$) to previous vials. The pH and temperature were re-adjusted. The solution is brought to final volume (20 mL). The vials were agitated again continuously for a period of 24 hours. At the end of the contact period, the solutions were filtered up to 0.45 microns, decanted, acidified and stored at $5 \text{ }^\circ\text{C}$ until analysis. Determination of the elements was carried out using ICP-OES on a Jobin-Yvon JY2000 device for Zn and Pb. As anion was analysed by ion chromatography on a Dionex DX500. Then analysed by furnace atomic absorption on a Unicam (Thermo) 989QZ. To validate the As calibration on AA furnace, a certified sample (TMDA64-2) was used. The experiments were performed in triplicate and the mean values were considered. Blanks and control solutions were also prepared.

Selective sequential extraction experiments

The chemical speciation was conducted in order to study the distribution of trace metals among the geochemical phases. We selected the items with the major and lesser affinity adsorption, As and Zn respectively. Since these metals are already naturally present in the BR, it was decided to compare the statements relating to speciation before and after adsorption.

The sequential extraction tests were performed according to the protocol proposed by Leleyter and Probst¹⁶ based on the principles of conventional protocols Tessier et

al.¹⁷ The samples selected for testing matched the sorption maximum point identified during the adsorption experiments.

Results

Adsorption Langmuir isotherms

The adsorption isotherms (Figure 1) showed that As(V), Pb²⁺ and Zn²⁺ reacted differently to the adsorbent (BR). The shapes of the isotherms were largely positive and concave with respect to the concentration axis. Plots adsorption isotherms were performed using the Langmuir equation:

$$q = \frac{kCb}{1 + kC}$$

where q is the amount adsorbed at equilibrium, C represents the concentration of the adsorbate at equilibrium, k is the constant of adsorption energy and b is the maximum adsorption capacity.¹⁸

Pb isotherm had a well-marked plateau. Its distribution follows the Langmuir model. A decrease in the amount of lead adsorbed is observed as the initial concentration in solution increases and the available adsorption sites become occupied. Pb, Zn and As had good correlation with the Langmuir model at low initial concentrations. However at high initial concentrations a deviation from the ideal curve is observed, in particularly for Zn and As(V) isotherms (Figure 1).

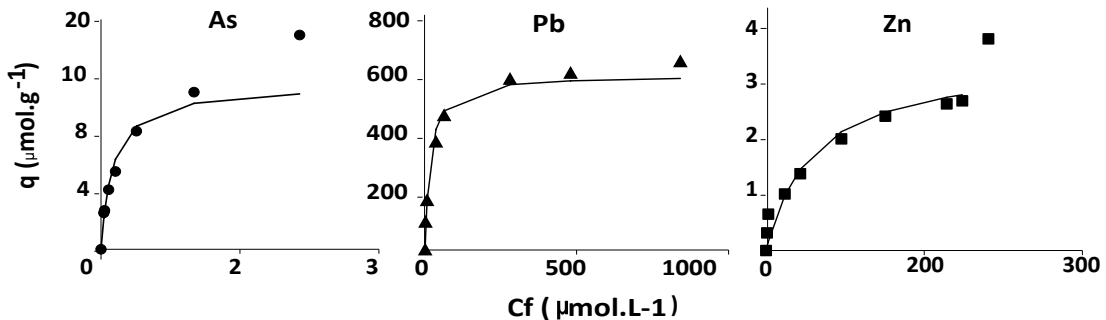


Figure 1: Langmuir adsorption plots for arsenate, lead and zinc. Reaction conditions: bauxite residue dosage 50g.L⁻¹, Ionic strength= KNO₃ 0.01M, pH 4.5±0.1 and temperature of 22 ± 1 °C

The Langmuir isotherm for Zn reflects that two different mechanisms operate for Zn sorption. At low concentrations a surface mechanism (adsorption) is controlling the removal of Zn from the solution. At higher concentrations the formation of a Zn-Al

hydroxide precipitate could be the mechanism involved in trace metals retention. Previous works reported that the formation of mixed-metal Zn (II)-Al (III) hydroxide co-precipitate at significantly lower total Zn concentrations in alumina powders¹⁹, or at low-surface area of gibbsite.²⁰ Recently, Collins et al.²¹ observed that the trace metal removal (e.g. Zn) in modified BR (pH 7.5) is dominated by mineral surface precipitation and signaled hematite, gibbsite and hydrotalcite as the mineral phases involved in the process. Moreover, the dissolution in acid conditions of parts of the amorphous or semi-amorphous components of BR, particularly Al-amorphous, could allow the interaction of some of these components with the Zn²⁺ in solution (Zn >309 µmol/L) resulting in co-precipitation. The decrease of amorphous phases observed in this work from 55 to 35 % after acid neutralisation (XRD analysis not showed) shows that these dissolved Al-Fe compounds are available to react.

The As(V) isotherm shows that the adsorption of this metal did not reach a defined plateau, which could suggest that As(V) was still reacting with the surfaces of mineral phases that control the adsorption. When the As concentration was the highest (748 µmol/L) the percentage of As(V) adsorption was 99 % (for a S/L ratio of 50 g.L⁻¹). The value of adsorption capacity calculated in this study was 11.4 µmol.g⁻¹ for an initial concentration ranging between 135 to 748 µmol/L. The estimated sorption site density for untreated BR is 132 µmol.g⁻¹ and 175 µmol.g⁻¹ for seawater neutralised BR.²¹ In agreement with the Langmuir isotherm, this suggests that the BR could adsorb more arsenate, the adsorbent has not yet reached its maximum sorption density.

