

Waste bauxite residue valorization as trace metal sorbent: application to acid mine
drainage remediation

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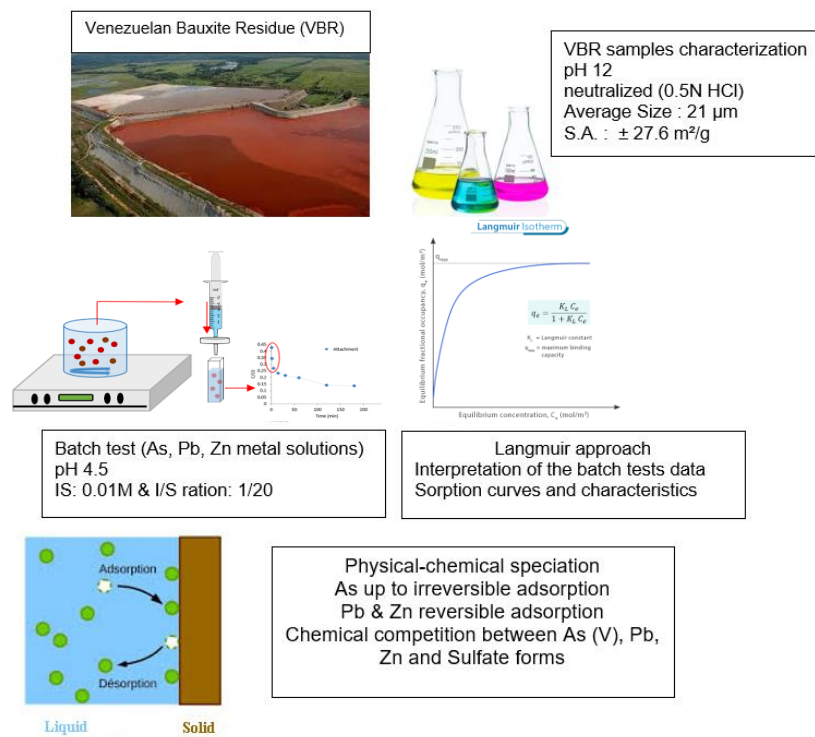
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Abstract.. With more than two millions of tons of alumina per year, Venezuela is an important producer. As observed the mining extraction activity generates a large number of by-products poorly valorized for many reasons (economic, technical, environmental standard and regulation) Venezuela production generates wastes (more than 15 million of m³) called red muds, which are dumped in old lagoons, near the Orinoco river or stored. This sludge has a high alkalinity (pH between 10 and 13) and a chemical composition containing some heavy metals (40 ppm Cr, 107 ppm La, 178 ppm Ce) that means it is considered environmentally problematic waste. However, their mineralogical, textural and structural characteristics make them adsorption materials. So, the aim of the study presented here was to investigate the sorption properties of these residues in the case of treatment of water from acid mine drainage. In fact, with an important reactive surface, their capacities to trap by adsorption trace elements such as cadmium, lead or zinc has been studied. Batch sorption tests revealed significant

retention of contaminants such as Pb, Zn and As. These retention processes were interpreted using the Langmuir isotherm model. The promising first results indicate that the red mud named Venezuelan Bauxite Residue (VBR), reveal a great potential as a sorbant of inorganic pollutants. The sorption is chemically dependent and efficient for certain pH and IS range. In addition, the material showed a strong affinity for the adsorption of arsenate (As^{5+}). This was observed during the post adsorption chemical speciation experiments, through the very high affinity of this element for the least mobile fractions, including oxyhydroxides mobile fractions, including Fe oxyhydroxides (amorphous). Nevertheless, these mining by-products could be considered as valuable absorbent materials. Despite this promising results, further studies are required to evaluate their potential in different conditions (dynamic tests, pH, IS, inorganic and organic contaminants, concentration and time effect).

Keyword : red mud - sorption - heavy metals - acid mine drainage – physical speciation – reactivity – Langmuir- Venezuelan Bauxite Residue (VBR)

Graphical Abstract



Our approach consisted in studying the capacity of Venezuelan bauxite residues (VBR) stored by lagooning as a means of treating water from acid mine drainage.

