Factors Governing the Performance of Bauxite for Fluoride Remediation of Groundwater

Katya Cherukumilli,*,[†] Caroline Delaire,[†] Susan Amrose,[†] and Ashok J. Gadgil[†,‡]

[†]Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720-1710, United States
[‡]Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Ⓢ *Supporting Information*

ABSTRACT: Globally, 200 million people drink groundwater contaminated with fluoride concentrations exceeding the World Health Organization's recommended level (WHO-MCL = 1.5 mg F^-/L). This study investigates the use of minimally processed (dried/milled) bauxite ore as an inexpensive adsorbent for remediating fluoride-contaminated groundwater in resource-constrained areas. Adsorption experiments in synthetic groundwater using bauxites from Guinea, Ghana, U.S., and India as single-use batch dispersive media demonstrated that doses of ~10−23 g/L could effectively remediate 10 mg F^-/L. To elucidate factors governing fluoride removal, bauxites were characterized using X-ray fluorescence,

X-ray diffraction, gas-sorption analysis, and adsorption isotherms/envelopes. All ores contained gibbsite, had comparable surface areas (~14−17 m^2/g), had similar intrinsic affinities and capacities for fluoride, and did not leach harmful ions into product water. Fluoride uptake on bauxite -primarily through ion-exchange- was strongly pH-dependent, with highest removal occurring at pH 5.0−6.0. Dissolution of $CaCO_3$, present in trace amounts in India bauxite, significantly hindered fluoride removal by increasing solution pH. We also showed that fluoride remediation with the best-performing Guinea bauxite was ~23−33 times less expensive than with activated alumina. Overall, our results suggest that bauxite could be an affordable fluoride-remediation adsorbent with the potential to improve access to drinking water for millions living in developing countries.
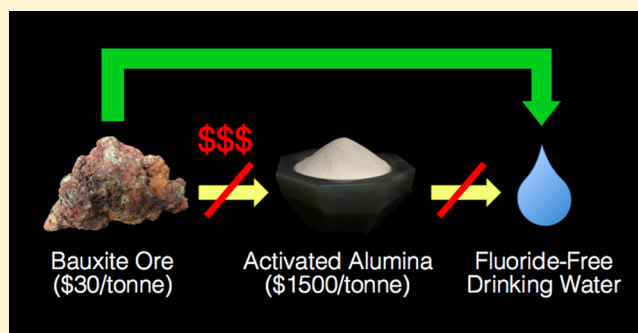
1. INTRODUCTION

Over 200 million people worldwide drink groundwater containing naturally occurring[1] fluoride concentrations[2] surpassing the World Health Organization's maximum recommended contaminant level (WHO-MCL) of 1.5 mg F^-/L.[3] Although fluoride at low concentrations (<1 mg F^-/L) is often intentionally added to drinking water supplies to prevent dental caries,[4] exposure to excessive fluoride concentrations can cause lower IQ,[5] mottling of tooth enamel (dental fluorosis), irreversible bone deformities in children (skeletal fluorosis), and anemia attributed to poor nutrient absorption.[6] Fluoride-affected areas include arid regions of India, China, the East African Rift Valley, the Middle East, northern Mexico, and central Argentina.[6,7]

Many defluoridation technologies have proven to be effective in the lab, but most are neither sustainable nor effective in remote rural regions of developing countries because they are cost-prohibitive and dependent on intensive skilled labor for maintenance (e.g., Nalgonda technique,[7] reverse osmosis, activated alumina, and aluminum electrocoagulation),[8] difficult to source and culturally inappropriate in India (e.g., bone char),[8] or unreliable and challenging to scale up in rural communities (e.g., rainwater harvesting).[9] Activated alumina (AA) filters are widely used due to their effectiveness and relative affordability for the upper middle class.[10] AA is