The Langmuir constants, maximum adsorption capacity (b) expressed as µmol g⁻¹ and adsorption intensity (K) expressed in L.µmol⁻¹, were calculated by linear regression and correlation with an r² always greater than 0.9. The constants obtained are shown in Table 2. Pb and As(V) have the highest adsorption capacity and intensity adsorption values respectively of the three metals. The difference between these constant values and those reported in other works^{7,10,12,22} may be due to experimental conditions (pH, ratio S/L, concentration range) that differ from those used in this work.

Table 2: Calculated Langmuir constants b (adsorption capacity), K (intensity) for arsenate, lead and zinc adsorption by the neutralised bauxite residue

Element	Initial Conc. ($\mu\text{mol.L}^{-1}$)	pH	b ($\mu\text{mol.g}^{-1}$)	K ($\text{L.}\mu\text{mol}^{-1}$)	r^2
As	135-748	4.6	11.4	7.71	0.97
Pb	472-4480	4.5	59.3	0.06	0.99
Zn	15.4-309	4.4	1.97	0.19	0.97

In addition, the affinity of the reaction with the Langmuir model was determined using the parameter " R_L " which is defined as $R_L = 1/(1 + kC)$. This constant describes if the metal adsorption process by the BR was favorable or unfavorable to the Langmuir model, making possible to determine the affinity of the adsorbent to adsorption.^{10,12}

Depending on the value of R_L the affinity can be described as non-favorable ($R_L > 1$), favorable ($0 < R_L < 1$) or irreversible for a zero value of R_L .¹² R_L values calculated for As(V), Pb and Zn are respectively 0.0002, 0.004 and 0.02; based on these values, Pb and Zn exhibit similar behavior, indicating favorable affinity towards adsorption. The R_L value of As(V) was close to 0 ($R_L = 0.0002$), this is clear indication of the tendency of As(V) towards an irreversible adsorption process at low pH (around 4.5).

Trace metal speciation

The distribution of As(V) and Zn among different adsorbent phases, was reported as a percentage of metal extracted. The results (Figure 2) show that the overall trend of the distribution is very similar before and after adsorption. Most of the metals (> 90 %) were associated with the less mobile fractions such as Fe and Al hydroxides (step 5 and 6). Zn is also associated (7.4 % before sorption and 10.9 % after sorption) with the more leachable fractions, considered the potentially mobile fraction (steps 1 to 3).

It is important to note the high percentage of Zn (27.1 %) associated to the amorphous iron oxide fraction after adsorption (Figure 2A). The higher specific surface areas and porosity structure of amorphous or poorly crystallised phases, compared to crystallised phases, can explain this fact.²³ This high concentration of Zn released at this step, could be also caused by the dissolution of new poorly ordered Zn precipitates, which would be consistent with Batch tests results. Arsenate was also associated to the amorphous phase but in a lesser extent (6.7 %).

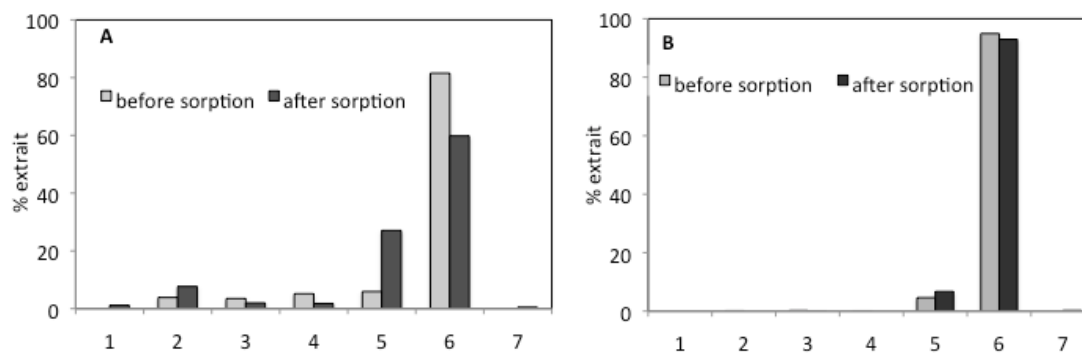


Figure 2: Distribution of zinc (A) and arsenate (B) on neutralised bauxite residue samples before and after adsorption experiences. Geochemical phases: water-soluble (step 1) exchangeable (Step 2); acid-soluble (Step 3); bound to manganese oxides (Step 4); bound to iron amorphous oxides (Step 5); bound to crystallised oxides (Step 6); bound to organic matter (Step 7)

Conclusions

The solid acid neutralised fraction of BR was studied to find out its potential as a sorbent of three trace metals typically found in acid mine drainages. The results of this study show that the adsorption is the main retention mechanism of As(V), Pb and Zn by the BR. The co-precipitation mechanism should not be neglected, especially for Zn. The sequential extraction experiments showed that the Fe and Al hydroxides, are the phases involved in the sorption (adsorption + co-precipitation) process on BR. The metals studied are mainly associated to the less reactive phases, suggesting that the trace metals would not readily release under acidic conditions. Thus, the Venezuelan bauxite residue could be a useful remediation agent for the treatment of acid mine drainage polluted by these metals, especially for As(V) contamination.

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Recovery of Fe, Al, Ti