Batch sorption tests were carried out on model waters with different concentrations of As, Pb and Zn. Langmuir-type sorption isotherms were applied to determine the physical and chemical speciation mechanisms of these industrial by-products.

Introduction

The chemical process used for alumina production from bauxite ores called Bayer produced by-product name Red mud or Bauxite residue (BR). In fact, it is estimated that the production of one ton of alumina generates between 0.3 and 2.5 tons of bauxite residue [1-2]. This industrial by-product has physical and chemical properties induced by the initial bauxite and the process itself. BR exhibits a high alkalinity (pH between 10 and 13) and a particle size distribution from 2 to 100 μm . Their structure is mainly crystalline (70% w/w) and an amorphous phase (30% w/w). The mineralogy [3-4] is composed of gibbsite $[\text{Al}(\text{OH})_3]$, boehmite ($\gamma\text{-AlOOH}$), hematite (Fe_2O_3), goethite ($\alpha\text{-FeOOH}$), magnetite (Fe_3O_4), calcite (CaCO_3), quartz (SiO_2), rutile (TiO_2) and anatase (TiO_2). Secondary products can also form, particularly during the desilication stage (DSP), aluminosilicates type of calcium or sodium such as sodalite $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}]\cdot 2\text{NaOH}$, Na_2SO_4 and cancrinite $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}]\cdot 2[\text{CaCO}_3]$.

Storage of this by-product was found to be a major environmental problem mainly because of the caustic nature of the material and quantities generated, between 0.7 and 2 tons of bauxite residue per ton of alumina product. The management of bauxite residue at a global scale is to valorize them to reach zero waste production or classification. A means for allowing a reduction of this environmental problem could be in the conversion as raw material for various applications in engineering, chemistry, metallurgy, environmental domain. Such strategy makes them to be considered as valuable material. The physicochemical characteristics of bauxite residue (BR) offered a significant reactive surface allowing the adsorption of trace elements such as cadmium, lead, zinc, arsenic, among others [5-7].

The BR has indeed worldwide researches. Most of these studies have focused on the adsorption capacity of contaminant metals, to assess the potential use of this industrial by-product for the

remediation of contaminated soil [8-9] and water [10-12]. The study of Santona et al. [13] is focused on the adsorption of cadmium, lead and zinc by the BR. It shows that this material is an effective adsorbent for heavy metals removal in solutions. Indeed, the sludge seems to promote the reduction of the solubility and bioavailability of the metal in soil contaminated by Trace Metal (Cd, Pb & Zn). Several authors [10,12,13] also studied, the use of BR as an adsorbent of arsenic and some so-called heavy metals (Cd, Cu, Pb) in aqueous solutions. They also reported that this material is a very effective sorbent for the remediation of water polluted by these elements. The use of BR in the field remediation, would constitute a great contribution to this theme, it also would solve this material management issues as well as its environmental impact. Moreover, its application as a useful by-product would offer new economic and / or industrial value.

In the case of acid mine drainage (AMD), and soils with acidity problems (eg. Acid sulphate soils), the use of untreated bauxite residue ($\text{pH} > 10$) is one of the solutions envisaged for neutralizing these solutions and acidic soils. The presence, in excess, in the BR of hydroxides (OH^-), carbonates (CO_3^{2-}) and aluminates ($\text{Al}(\text{OH})_4^-$) can reduce acidity by a buffer effect. In addition, the BR contains too Fe and Al oxyhydroxides which can play a role of the substrate able to trap, by a sorption mechanism metal, ion contaminants present in the AMD or in the soil, [15-17].

Venezuela is, with Brazil and Suriname, one of the major south American alumina producers. Venezuela alumina is produced by the refinery CVG Bauxilum, south-east of Venezuela, on the banks of the Orinoco River. In this plant, the ratio BR/per ton of Al produced is around 0.6 [18]. The tailings are deposited in former lagoons specially designed for this purpose (lagooning method). Such method is problematic due the high concentration of many contaminants like heavy metals.

