



# Effect of strong acids on red mud structural and fluoride adsorption properties



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## ABSTRACT

The removal of fluoride using red mud has been improved by acidifying red mud with hydrochloric, nitric and sulphuric acid. The acidification of red mud causes sodalite and cancrinite phases to dissociate, confirmed by the release of sodium and aluminium into solution as well as the disappearance of sodalite bands and peaks in infrared and X-ray diffraction data. The dissolution of these mineral phases increases the amount of available iron and aluminium oxide/hydroxide sites that are accessible for the adsorption of fluoride. However, concentrated acids have a negative effect on adsorption due to the dissolution of these iron and aluminium oxide/hydroxide sites. The removal of fluoride is dependent on the charge of iron and aluminium oxide/hydroxides on the surface of red mud. Acidifying red mud with hydrochloric, nitric and sulphuric acid resulted in surface sites of the form  $\equiv\text{SOH}_2^+$  and  $\equiv\text{SOH}$ . Optimum removal is obtained when the majority of surface sites are in the form  $\equiv\text{SOH}_2^+$  as the substitution of a fluoride ion does not cause a significant increase in pH. This investigation shows the importance of having a low and consistent pH for the removal of fluoride from aqueous solutions using red mud.

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## 1. Introduction

At the end of 2010, around 3 billion tonnes of bauxite refinery residue (red mud) had been produced globally using the Bayer process to convert aluminium oxides in bauxite ore to alumina [1]. It is estimated that an additional 120 million tonnes is produced each year [2,3]. The magnitude of waste generated by this industry clearly demonstrates the need for future developments that find a beneficial use for this material. Due to the complexity and classification (hazardous material under the Basel Convention) [4] of bauxite residue, numerous researchers are trying to utilise the waste residue in water purification applications.

Red mud (generally a slurry) is comprised of iron oxides, titanium oxides, silicon oxides and undissolved alumina, along with a wide range of other oxides depending on the country of origin [5–7]. Trace levels of metal oxides, such as arsenic, cadmium, chromium, copper, gallium, lead, mercury, nickel and in some cases thorium and uranium, are of particular concern [8]. Apart from heavy metal contamination, the alkalinity of red mud also constrains viable applications due to the cost of neutralisation.

Alkalinity in the residue exists in both solid and solution as: (1) entrained liquor (sodium hydroxide, sodium aluminate and sodium carbonate), (2) calcium compounds, such as hydrocalumite, tri-calcium aluminate and lime, and (3) sodalite ( $(\text{NaAlSiO}_4)_6(\text{Na}_2\text{X})$ ), where X can be  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{Al}(\text{OH})_4^-$  or  $\text{Cl}^-$  [9].

The potential environmental implications of seepage, dam failures and flooding can have a large negative impact on the surrounding water bodies, including groundwater, lakes and rivers, when soluble caustic chemicals are released. Mining industries employ precautionary measures to minimise environmental risks such as lining dams, however during natural disasters such as flooding there are no measures that can be taken to prevent spillage. Apart from the potential risks of tailing dams, there also exists the problem that large areas of land are being transformed into landfill to contain red mud residue. The discovery of a viable application (in-expensive and uses large quantities) for the reuse of red mud will significantly minimise environmental impacts caused by tailings dams and the associated costs of storage facilities (more than \$80 million a year) [10].

In recent years, many researchers have focused on utilising red mud as an adsorbent material, and have had success in the adsorption of heavy metals [11,12], arsenate [13–18], phosphates [19–21] and to a lesser extent fluoride [22–24]. Fluoride is naturally found in groundwater due to the dissolution of fluoride bearing minerals

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over long periods of time [25]. However, elevated levels of fluoride in groundwater can generally be traced back to a number of industries, including but not limited to, glass and ceramic production, electroplating, coal fired power stations, brick and iron works, and aluminium smelters [22,26]. It is estimated that more than 200 million people rely on contaminated drinking water containing more than  $1.5 \text{ mg L}^{-1}$  of fluoride (World Health Organisation safe level) [27]. Continual and excess exposure to fluoride results in diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer and thyroid disorders in humans [22].

