Applied Geochemistry 76 (2017) 112–123

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Assessing changes in the physico-chemical properties and fluoride adsorption capacity of activated alumina under varied conditions

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ARTICLE INFO

Article history:
Received 10 February 2016
Received in revised form
13 July 2016
Accepted 16 November 2016
Available online 19 November 2016

Keywords:
Activated alumina
Fluoride
Adsorption
Surface complexation

ABSTRACT

Adsorption using activated alumina is a simple method for removing fluoride from drinking water, but to be cost effective the adsorption capacity must be high and effective long-term. The intent of this study was to assess changes in its adsorption capacity under varied conditions. This was determined by evaluating the physico-chemical properties, surface charge, and fluoride (F^-) adsorption capacity and rate of activated alumina under conditions such as hydration period, particle size, and slow vs. fast titrations. X-ray diffraction and scanning electron microscopy analyses show that the mineralogy of activated alumina transformed to boehmite, then bayerite with hydration period and a corresponding reduction in adsorption capacity was expected; while surface area analyses show no notable changes with hydration period or particle size. The pH dependent surface charge was three times higher using slow potentiometric titrations as compared to fast titrations (due largely to diffusion into pore space), with the surface acidity generally unaffected by hydration period. Results from batch adsorption experiments similarly show no change in fluoride adsorption capacity with hydration period. There was also no notable difference in fluoride adsorption capacity between the particle size ranges of 0.5–1.0 mm and 0.125–0.250 mm, or with hydration period. However, adsorption rate increased dramatically with the finer particle sizes: at an initial F^- concentration of 0.53 mmol L^{-1} (10 mg L^{-1}), 90% was adsorbed in the 0.125–0.250 mm range after 1 h, while the 0.5–1.0 mm range required 24 h to achieve 90% adsorption. Also, the pseudo-second-order adsorption rate constants for the finer vs. larger particle sizes were 3.7 and 0.5 g per mmol F^- per min respectively (24 h); and the initial intraparticle diffusion rate of the former was 2.6 times faster than the latter. The results show that adsorption capacity of activated alumina remains consistent and high under the conditions evaluated in this study, but in order to increase adsorption rate, a relatively fine particle size is recommended.

1. Introduction

Adsorption is often recommended as a low-cost and simple method for removing excess fluoride from drinking water (Ayoob et al., 2008; Mohapatra et al., 2009; Bhatnagar et al., 2011). This is particularly important in poor regions of the world where advanced water treatment facilities are not an option. Activated alumina, which is synthesized at the industrial scale, is well established as an effective adsorbent for fluoride removal from water (Hao and Huang, 1986; Farrah et al., 1987; Fletcher et al., 2006). It is more effective than untreated natural sorbents, such as bauxite and laterite, due to a very high specific surface area and high fluoride adsorption at the near neutral pH range of most groundwater (Craig et al., 2015a, b). Unfortunately, activated alumina can also be a costly choice for use in fluoride adsorption filters in rural areas of the developing world where fluorosis is endemic. Given that activated alumina must be purchased (and in many countries also imported), it would almost certainly need to be used for extended time in order to be considered practical and cost-effective. Therefore, understanding activated alumina's surface characteristics and its long-term effectiveness as a sorbent for fluoride removal are needed in order to determine, in part, whether it is an economically feasible sorbent.

Studies on activated alumina adsorption generally utilize fast titrations, with the sorbent first hydrated in deionized water up to

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http://dx.doi.org/10.1016/j.apgeochem.2016.11.011
0883-2927/

two weeks (Huang, 1981; Hao and Huang, 1986; Craig et al., 2015a), and do not consider possible changes in adsorption capacity and surface reactivity with varied hydration period and or with slower titrations. Changes in surface reactivity with hydration period were observed at upper and lower pH values by Lefèvre et al. (2002) who documented a decrease in surface reactivity of activated alumina with increased hydration periods as it transformed to bayerite. Lefèvre et al. (2002) also speculated that a decrease in surface reactivity may adversely affect adsorption capacity which is important for practical applications of activated alumina. In addition, Rosenqvist et al. (2002) proposed that the fast acid-base titrations (2–8 min) typically used to determine surface acidity under-estimate the surface charge of gibbsite and other oxides because the readings are taken before reaching equilibrium. Craig et al. (2015a) also observed that the pH of activated alumina frequently did not stabilize well during fast titrations, and assumed the resultant surface acidity was under-estimated.

This study evaluated surface characteristics of activated alumina under varied initial conditions to determine, ultimately, if observed changes would result in a decrease in fluoride adsorption capacity. The major components were as follows: (1) fast and slow potentiometric titrations were conducted to document whether surface acidity increased notably with slower titrations; (2) hydration periods were varied from 24 h to 16 weeks to observe changes in surface acidity, physico-chemical structure of activated alumina, and or fluoride loading capacity (sorbent hydrated up to 30 weeks); and (3) fluoride adsorption capacity and rate were compared at two particle size ranges to determine the extent to which particle size influenced adsorption. The results are intended to contribute to the understanding of surface complexation processes, aid in the design of small-scale de-fluoridation filters (e.g. by evaluating the influence of particle size), and help determine the economic viability of using activated alumina filters in communities with drinking water fluoride concentrations above the World Health Organization recommended limit of 1.5 mg L^{-1} (0.079 mmol L^{-1}) (WHO , 2008).