This study is focus on the sorbent properties of the solid Venezuelan bauxite residue in acid conditions close to those of acid mine drainage. This choice was considered due to the existing mining context in the state of Bolivar, a region where the Venezuelan BR storage lagoons are located. Acid mine drainage from mining, are characterized by pH values generally between 1 and 4, and an enrichment of mine water with heavy metals such as zinc and arsenic but also anions, such as sulfates or arsenate. In this study, tests in batch for the study of the adsorption and desorption, as well as sequential chemical adsorption after extraction, have been made. All testing has been performed on the portion of the VBR neutralized with acid (pH 4.5-5). The idea was to recreate, in laboratory scale, the contact conditions between VBR and acid mine drainage, to study the sorption properties of the material under this scenario.

Materials and Methods

Venezuelan bauxite residue

Venezuelan bauxite residue (VBR) slurry comes from CVG Bauxilum alumina refinery, located in Guayana city (South-East of Venezuela). The slurry was dried at 40°C. A fraction of the material (pH 12) was neutralized with 0.5N HCl in a 1:20 [13] to carry out various experiments in batch realize later controlled pH.

Triplicate pH measurements have been performed on a diluted (1:5 in volume) suspension of VBR using deionized water after stirring for 10min [19]. The mineralogical phases were identified by X-ray diffraction (Bruker-AXS spectrometer model D4) equipped with a copper anticathode ($\lambda = 1,541\text{\AA}$) and a LynxEye fast detector. The elementary composition of major elements was determined by X-ray fluorescence (Panalytical Axios wavelength dispersive XRF

Advance) after the fusion of the BR powders by the fusion with lithium metaborate and lithium tetraborate plus bromide as a releasing agent.

The size distribution was performed by the Mastersizer 2000 particle size analyzer version 5.60 (Malvern Instruments Ltd.). After wet sieving (40 μm cut-off fraction), we determined the average particle size distribution of treated VBR (21 μm average size). The surface area, performed using a Quantachrome Nova 2220, was found at $27.6 \pm 0.2 \text{ m}^2.\text{g}^{-1}$. The data analysis is done by using BET model [20].

Batch experiments

Static tests are frequently used to determine sorption properties and the kinetic adsorption trend or characteristics on different materials, including BR [5, 10-12].

These types of tests are characterized by introduction under controlled conditions (physico-chemical parameters such as pH, temperature, etc.), in closed reactors, agitated, and in the absence of flow.

Adsorption of metal / metalloid (As, Pb and Zn) on the Venezuelan Bauxite Residue (VBR) by batch tests in static conditions has been performed. The idea was to study the adsorption process in these three elements (As, Pb and Zn) individually then through the competitive effect due to the presence of another element in the system [10]. To do so, we followed cation-cation (Zn-Pb) or cation-anion pairs (Zn-As, Zn-SO₄) to highlight this potential competition. The sulfate ion was added in this experiment to be among the most present species in the AMD.

The concentration ranges for each component were chosen taking into account the reference values in the literature (Table 2). The concentration ranges for competition assays between elements are shown in Table 3.

A pH of 4.5 ± 0.1 and an ionic strength (IS) of 0.01 M were considered and based on prior results obtained. The L/S ratio 1:20 (50g. L⁻¹) was used i.e. 1g VBR in 20mL of solution (15mL KNO₃ solution and 5 mL of metal solution). Metal solutions were prepared using salts of Na₂HAsO₄.7H₂O for arsenic; PbNO₃ for Pb and Zn (NO₃).6H₂O for Zn.

The experimental approach used for each of the elements studied can be divided into two stages:

pre-equilibrium solution-phase adsorbent: the mass of solid weighed, 1g of dry VBR (neutralized sieved <40 µm) is filled, with 15mL of 0.01M KNO₃ electrolyte solution, in chemically inert polyethylene bottles. The potassium nitrate solution was chosen as the ideal electrolytic solution in these tests, allowing to fix the ionic strength [24]. The pH is monitored at ± 4.5 by few drops of HNO₃ or 0.1M KOH solution. The temperature was set at 22 ± 1 ° C during continuous flasks stirring during 24 hours [13].

Adsorption step: The metal solutions (increasing concentration of As, Pb or Zn) consisted of the addition of ± 5 mL to previous vials. The pH and temperature are monitored respectively at ± 4.5 and ± 22 ° C; while the final volume reach 20 mL. Each vial is continuously agitated during 24 hours.