produced by first extracting aluminum oxides from bauxite, a composite ore that also contains oxides of iron, silicon, and titanium as well as other trace minerals. Industrial refining methods such as the Bayer process, aiming to concentrate the Al fraction of bauxite and eliminate impurities, utilize pressurized sodium hydroxide and temperatures exceeding 1000 °C and are therefore extremely resource-intensive in terms of capital and operating costs, energy, and greenhouse gas emissions.[11] Per tonne, alumina ($300/tonne) costs approximately 10× more than raw bauxite ore ($30/tonne), due to expenses associated with processing and purifying the bauxite.[12] Alumina (Al_2O_3) is then thermally activated to make the commonly used AA filter media ($1500/tonne),[13] a highly efficient fluoride adsorbent[14,15] with a final material cost 50× higher than raw bauxite ore. Fluoride also has a strong adsorption affinity for gibbsite ($Al(OH)_3$),[15−17] the primary component of bauxite, AA's parent ore. In addition, bauxite deposits are present worldwide, including in countries with fluoride-contaminated regions (e.g., India, Ghana, and China). For instance, India has over 66 million people facing risk of

developing fluorosis[18] and it is also home to the fifth largest bauxite deposit (3037 million tonnes).[19] Hence, replacing AA with mildly processed bauxite (e.g., dried/milled) ore has the potential to create a fluoride removal method that is more (a) effective at remediating contaminated groundwater in \$/volume of water treated, (b) affordable to low-income households, and (c) widely available in affected regions.

Although several studies have observed fluoride adsorption on bauxite,[20−28] existing literature does not rigorously demonstrate that mildly processed bauxite can produce the level of fluoride removal required to meet the WHO-MCL, nor does it investigate the fluoride removal performance of bauxites of diverse origins with significantly different chemical compositions. The adsorption of numerous cationic (e.g., Cu^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+}, Ca^{2+}, Zn^{2+}, $Hg(OH)_2$, UO_2^{2+}, Th^{4+}), and anionic (e.g., PO_4^{3-}, AsO_4^{3-}, SO_4^{2-}, MoO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}, H_3BO_3, $H_2SiO_4^{2-}$) species on gibbsite has been reported,[29] but very few studies have focused on the adsorption of fluoride (F^-) on pure gibbsite[16] or on its composite bauxite ore.[27,23] More generally, the adsorption behavior of composite mineral assemblages such as bauxite is not well understood because published surface complexation and spectroscopic studies have primarily focused on surface interactions with pure mineral phases. Specifically, the effect on fluoride removal of non-Al minerals present in bauxite (e.g., hematite, goethite, kaolinite, calcite, etc.), which could impact adsorption through modifications in the adsorbent's elemental composition, surface area, and affinity for fluoride, has not been investigated in prior literature. Thus, characterizing and elucidating the performance of diversely sourced bauxite ores with different compositions may allow for the design of an effective and low-cost solution to remediate fluoride-contaminated groundwater.

Therefore, the objectives of this study are (1) to demonstrate and compare fluoride removal performance of diversely sourced bauxite ores used as dispersive batch media, (2) to elucidate factors governing fluoride removal with mildly processed bauxite ores, and (3) to conduct a rigorous, controlled, cost comparison of treating fluoride-contaminated groundwater with AA and bauxite. To meet these objectives, we conducted batch fluoride adsorption experiments with four bauxite ores originating from India, Guinea, Ghana, and the U.S. Except for U.S. bauxite, which was convenient to obtain, the other regions were selected because of the severity of their fluoride contamination problem and their large share in global bauxite production.[19,30,31] Furthermore, molecular-level and macroscopic experimental techniques were used to characterize the ores in terms of elemental and mineral composition, adsorption affinity and capacity, surface area, and equilibrium suspension pH. Our results elucidating factors influencing fluoride removal efficiency strongly suggest that mildly processed bauxite ore is a cost-competitive alternative to AA and consequently has the potential to substantially improve access to safe water in fluoride-affected low-income communities.