2. Materials and methods

2.1. Sorbent preparation

The activated alumina with a manufactured particle size range of 0.5–1.0 mm was provided by World Vision Ghana. Field adsorption tests previously conducted by World Vision Ghana used activated alumina at its manufactured particle size range. For this reason, the bulk of experiments in this study were also conducted at the manufactured particle size, with the sorbent first cleaned and sieved to remove fine powder. To compare changes in adsorption with changes in particle size, some of the activated alumina was also ground by hand with a pestle and mortar and sieved to a particle size range of 0.125–0.250 mm. Another small portion of the activated alumina was ground and sieved to a particle size range of 0.063–0.125 mm but only to determine the specific surface area. The activated alumina was rinsed well with deionized water to remove fine powder, followed by an acid-base wash to increase sample purity and reproducibility of the titrations and batch adsorption experiments (Huang, 1981). It was first soaked in 0.01 M NaOH, stirred for 30 min, centrifuged for 30 min at 26,890 g relative centrifugal force (RCF) using a Sorvall® RC-5B centrifuge, and rinsed again with deionized water by pouring off the supernate until the electrical conductivity was less than 5 μS cm^{-1}. The activated alumina was soaked once more for 30 min with 0.01 M HCl, centrifuged, and rinsed as described for the 0.01 M NaOH. Once clean, it was left to dry and sieved again to remove traces of powder finer than the smallest particle size. The clean, dry, sieved 0.5–1.0 mm sorbent was stored in a plastic container for six months or more before using. The portion that was ground to 0.125–0.250 mm, sieved, cleaned, and dried was stored in a plastic container for one month before using.

2.2. Sorbent physico-chemical properties

The specific surface area, pore surface area, pore volume, and average pore diameter of dry samples were determined using a Micromeritics® TriStar 3000 static pressure surface area analyzer with $N_{2(g)}$ as the sorbate. The 10-point Brunauer, Emmett, Teller (BET) method was used to determine specific surface area (Brunauer et al., 1938; Lowell and Shields, 1991), and the Barrett, Joyner, Halenda (BJH) adsorption method was used to determine pore area and diameter for pore sizes between 1.7 and 300 nm (Barrett et al., 1951; Lowell and Shields, 1991). Samples were also evaluated for evidence of micropores (<2 nm) by creating *t*-plots from the adsorption and desorption data used to calculate the BET surface area, and BJH pore area and diameter (Gregg and Sing, 1982; Hay et al., 2011). The *t*-plot was created by plotting the statistical film thickness (t) on the x-axis and the volume of liquid nitrogen adsorbed to the surface (liquid nitrogen density of 0.808 g ml^{-1} at 77 K) on the y-axis. The statistical film thickness was calculated from the Harkins-Jura equation:

$$t\left[\text{Å}\right] = \sqrt{\frac{13.99}{0.034 - \log\left(\frac{p}{p^{o}}\right)}} \quad (1)$$

Exposed surface area, evidence of micropores, and small-pore volumes were determined by the linear portions of the *t*-plot and y-intercepts (see Gregg and Sing, 1982; Leofanti et al., 1998; Hay et al., 2011). The statistical film thickness (t) was presented in nanometers (nm), where 1 nm = 10 angstroms (Å); and p/p° is the relative pressure used to create the $N_{2(g)}$ sorption isotherms.

The mineral content of activated alumina samples hydrated 2, 16, or 30 weeks, was determined using X-ray diffraction (XRD). The original pre-hydrated activated alumina (γ-Al_2O_3) contained some boehmite (γ-AlOOH), with the relative abundance not determined (Craig et al., 2015a). The samples were prepared by hand grinding ~5 g of the bulk sample to a particle size <500 μm, then grinding to a powder in a McCrone mill for 8 min in 10 ml of methanol. Samples were air dried overnight, re-crushed to break up aggregates formed during drying, and side-loaded into sample holders. The samples were run on a Bruker D8 Advance XRD equipped with a Vantec PSD detector, and the XRD scans were interpreted using the software, EVA®. The minerals were identified by matching reference mineral patterns stored in the ICDD (International Centre for Diffraction Data) database to the observed peaks. The described method used for semi-quantitative analysis is based on the method of Chung (1975), which assumes the minerals are identified correctly with no unidentified phases in the sample.

The surfaces of activated alumina samples were observed using scanning electron microscopy (SEM) with a Hitachi S-4700 II Scanning Electron Microscope. Dry samples were placed in the Emitech K-575X sputter coater and coated with platinum to make particles electronically conductive before being inserted in the microscope chamber for imaging. The images were taken with a Hitachi cold field emission scanning electron microscope model S-4700-II equipped with the Oxford Energy Dispersive Spectroscope detector for chemical composition analysis.

2.3. Acid-base titrations

The method for acid-base titrations was modified from Huang and Stumm (1973), Huang (1981), Hao and Huang (1986), and