Finally, the solutions were filtered to 0.45 microns (Millipore brand micro-filters); then decanted, acidified before their storage at 5 ° C, until analysis. The dosage of the elements was performed at BIOEMCO laboratory, University Pierre and Marie Curie, Paris. The cation forms of lead (Pb) and zinc (Zn) were quantified using ICP-OES (Jobin-Yvon JY2000). Ionic form of Arsenic (As) was analyzed by ion chromatography (Dionex DX500 equipped with conductimetric detection cell), then quantified by atomic absorption (Unicam, Thermo 989QZ). As calibration during Absorption Atomic furnace, is achieved using certified standard (TMDA64-2)

Speciation after sorption

The physical speciation [25,26] after sorption allows to know the combination of sorbed element according to the different fractions in term of the size of the reactive phase of the VBR, which provides information on setting mechanisms occurring. Physical speciation depends of the reactional site(location and size) of the different minerals but also of the size of the crystalline phases. The sequential extraction tests followed the protocol [27] and based on the principles of conventional protocols [28]. Each experiment was performed in triplicate on 2g of solid VBR. The liquid/solid ratio used for all steps was 1/10. This ratio was indeed mentioned as optimal during speciation studies on BR samples from Ajka, Hungary [29]. Maximum sorption points were identified during adsorption tests for each sample. The dosage of the elements was done using the same protocols as those used for the tests in batch. To ensure the quality of the results, three replicas were systematically performed for each test. In addition, a blank containing the electrolyte solution over the solid KNO_3 was prepared, and also a few control solutions containing only the solutions (electroplating and metal).

Results

Material characterization

The XRD analysis (figure 1) revealed the presence of the four major crystallized phases which are Gibbsite, Hematite, Goethite, Quartz, and the presence of amorphous phases (approximately 35%). The results of chemical composition (Table 1) show the following order of abundance

of major elements in the VRB treated: Fe> Al> Si> Na> Ti> Ca elements Ca and Na are virtually undetectable.

Pb, As and Zn sorption depending on the concentration: Langmuir isotherms

The adsorption batch tests were performed by varying the initial concentration of the metal solution in contact with a fixed mass of VBR neutralized under controlled conditions of pH, IS and temperature.

Adsorption isotherms plots were calculated using equations 1, 2 and 3 and showing the variation in function of C_f (q corresponds to the quantity of the metal adsorbed by the VBR, expressed in mol. g⁻¹ and C_f the metal concentration in solution, at the equilibrium, in mol L⁻¹. These isotherms are shown in Fig. 2.

$$q = \frac{k \cdot C_f \cdot b}{(1 + k \cdot C_f)}$$

or in the linear expression:

$$\frac{1}{q} = \frac{1}{C_f \cdot k \cdot b} + \frac{1}{b}$$

Where q is the amount adsorbed at equilibrium

C_f is the concentration of the adsorbate at equilibrium (or final concentration in solution)

k is the constant of adsorption energy and

b is the maximum adsorption capacity [29].

Equation 3 : $q = \frac{(C_i - C_f) \cdot V}{m}$

Where q is the amount of lead adsorbed (mol L^{-1}),

C_i and C_f are the initial and final concentrations,

V the volume of solution used

m is the mass of the adsorbent [7].

Positive adsorption isotherms were obtained with concave curves with respect to the concentration axis; And a plateau well marked in the case of the distribution of Pb. A feature common to the three components is a good correlation with the Langmuir model, at low initial concentrations. This fact is evidenced by the rapid and strong adsorption of the metal that can be visually distinguished by the stack points to the top of each isotherm. The rights of lineal regression also show the same trend. However, for higher concentrations, some deviations with the ideal curve are observed.

These facts lead us to believe that there are indeed two different distributions. A first distribution which corresponds to the Langmuir model very well and would be characterized by a decrease of the measured slope as the solution concentration increases and the available adsorption sites are exhausted. And a second distribution to higher concentrations (more points spaced with respect to the ideal curve) which no longer corresponds to Langmuir. The presence of multiple simultaneous adsorption sites could explain this fact. The mineralogical heterogeneity of BR (particularly adsorbent phases such as hematite, gibbsite, goethite, amorphous iron, etc.) would be consistent with this argument.

