



Adsorption of inorganic pollutants on bauxite residues: An example of methodology to simulate adsorption in complex solids mixtures



Mehwish Taneez ^a, Charlotte Hurel ^b, Nicolas Marmier ^a, Grégory Lefèvre ^{c,*}

^a Université Nice Sophia Antipolis, CNRS, FRE 3729 ECOMERS, Parc Valrose 28 Avenue, 06108 Nice, France

^b Université Nice Sophia Antipolis, CNRS, LPMC, UMR 7336, Parc Valrose 28 Avenue, 06108 Nice, France

^c PSL Research University, Chimie ParisTech — CNRS, Institut de Recherche de Chimie Paris, 75005, Paris, France

ARTICLE INFO

Article history:

Received 23 May 2016

Received in revised form

9 November 2016

Accepted 9 January 2017

Available online 11 January 2017

Editorial handling by Prof. M. Kersten.

Keywords:

Surface complexation model

Red mud

Iron oxide

Aluminum oxide

ABSTRACT

Bauxite residue rich in iron and aluminum oxide is good adsorbing material for inorganic pollutants. Composition and physic-chemical parameters of 2 bauxite residues (Bauxaline[®] and Bauxsol) were determined. Adsorption of arsenic and cadmium from aqueous solutions on Bauxaline[®] and Bauxsol was studied as a function of solid to liquid ratios, pH and initial adsorbate concentrations. Both solids showed optimum removal of As and Cd at near to neutral pH. Adsorption data were modeled using 2-pK/Double Layer Model. In the model, the complex composition of bauxite residues was simplified by considering that Bauxaline[®] and Bauxsol were made of a binary mixture of iron and aluminum oxides. Considering acid-base and surface complexation (for As and Cd) equilibria and constants from the literature, the model proposed in this work has shown to be predictive. Adsorption mechanism was found consistent with the formation of a surface complex along with surface precipitation for cadmium.

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1. Introduction

Arsenic (As) and Cadmium (Cd) are ones of the priority toxic pollutants present in the environment. Elevated concentrations of both trace elements can be detrimental to living systems. The main sources of arsenic contamination are geological, industrial and agricultural use of arsenic pesticides (Müller et al., 2010; Silva et al., 2010). Significant health problems are reported due to As contamination in the environment. Inorganic forms of arsenic such as As(III) (arsenite) and As(V) (arsenate) are present in water supplies. Under aerobic environment, arsenate is more stable and dominant over a wide pH range and occurs as oxyanions of arsenic acid (H_2AsO_4^- and HAsO_4^{2-}). US-EPA set maximum concentration level of 10 ppb (0.01 mg/L) for As in drinking water. However, many countries including China and Bangladesh have retained the old WHO guideline of 50 ppb as their standard (EPA, 2001). Cadmium is a highly toxic element that enters into environment mainly through anthropogenic industrial effluents (Luo et al., 2011). The regular exposure of cadmium causes serious human health problems such as lung cancer and kidney failure. US EPA set permissible

limit of 5.0 ppb (0.005 mg/L) for Cd in drinking water due to its carcinogenic effects (ATSDR, 1997; Järup, 2002). Thus, it is imperative to identify remediation technologies for contaminated environments. Commonly employed methods to remove trace elements from water are chemical precipitation, adsorption, ion-exchange, reverse osmosis, electrochemical reduction, etc. Adsorption is being the most commonly used method for the treatment of contaminated media (Papandreou et al., 2007). Industrial by-products received considerable attention as alternative adsorbents to activated carbon due to their low cost and mineralogical composition. Bauxite residue (red mud) is a waste generated by aluminum industries in huge quantities (1 ton of alumina production generates 1–1.5 tons of red mud). Raw bauxite residue is highly alkaline in nature (pH 10–13) due to Bayer process used for aluminum extraction. It is mainly composed of Fe, Al, and Ti oxides. Neutralization of bauxite residue is required for safe disposal and utilization purposes. Common neutralization methods involve addition of acids, hard groundwaters, magnesium and calcium chloride salts, saline brines, or seawater (Genç et al., 2003). Bauxite residue is a promising adsorbent for the removal of trace elements from water, and/or wastewater. It is often utilized as amendment in contaminated soils to immobilize trace elements (Lombi et al., 2002; Santona et al., 2006; Wang et al., 2008). Modelling the adsorption mechanisms has been made in a few works. The

* Corresponding author.

E-mail address: gregory.lefevre@chimie-paristech.fr (G. Lefèvre).

reactivity of the surface has been modeled assuming a single homogeneous surface for the sake of simplicity (Genç-Fuhrman et al., 2004; Güçlü and Apak, 2000, 2003) with one amphoteric site $>S-OH$ following a 2-pK approach. A non-electrostatic model has been chosen to fit heavy metal complex-bound EDTA adsorption on red mud (Güçlü and Apak, 2000, 2003). On Bauxsol, a Diffuse Layer Model has been used to fit As(V) adsorption (Genç-Fuhrman et al., 2004). Even though the complexity of the mixture composing the bauxite residues makes difficult to characterize and describe separately the reactivity of each surface reactive groups, the simplicity of the published approach can be questionable. Thus, four adsorption constants for As(V) have been used in the model (Genç-Fuhrman et al., 2004), correlated to four different surface complexes ($>SH_2AsO_4$, $>SHAsO_4^-$, $>SAsO_4^{2-}$, $>SOHAsO_4^{3-}$) to fit the experimental data. Another interpretation could be to consider a smaller number of arsenate geometries but several different surface sites, connected to different mineral surfaces, as usually assumed in the modelling of mixtures (Lützenkirchen and Behra, 1997). Moreover, the predictive capacity of these works (Genç-Fuhrman et al., 2004; Güçlü and Apak, 2000, 2003) has not been shown, since their objective was to fit experimental sorption data. However, building surface complexation models has two purposes: (1) a speciation purpose where possible structures of surface complexes were tested, and (2) an application purpose where surface complexation constant can be used in a reactive transport model.