2. MATERIALS AND METHODS

2.1. Adsorbent Materials. Bauxite ores were received from mines in India (Visakhapatnam, Telangana), Guinea (Boke), Ghana (Western Region), and U.S. (Eufaula, Alabama). After oven-drying raw bauxite at 100 °C for 24 h to remove moisture, 5 g of each sample was milled for 60 min in an agate milling jar of a shaker ball mill (SPEX8000) to generate submicrometer-sized powders, as confirmed by scanning electron microscopy

(SEM) and dynamic light scattering (Malvern Zetasizer Nano ZSP). In a number of experiments, we used as-received AA powder (0.58 ± 0.56 μm, Sigma-Aldrich, MO) with a comparable particle size to that of the bauxite ores from India, Guinea, Ghana, and U.S. (respectively 0.71 ± 0.10, 0.76 ± 0.08, 0.55 ± 0.27, and 0.91 ± 0.84 μm). Images of each bauxite ore (as-received, after milling, and with SEM) are shown in Supporting Information (SI) Figure S1. The zetapotentials of these bauxite ores and AA measured between pH 2 and 12 in deionized (DI) water are reported in SI Figure S2, along with points of zero charge (PZC).

2.2. Materials Characterization. Bulk elemental composition was measured by energy dispersive X-ray fluorescence spectroscopy using the parameter-free Turboquant method (Spectro Xepos ED-XRF), which does not account for light elements such as C and N in the total mass. Bulk crystalline mineral composition was determined from X-ray diffraction (XRD) patterns obtained using a Bruker D8-Discover diffractometer with a Co source (Co Kα = 1.79 Å) and a Vantec-500 area detector. Multipoint Brunauer−Emmett−Teller (BET) measurements were made using a Micromeritics Tristar II 3020 to determine the specific surface area (SSA) of the milled bauxite ores. Additional details regarding sample preparation and data processing are provided in the SI.

2.3. Batch Adsorption Experiments. Standard batch adsorption experiments were designed to determine the respective effects of the solid:liquid ratio (referred to as "dose" henceforth), initial fluoride concentration, pH, ionic strength, and reaction time on fluoride removal with the 4 bauxite ores. Adsorbents were added to select electrolytes in 15 mL polypropylene centrifuge tubes at doses differing for each experiment. An Analog Rotisserie Tube Rotator (Scilogex, MX-RL-E) allowed maintenance of well-mixed suspensions during the full duration of the batch adsorption experiments, which were conducted for 24 h for consistency with other studies,[15,32] and after confirming through kinetics studies that concentrations were independent of time after 3 h (SI Figure S4). Upon completion of each adsorption experiment, a 5 mL aliquot of the slurry was collected in a syringe and filtered using 0.2 μm filters before analysis. Filtered aliquots were then mixed with equal volumes of Total Ionic Strength Adjustment Buffer (TISABII) to complex aluminum and iron, and free-fluoride (F^-) was measured using a fluoride ion-selective electrode (Mettler Toledo SevenMulti, perfectION). A Consort meter (R3620) was used to measure pH. SI Table S1 provides a detailed summary of experimental conditions. SI Table S2 provides the composition of real and synthetic groundwater matrices used in batch experiments designed to be representative of real treatment conditions (including ionic strength, which is mostly unaffected by fluoride adsorption). Binary-solute buffered electrolytes were used mainly in bauxite characterization experiments and were not designed to be representative of drinking water.