The affinity term of the reaction using a Langmuir model can be determined by the parameter " r ". This dimensionless constant (eq. 3) allows to describe, using isotherms shape, if the metal

adsorption process by the BR followed or not the Langmuir model approach. This makes it possible to determine the affinity of the adsorbent for a specific adsorption mechanism. [10,12].

$$r = \frac{1}{1 + k \cdot C_0}$$

with C_0 = Initial concentration (μmol^{-1}) and k = sorption energy ($\text{L} \cdot \mu\text{mol}^{-1}$)

Depending on the value of r , the affinity is considered non-favorable ($r > 1$), favorable ($0 < r < 1$) or irreversible for a zero value of r [12]. The values of r have been calculated for As, Pb and Zn. With values respectively of 0.0009; 0.03 and 0.08, Pb and Zn exhibit similar behavior (a favorable affinity toward solid adsorption). In the case of As, the r value obtained, closest to zero, will be indicative of the tendency of irreversible adsorption process for this element. High affinity can thus mean that our material has a strong affinity to adsorption of these metals studied, and more particularly to arsenic, low pH (around 4.5).

The adsorption capacity of the VBR would be greater for the material in the neutralized form (acid), because of the increase of the specific surface area (from 23.1 to 27.6 $\text{m}^2 \cdot \text{g}^{-1}$) upon treatment with the acid solution (HCl).

In addition, Langmuir constants, maximum adsorption capacity (b) expressed as $\mu\text{mol g}^{-1}$ and adsorption energy (K) expressed in $\text{L} \cdot \mu\text{mol}^{-1}$, were determined by linear regression. A correlation value always greater than 0.9 is considered. The various constants (a) are given in Table 3.

Chemical speciation after adsorption

As arsenic and zinc are already naturally present in VBR, it was decided to compare their distributions in the phases involved in speciation before and after adsorption. The results (Fig. 3) show similar distributions both before and after adsorption.

Arsenic and Zinc already naturally present in the VBR, it was decided to compare the statements relating to speciation before and after adsorption. The results (Fig. 3) show that the overall trend of the distribution is very similar before and after adsorption. The vast majority of these elements is indeed associated with less mobile fractions such as iron oxyhydroxides. In the case of Zn, this element is also associated, to a lesser extent, considered the most mobile fractions (exchangeable).

The most interesting aspect of these results is that after adsorption the amorphous iron oxides show a significant higher percentage of Zn and less fixing arsenate thereon, in accordance with higher specific surface areas as compared to crystalline oxides and other fractions of the solid [31]. This allows to highlight that the type of surface adsorption phenomena is responsible for fixing these elements on the BR [31-32].

In addition, the similarity of speciation before and after adsorption, shows that the elements "naturally" present in the material and extracted by the sequential extraction method, rather correspond to fractions sorbed in the solid.

Effect of the presence of various ions

A special attention concerns the remediation of acid mine drainage mainly due to the presence of several cations and anions, which can greatly change the BR sorption properties by a potential competition between the different chemical species of the leachate and the BR.

The objective of this work was to follow cation-cation or cation-anion pairs in order to highlight this potential competition. The choice of the principal cation has focused on zinc in that this cation is, among our three elements, the most present study in drainage waters [33]. This element also has an interesting mobility in the case of our study. Interactions with other three elements were tested: lead, arsenic and sulfates. This choice has the advantage of following a competition both between two cations but also between a cation and an anion. Furthermore, sulfates are among the most present species in an AMD. The selected protocol is similar to that previously developed in the case of tests in single batch. The concentrations used are shown in Table 4.

Results show an effect of competition between these elements. Indeed, the isotherms calculated for each of the pairs (Fig. 4) show a decrease of sorption compared to the single zinc element. We thus observe the following distribution Zn; Zn-SO₄; Zn-As and Zn-Pb with further lower slopes. This would suggest that the intensity of adsorption is the lowest in the case of the couple Zn-Pb, reflecting a competition effect between these two cations.

Analysis of Langmuir constants Q adsorption capacity and adsorption energy b (Table 4) corroborates this hypothesis. Thus, in the case of the simultaneous sorption for the couple Zn-Pb the maximum quantity sorbed zinc is 1.71 $\mu\text{mol g}^{-1}$, while it is 1.75 $\mu\text{mol g}^{-1}$ for Zn-As couple; 2.19 $\mu\text{mol g}^{-1}$ for Zn-SO₄; and 3.18 $\mu\text{mol g}^{-1}$ for the zinc alone. A competition effect occurs when sorption is initiated in the presence of another ions. This competition increases further in the presence of a cation with respect to an anion [34]. An interesting aspect of these results is that high concentrations initially brought into play for lead and sulphate (100 mg L⁻¹), do not cause saturation of sorption sites on the surface of BR in spite of extremely low pH.