In the present work, two formulations of bauxite residue (Bauxaline[®] and Bauxsol) were investigated for their sorption potential of As(V) and Cd(II) and for their possible use as immobilizing agent for inorganic pollutants in sediments. Adsorption of these inorganic pollutants on bauxite residues was modeled using a surface complexation approach based on the assumption that the most reactive phases were responsible of As and Cd surface retention. Hence, data from the literature were introduced in the model for each individual phase. The final objective of this work is to evaluate the predictive capacities of such model.

2. Experimental

2.1. Bauxaline[®] and Bauxsol

Bauxaline[®] and Bauxsol were provided by ALTEO Gardanne plant, (France) that supplies specialty alumina. Bauxaline[®] is a press-filtered bauxite residue; Bauxsol is a press-filtered bauxite residue previously washed with brine to lower alkalinity. The pH and electrical conductivity (EC) values of Bauxaline[®] and Bauxsol were measured in suspension of (100 g/L) using pH (Consort bvba, Belgium) and electrical conductivity meter (Crison, Barcelona, Spain) respectively. ISO standard BET method was used to determine the specific surface area (ISO, 2010). Hexamminecobalttrichloride solution was used to determine the cation exchange capacity (CEC) of solids (ISO, 2007). Properties of adsorbent materials are presented in Table 1.

Table 1
Properties of adsorbents.

	Bauxaline [®]	Bauxsol
Suspension pH ^a	10.60	9.40
Electrical conductivity (mS/cm) ^a	0.915	1.187
Cation exchange capacity (meq/100 g) ^a	6.18	4.15
Specific surface area (m ² /g) ^a	23.06	
Isoelectric point ^b	6.9	6.9

^a (Taneez et al., 2015).

^b This study.

2.2. Sorption experiments

All the chemicals used in adsorption experiments were of analytical grade. Adsorption experiments were carried out according to the US EPA protocol based on batch type adsorption tests at room temperature (EPA, 1991). Influence of liquid to solid ratios, pH, and initial adsorbate concentrations was studied. Stock solutions of As(V) and Cd(II) (1 g/L) were separately prepared using AsHNa₂O₄·7H₂O (Fluka ≥ 98.5%), and Cd(NO₃)₂·4H₂O (Sigma-Aldrich, ≥ 99%) dissolved in Milli-Q pure water (Milli-Q Academic A10, France) and acidified with 1% HNO₃ (Fluka, ≥ 69.0%) for a better conservation. Adequate dilution factors were applied to these stock solutions for adsorption experiments. Adsorption experiments as a function of solid to liquid ratios were conducted in polypropylene tubes (50 ml) filled with 0.01 g to 0.2 g of Bauxaline[®] or Bauxsol in 40 ml of NaNO₃ (Acros Organics, ≥ 99%) (0.01 M) solution spiked with the adequate volume of Cd (II) or As (V) stock solutions previously prepared. The pH was kept constant (pH: 6.9–7.0 ± 0.1) by adding drops of 1M HNO₃ in each suspension. The adsorption as a function of pH (between pH 2 to 10) was studied using 0.05 g of solid mass in 40 ml of solution. The pH adjustments were made by adding drops of 1M HNO₃ or 1M NaOH solutions. Then, the suspensions were agitated on circular rotator at 50 rpm for 24 h, centrifuged at 5000 rpm for 10 min, and supernatants were separated using 0.45 μm cellulose acetate filters. Before measuring final concentrations of Cd (II) and As (V) on ICP-OES (Optima 7300, Perkin Elmer corporation, Massachusetts, USA), filtrate solutions were acidified (1%) with HNO₃.

2.3. Modelling procedure

The model used in this study is based on a 2-pK approach to represent the surface reactivity, and a Diffuse Layer Model (DLM) to describe the electrostatics. 2pK-DLM was amongst the simplest surface complexation models (SCM) and was extensively used in literature (Dzombak and Morel, 1990; Karamalidis and Dzombak, 2011). In this model, adsorption constant reactions between adsorbate (Cd²⁺ or AsO₄³⁻ here) and the hydroxyl surface groups. Such reactions are given below (Table 4). Likewise, acido-basicity of the surface results from the adsorption of proton and hydroxide ions on hydroxyl groups. In comparison with the isotherm modelling approach, this model assumes a Langmuir behavior for the adsorbed species (including protons and hydroxide ions). An exception to Langmuir isotherm is the surface precipitation which can be represented as a bulk precipitation reaction with a different equilibrium constant (approach developed in this article), or as the formation of a solid solution (Farley et al., 1985). The strength of 2-pK model is able to reproduce the amphoteric nature of the surface, and the effect of the pH on the sorbed amounts of species, whatever their charge. It can be associated with different models for electrostatics (including its absence in a “non-electrostatic” model) which describe the double layer structure with more or less details. A strength of the DLM is the absence of fitting parameters (as it is the case for capacitances values in Basic Stern Model or Triple Layer Model), but its weakness is that only inner sphere complexes (i.e. complexes where adsorbed species are directly bound to the surface) can be taken into account. Formation of outer-sphere surface complexes cannot be distinguished due to electrostatic attraction, and more complex models as Basic Stern Model are needed in this case.

The software ECOSAT 4.9 (Keizer and Van Riemsdijk, 2009) has been used to make the simulations, with the associated thermodynamic database for aqueous species and minerals.

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