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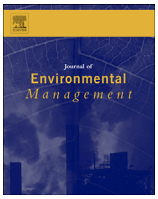

Research article

# Defluoridation of groundwater using aluminum-coated bauxite: Optimization of synthesis process conditions and equilibrium study

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ABSTRACT

There is no known effective treatment for fluoride-related health disorders, hence prevention through water defluoridation is necessary. This study explored the possibility of modifying the physico-chemical properties of bauxite, a locally available material in many countries including Ghana, by thermal treatment and an aluminum coating, for water defluoridation. The study mainly focused on investigating the effects of varying synthesis process conditions on the defluoridation efficiency of Granular Aluminum Coated Bauxite (GACB). GACB performed better than raw bauxite (RB) and was able to reduce fluoride concentration in groundwater from 5 ± 0.2 mg/L to ≤ 1.5 mg/L, World Health Organization (WHO) guideline. Based on nonlinear Chi-square ($\chi^2$) analysis, the best-fitting isotherm model for the fluoride-GACB system was in the order: Freundlich > Redlich-Perterson ≈ Langmuir > Temkin. The fluoride adsorption capacity of GACB ($q_{max} = 12.29$ mg/g) based on the Langmuir model was found to be either comparable or higher than the capacities of some reported fluoride adsorbents. Aluminum (Al) coating procedures optimized in this study could therefore be a useful approach for synthesizing an effective fluoride adsorbent using bauxite, a locally available material. Kinetic and isotherm analysis, thermodynamic calculations, as well as FTIR and Raman analysis suggested the mechanism of fluoride adsorption onto GACB was complex and involved both physical adsorption and chemisorption processes.

## 1. Introduction

Millions of people, particularly in developing countries including Ghana, rely on groundwater with excess fluoride (beyond 1.5 mg/L, World Health Organization (WHO) guideline) for drinking, and are hence exposed to many related health hazards, including fluorosis, changes of DNA structure and lowering of IQ of children (WHO, 2008; Chen et al., 2010; Salifu et al., 2013). Water defluoridation in such situations therefore become necessary, as a preventive measure (Sahli et al., 2007).

Among the available fluoride removal methods (Fawell et al., 2006; Sahli et al., 2007), the adsorption technique is generally considered one the viable options due to its many advantages, including the simplicity of design and relative ease of operation (Maliyekkai et al., 2006; Chen et al., 2010). Its appropriateness, however, largely depends on availability of a suitable adsorbent.

A large number of studied materials have exhibited certain degrees of fluoride adsorption potential. These include activated carbon, quartz, clay, fly ash, calcite; sodium exchanged montimorillonite-$Na^+$, bauxite, bone charcoal and activated alumina (Chaturvedi et al., 1990; Bhargava and Killedar, 1991; Fan et al., 2003; Ghorai and Pant, 2005; Ramdani et al., 2010; Sujana and Anand, 2011). The applicability of some, however, have limitations including lack of acceptability due to customs and beliefs, high cost and/or require pH adjustment to function effectively, which could be problematic. Moreover some studied materials are

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either of fine particles or powders, which makes separation of adsorbent from aqueous solutions difficult. Such adsorbents could also cause clogging and/or low hydraulic conductivities when applied in fixed-bed adsorption systems (Fan et al., 2003; Fawell et al., 2006; Han et al., 2009). Considerable attention therefore continues to be devoted to the search for alternative suitable adsorbents. Modifying the physico-chemical properties of locally available materials for water defluoridation is also of interest, as that could have a potential for cost reduction and sustainability, particularly in developing countries. Bauxite is one such local material in many countries including Ghana that could be used as a raw material for synthesizing a fluoride adsorbent. Raw bauxite (RB) has known defluoridation properties (Sujana and Anand, 2011). Bauxite is robust, possess sufficient mechanical strength and could overcome limitations such as clogging and/or low hydraulic conductivities in fixed-bed adsorption systems. Fluoride adsorption capacity of raw bauxite is, however, limited and modifications of the physico-chemical properties for improved performance, appear not to have been well studied.

The properties of a material which may contribute to the number of available active sites for fluoride adsorption is expected to include both the surface area, as well as the nature of the surface (i.e. its reactivity/affinity for fluoride ions) (Cater et al., 1986). The objectives of this study were therefore to; (i) explore the possibility of synthesizing granular aluminum coated bauxite (GACB) as a novel fluoride adsorbent, with a focus on investigating the influence of synthesis process conditions (coating pH and thermal treatment) on the amount of aluminum coated onto GACB, as well as the surface area and (ii) study the fluoride adsorption potential of the synthesized adsorbent.

Series of batch adsorption experiments were conducted for evaluating the fluoride removal efficiency of GACB produced under the different process conditions, namely; varying coating pH and varying process temperatures for thermal pre-treatment of raw bauxite(RB) prior to surface modification by Al coating.