Conclusion

The example of an acid mine drainage has been selected as part of this work in order to approach the environmental context related to mining activities in Venezuela to monitor their impact on the soil and water environment. A pH between 4-5 simulating mine water in the presence of Venezuelan Red Bauxite (VRB), adsorption appears to be very effective for the main components simulating the ideal composition of these waters (As, Pb, Zn, SO_4^{2-}). During the retention process of elements like As (V) Pb and Zn, two different types of distributions or fractionation of these elements are concerned [35]. At low concentrations, the Langmuir model perfectly fits with the process involved. Nevertheless, at high concentrations, there is an offset to this model. One explanation could be due to the fact that VRB is a polycrystalline material very heterogeneous in term of the chemical composition, physical state between crystalline and amorphous phases size of the mineralogical phases, specific surface, etc.) and thus multiple adsorption sites with a very high reactivity can existed. Here, the Langmuir model should only be used as an empirical approach to the study of the adsorption phenomenon in the Venezuelan alumina material. Our experimental tests (in batch conditions) on the reversibility and the efficiency of adsorption show firstly that physical adsorption is the main metal attachment mechanism on VBR. And secondly that the chemisorption (inner sphere) would appear as a possible type of connection of these surface phenomena. From these data, our opinion about the potential of VBR for the remediation of soils and waters contaminated by trace metals such As, Pb and Zn could be developed and studied. In general, such studies like this one are very promising but reveal also many limitations. We are concerned by the scale of the study which has been conducted at a laboratory scale, for limited volume and quantities and specific conditions. Before application for soil and water remediation sites only holistic approaches has to be achieved to avoid not expected secondary effects.

Validation of the concept of using these fine residues as a sorbent for contaminated environments will require a second stage in which the behavior is monitored dynamically rather

than statically. Column percolation tests will be used to monitor the reaction and kinetic processes that may occur during fluid transfer. The results of these chemistry-transport reactions, combined with those from batch experiments, can then be fed into a numerical model with a view to modelling the behavior of these materials over the medium and long term.

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Table 1 Chemical Composition (determined by fusion XRF) of acid neutralised bauxite residue from Venezuela

Majors Elements	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	TiO ₂	CaO	K ₂ O	Na ₂ O	MgO	P ₂ O ₅	MnO	V ₂ O ₅	Cr ₂ O ₃	LOI
(% w/w)	42.73	27.1	13.78	3.81	0.12	0.04	0.01	<0.01	0.17	0.08	0.02	<0.01	11.03

Table 2 Typical values of AMDs (pH $\pm$ 3, Eh> 1mV) for As, Zn and Pb. Intervals presented are used for this work.

Element	Reference concentration values ($\mu\text{mol.L}^{-1}$)	Range value for the experiments ($\mu\text{mol.L}^{-1}$)
As	0.05 to 220 [21] 2.7 (pH 3.6 Eh 620mV) [21] 0.67 to 27 [22]	135 to 748
Zn	180 to 700 [21] 30 to 3000 [23]	15.4 to 309
Pb	96 [21] 1400 [21]	472 to 4480

Table 3 Langmuir parameters: b (adsorption capacity) and K (intensity) relating to arsenate, lead and zinc adsorption by the neutralized 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	3.18	0.02	0.97

Table 4. Results of Langmuir parameters for competition test Zn-Pb; Zn-As and Zn-SO₄

couples.