Traditionally, contaminated fluoride drinking waters have been treated using lime, which results in the precipitation of fluorite. However, due to the slight solubility of calcium fluoride ( $\text{CaF}_2$ ), it is difficult to treat fluoride ( $\text{F}^-$ ) ions levels below  $20 \text{ mg L}^{-1}$  [28]. Other precipitating and coagulating reagents have been used and include iron (III), alum, calcium and activated alumina [22]. More involved processes, such as ion exchange, reverse osmosis and electrodialysis, have also been explored, but have subsequent waste disposal issues and high operating and maintenance costs [22,29].

Of particular interest, is the removal of fluoride using activated alumina and iron-based materials, schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)_n\text{H}_2\text{O}$ ), granular ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ), and goethite ( $\alpha\text{-FeOOH}$ ) [22,29], as they are found in red mud and thus suggest red mud can potentially be an adsorbent. Fluoride sorption using iron-based sorbents is facilitated by exchange reactions involving  $\text{F}^-$  and  $\text{OH}^-$  with  $\text{FeOH}$  surface groups. A maximum Langmuir adsorption capacity of  $0.368 \text{ mmol/g}$  of fluoride on granular ferric hydroxide has been reported by Kumar et al. [30], in the pH range 6.0–7.0. Phosphate and sulphate (inner-sphere forming species) have been shown to have negative effects on the loading capacity of fluoride, while outer-sphere forming species (chloride and nitrate) improved fluoride removal slightly [22]. At pH values less than 3.7, fluoride removal generally decreases due to the formation of  $\text{AlF}_x$  soluble species, while in alkaline solutions  $\text{OH}^-$  displaced  $\text{F}^-$  [31]. A study by Cengeloglu et al. [24] investigated the adsorption capacity of untreated and hydrochloric treated red mud. The maximum removal capacity was obtained using the acid treated red mud and observed a Langmuir loading capacity of  $0.331 \text{ mmol/g}$  at pH 5.5 after 2 h equilibration. Granular red mud prepared by Tor et al. [32], exhibited a Langmuir loading capacity of  $0.339 \text{ mmol/g}$  at pH 4.7 after 6 h equilibration during a batch trial. Previous studies have also shown that the spent red mud satisfies the toxicity characteristic leaching procedure (TCLP) used to classify inert wastes [32].

The majority of papers in this field of research focus on the use of hydrochloric acid to activate red mud, however this can reduce the iron content available for subsequent adsorption applications. Consequently, this investigation will assess the structural changes and resulting adsorption capacities of Australian red mud untreated and treated with hydrochloric, nitric and sulphuric acid. Particular emphasis will be placed upon determining the reactions involved during acid activation and how the remaining mineralogical composition correlates with fluoride removal efficiencies.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Red mud preparation

Red mud from an Australian alumina refinery was dried over a period of 2 days at  $105^\circ\text{C}$  before being crushed to a fine powder using a Fritsch agate planetary ball mill. Using a Retsch AS200

sieving stack consisting of 10 sieves, ranging from 4 mm to  $64 \mu\text{m}$ , red mud was processed to give a size fraction  $<250 \mu\text{m}$ .

#### 2.1.2. Acid activated red mud

Hydrochloric ( $\text{HCl}$ ), nitric ( $\text{HNO}_3$ ) and sulphuric ( $\text{H}_2\text{SO}_4$ ) acid were prepared with a concentration of  $0.5 \text{ M}$  by the dilution of known amounts of corresponding concentrated acids (Rowe Scientific). Prepared red mud ( $12.5 \text{ g}$ ) was placed into seven  $250 \text{ mL}$  Nalgene bottles. To each bottle  $200 \text{ mL}$  of either DI water  $0.5 \text{ M HCl}$ ,  $32\% \text{ HCl}$ ,  $0.5 \text{ M HNO}_3$ ,  $70\% \text{ HNO}_3$ ,  $0.5 \text{ M H}_2\text{SO}_4$  or  $98\% \text{ H}_2\text{SO}_4$  was added. The seven bottles were then placed on a Ratek rotary stirrer for 2 h at  $200 \text{ rpm}$  to allow the acids to react with red mud. Once stirring was completed, the samples were centrifuged at  $4000 \text{ rpm}$  for 10 min using a C2041 Centurion centrifuge. The acid treated red mud samples were then placed in the oven to dry ( $90^\circ\text{C}$ ), while the supernatant was stored for analysis.