The effects of major co-anions on fluoride adsorption by GACB were also examined to obtain a preliminary assessment of its performance in natural groundwater.

## 2. Approach for synthesis of fluoride adsorbent

### 2.1. Conceptual approach

According to the hard-soft acid-base (HSAB) concept, due to their inherent electronic characteristics, hard acids prefer binding to hard bases to give predominantly ionic complexes, whereas soft acids prefer binding to soft bases to form predominantly covalent complexes. The soft-soft interactions with covalent character and hard-hard interactions with ionogenic character results in the most stable interactions and are therefore preferred (Pearson, 1993, Pearson, 1988; Makov, 1995; Alfarra et al., 2004; Pearson, 2005; Vigneresse et al., 2011). With a hardness value of 7.0 ev, a ranking order of hardness values determined for bases, shows $F^-$ as the hardest base and would therefore prefer to coordinate to a hard acid. A similar ranking of hardness values for hard acids also show $B^{3+}$ ($\eta = 110.72$), $Be^{2+}$ ($\eta = 67.84$), and $Al^{3+}$ ($\eta = 45.77$) as the hardest of the acids and would therefore have strong affinity towards $F^-$ in accordance with the HSAB concept (Pearson, 1988; Alfarra et al., 2004). $Al^{3+}$ is, however, considered to be readily available in Ghana, and presumably in most developing countries due to the use of aluminum bearing salts such as $Al_2(SO_4)_3$ for conventional water treatment. Thus a working concept in this study was that treatment of raw bauxite (RB) particle surfaces by aluminum coating can modify the surface hardness and make it a better fluoride scavenger, and that a higher amount of Al coating onto RB in the form of Al hydr(oxides) would result in higher amount of hard surface sites, hence increased fluoride adsorption capability. Additionally, the effect of thermal treatment on enhancement of the textural properties (i.e., surface area, pore size, pore volume) of the fluoride scavenger was investigated as part of the synthesis approach.

### 2.2. Reactivity of RB particle surfaces and potential for binding cations in aqueous solutions

Bauxite is a naturally occurring heterogeneous material composed primarily of one or more aluminum hydroxide/oxides minerals and other constituents including iron oxides, silica, titanium oxides, aluminosilicates, zirconium and water (Gow and Lozej, 1993). By its composition, pH-dependent variably-charged surfaces may exist on RB when in aqueous solution, along-side permanent (pH-independent) negatively charged-surfaces (GES, 2000; Rosenqvist, 2002; Mohammad, 2004; Grafe et al., 2009). Further details on the origin of the charges on the RB particle surfaces are presented in the supplementary materials (SM). The charge development on the bauxite particle surfaces would make it reactive and can consequently be involved in sorption-desorption reactions with ionic species at a bauxite-water interface (e.g. during an Al coating process). The charged state (i.e., charge density and sign) of the bauxite particle surfaces may also be a significant regulator for aqueous ionic species being either adsorbed from solution or desorbed into solution (Grafe et al., 2009).

## 3. Materials and methods

### 3.1. Coating Al onto RB particle surface at varying pH

RB used as base material in Al coating experiments for surface modification, was obtained from Awaso Bauxite Mines (Ghana). Bulk samples were crushed and sieved to a particle size range of 0.8–1.12 mm, a common size fraction for filter media used in drinking water production. RB was subsequently washed and air-dried for use in the Al coating process (without thermal pre-treatment). Coating of RB was done by completely soaking about 150 g of dried sample in sufficient amount of 0.5 M $Al_2(SO_4)_3$ in a Pyrex glass beaker and employing similar procedures as described in our previous work (Salifu et al., 2013). To investigate the effect of coating pH, however, Al coating was done at pH values of 1, 2, 4 and 6. NaOH and/or HCl was slowly added to the completely mixed RB-Al mixture for pH adjustment to the desired coating pH, using a small capacity peristaltic pump (Waston Marlow, 1014, U.K). The coated samples were well sieved and washed with water buffered at pH $7.0 \pm 0.1$, to remove any loosely bound coatings, to ensure that only the effectively coated RB was used for subsequent fluoride adsorption studies.

### 3.2. Thermal pre-treatment of RB prior to Al coating

Samples of dried RB were pre-treated by calcination at different process temperatures (200, 400, 500, 600 and 700 °C) in a muffle furnace for 2 h, before being used in the Al coating process. The aim was to improve on the textural proprieties (surface area, pore size, pore volume) as well as enhance the amount of Al coating, hence nature of coated bauxite surface. The combined effects were expected to result in increased fluoride uptake by the synthesized material.

### 3.3. Characterization of adsorbent

Morphological images of RB and GACB were obtained by