Ci (mg.L ⁻¹)	Sorbed (μmol.g ⁻¹)	b (μmol.g ⁻¹)	k (L.μmol ⁻¹)
Zn-Pb			
0.5-100	0.07	1.71	0.08
2-100	0.3		
10-100	1.09		
Zn-As			
0.5-100	0.07	1.75	0.06
2-100	0.29		
10-100	1.16		
Zn-SO ₄			
0.5-100	0.07	2.19	0.06
2-100	0.28		
10-100	1.14		

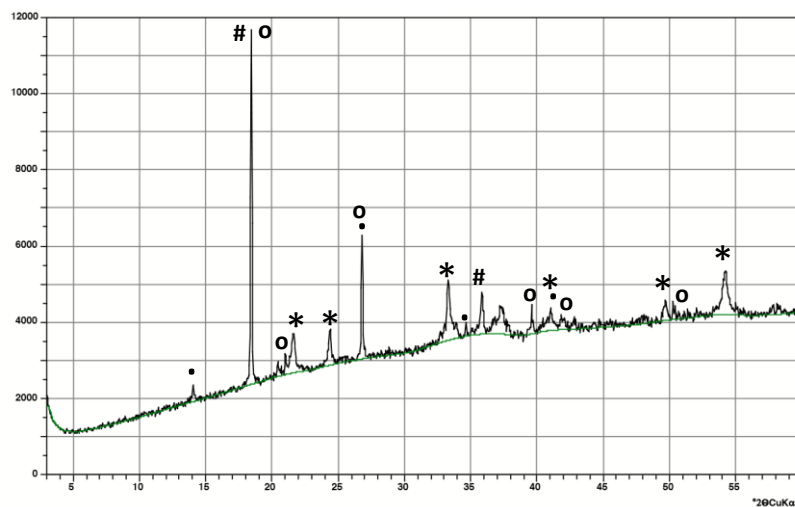


Figure 1. XRD pattern of the as received VBR (*: goethite; #: gibbsite; •: quartz; o: hematite)

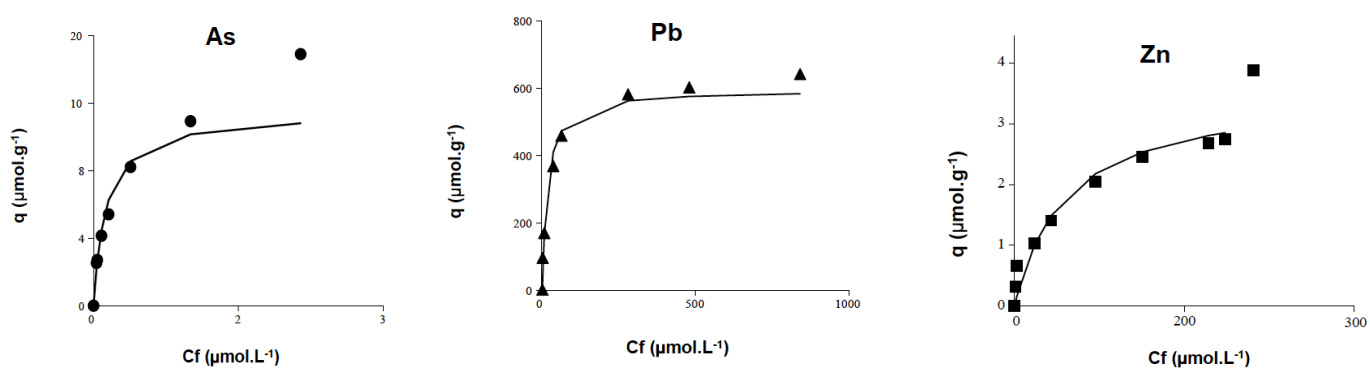


Figure 2. Langmuir adsorption plots for arsenate, lead and zinc. Conditions: bauxite residue dosage 50g.L⁻¹, Ionic strength = KNO₃ 0.01M, pH 4.5± 0.1 and temperature of 22± 1°C