#### 2.1.3. Fluoride adsorption

The  $100 \text{ mg L}^{-1}$  fluoride solution was prepared using AR grade sodium fluoride purchased from Sigma–Aldrich. Adjustment of the fluoride solution pH to 4.75 was achieved by the addition of a  $1 \text{ M}$  nitric acid solution that was added dropwise until the desired pH was obtained. The pH was monitored with a TPS WP40 pH metre and Sentek laboratory probe calibrated with pH 4 and 7 buffers. A known amount of acid activated red mud (ranging from  $0.025$  to  $2.000 \text{ g}$ ) was placed into  $50 \text{ mL}$  centrifuge tubes, followed by the addition of  $40 \text{ mL}$  of the  $100 \text{ mg L}^{-1}$  fluoride solution. The centrifuge tubes were then placed on a Ratek rotary stirrer at  $200 \text{ rpm}$  for 2 h. After equilibrium was reached, the tubes were removed from the rotary stirrer and subsequently centrifuged at  $4000 \text{ rpm}$  for 10 min using a C2041 Centurion centrifuge. The red mud was placed in the oven to dry ( $90^\circ\text{C}$ ), while the solution was stored for analysis. The supernatant was kept for fluoride analysis using a fluoride ion selective electrode (ISE).

#### 2.1.4. Point of zero net proton charge (PZNPC)

$0.1 \text{ M}$  sodium nitrate ( $\text{NaNO}_3$ ), nitric acid ( $\text{HNO}_3$ ) and sodium hydroxide ( $\text{NaOH}$ ) solutions were prepared using AR grade reagents (Sigma–Aldrich). Approximately  $25 \text{ mg}$  ( $\pm 0.0005 \text{ g}$ ) of dry, finely crushed red mud were measured into  $10$   $25 \text{ mL}$  conical flasks containing a  $1 \text{ cm}$  stirring bar. Known aliquots ( $10 \text{ mL}$ ) of the  $0.1 \text{ M}$   $\text{NaNO}_3$  solution were then added to each conical flask using a  $10 \text{ mL}$  Eppendorf pipette. The mixtures were then stirred at  $100 \text{ rpm}$  while known aliquots of  $0.1 \text{ M HNO}_3$  and  $\text{NaOH}$  were added to each conical flask to produce solutions with pH values ranging from 2 to 10. It was necessary to keep the total volume in each conical flask at  $15 \text{ mL}$ , therefore if  $1 \text{ mL}$  of  $\text{HNO}_3$  or  $\text{NaOH}$  was added a further  $4 \text{ mL}$  of DI water was also required. This was done to ensure the sorbent weight to solution volume ratio remained constant. The conical flasks were then covered with cling wrap and allowed to stir for 24 h before the pH was measured using a TPS WP40 pH meter (Labtek) and Sentek high alkalinity pH probe. The results obtained represent the pH curve for red mud. The blank solution curve was obtained by repeating the procedure described above except that the addition of red mud to the conical flasks was skipped.

### 2.2. Characterisation techniques

#### 2.2.1. Fluoride analysis

The removal of fluoride from solution was determined by using a TPS uniPROBE Fluoride ( $\text{F}^-$ ) ISE. A fluoride ISE buffer was prepared using  $1 \text{ M}$  of sodium chloride ( $\text{NaCl}$ ) and  $1 \text{ M}$  sodium citrate dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) dissolved in approximately  $1.5 \text{ L}$  deionised water. Sodium hydroxide ( $\text{NaOH}$ ) was used to adjust the solution pH to 5.5 before making the solution up to  $2 \text{ L}$ . Calibration

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