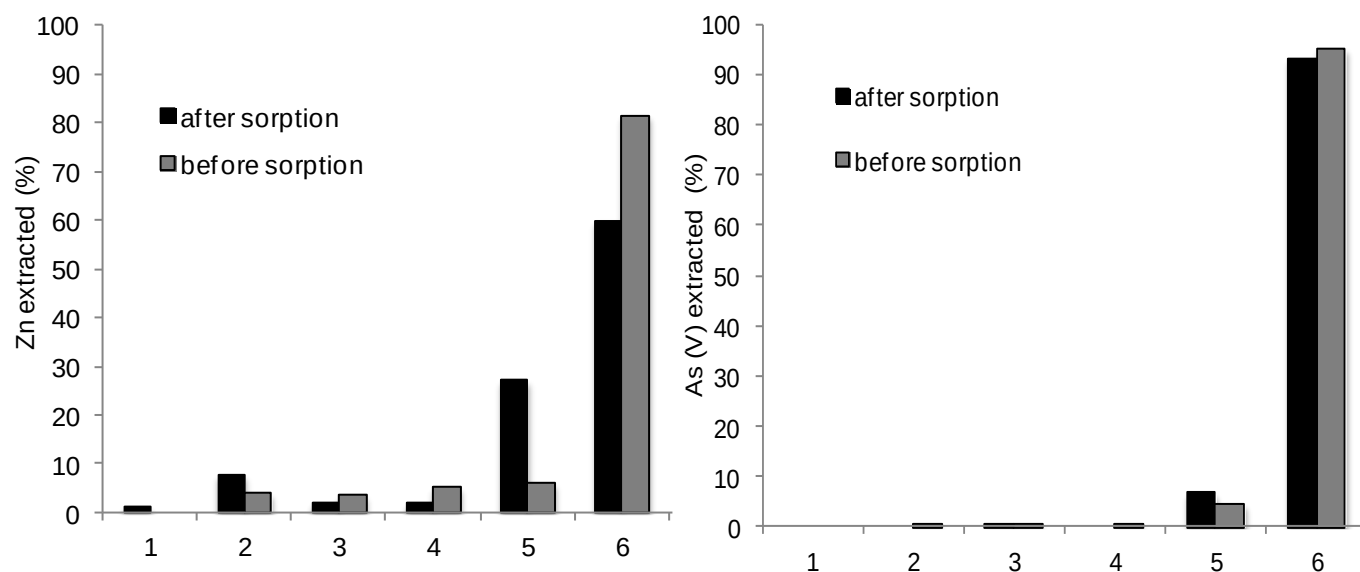


Figure 3. Zinc arsenic (V) distribution on neutralised bauxite residue samples before and after adsorption experiences. Extracted with nitrate magnesium $\text{Mg}(\text{NO}_3)_2$ (Step 1); sodium acetate NaOAc (Step 2); hydroxylammonium chloride NH_2OHCl (Step 3); ammonium oxalate-oxalate acid $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4$ (Step 4); $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4\text{-C}_6\text{H}_8\text{O}_6$ (Step 5); nitric acid-ammonium acetate $\text{HNO}_3\text{-NH}_4\text{OAc}$ (Step 6)

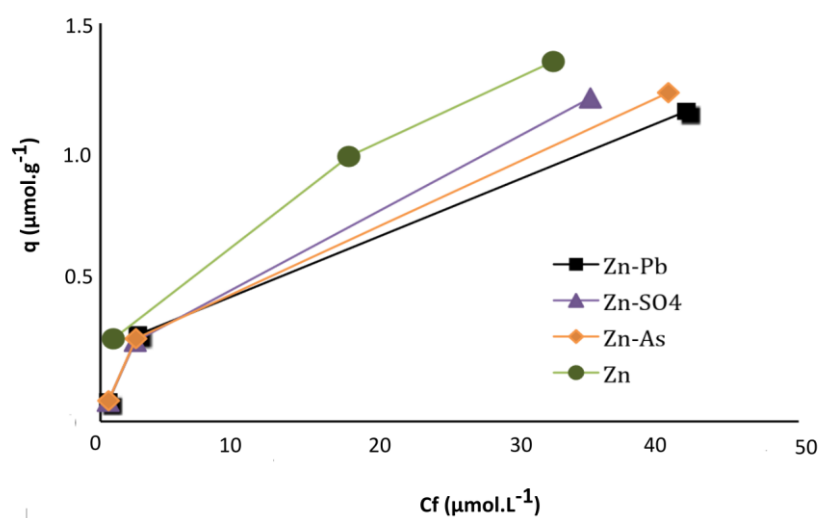


Figure 4. Effects of the presence of ions on zinc adsorption using neutralised bauxite residue at room temperature (Ionic strength= KNO_3 0.01M, pH 4.4 ± 0.1 ; Zn-Ion concentrations (mg.L^{-1})=0.5-100 ; 2-100 ; 10-100)