Experiments to determine the minimum bauxite dose (g/L) to remove an initial fluoride concentration of 10 mg F^-/L down to below the WHO-MCL (1.5 mg F^-/L) were conducted in a synthetic Sri Lankan groundwater matrix (4.3 mM Ca^{2+}, 7.5 mM Mg^{2+}, 8.5 mM HCO_3^-, 0.2 mM SO_4^{2-}, 1.6 mM Si, and 0.6 mM NO_3^- as N) derived from British Geologic Survey (BGS)[2] measurements to represent the average composition of groundwater in fluoride-contaminated regions in South Asia (SI Table S2). The pH was initially set to 6.0 ± 0.1 (near the pH of minimum solubility of gibbsite) and was not kept constant
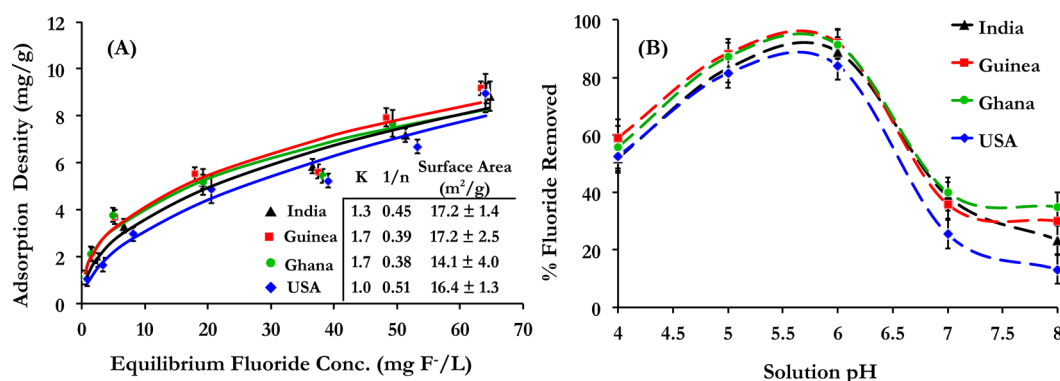
Figure 1. Characterization of globally diverse bauxite ores in terms of (A) Minimum doses required to remediate 10 mg F$^-$/L to below the WHO-MCL (1.5 mg F$^-$/L) in synthetic Sri Lankan groundwater; initial pH of 6.0, (B) Elemental composition as determined by X-Ray fluorescence, and (C) Mineralogy as determined by X-ray diffraction patterns. Unlabeled peaks represent gibbsite. In panel A, we present averages from duplicate experiments and error bars are the largest of the range from duplicate tests and measurement errors associated with the fluoride probe. In panel B, we present the measurement errors associated with the ED-XRF analysis.

during experiments (final pH values ranged between 6.3 and 7.5). Batch tests using incremental adsorbent doses allowed us to narrow down the range of the minimum required dose, which was determined by linear interpolation of three separate doses yielding an equilibrium fluoride concentration that tightly bracketed the target of 1.5 mg F$^-$/L (SI Figure S3). Dissolved aluminum (Al) and iron (Fe) concentrations were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 720 Series) upon bauxite's equilibration with a binary-solute matrix (5 mM HCO$_3^-$ + 35 mM NaCl + 10 mg F$^-$/L) for 3 h (SI Table S2). Additional studies described later in the paper (e.g., ionic strength, kinetics, FTIR, and treatment costs) were conducted using Guinea bauxite ore due to its high fluoride removal performance.

Experiments to determine the adsorption isotherm of each ore were conducted in 50 mM 2-(N-morpholino)-ethanesulfonic acid (MES, to maintain the pH at 6.0 ± 0.2) + 5 mM HCO$_3^-$ (to introduce a natural source of buffering/alkalinity) amended with 5, 10, 20, 40, 60, 80, and 100 mg/L of NaF. Ionic strength was kept constant at 61 mM by adding NaCl as necessary and a constant bauxite dose of 4 g/L (40 ± 0.1 mg/10 mL) was used in these experiments. Adsorption isotherms were fitted against the Langmuir and Freundlich models using ISOFIT (nonlinear regression). The intrinsic fluoride adsorption capacity and affinity of each ore were then determined using the best-fit model.

Experiments to determine the adsorption envelope of each bauxite ore were conducted in 5 mM HCO$_3^-$ amended with the following buffers: 50 mM NaCH$_3$COO/CH$_3$COOH (pH 4 and 5), 50 mM MES (pH 6), 14 mM Na$_2$HPO$_4$/NaH$_2$PO$_4$ (pH 7),

and 10 mM Na$_2$B$_4$O$_7$/H$_3$BO$_3$ (pH 8). Ionic strength was kept constant at 61 mM across experiments by adding NaCl as necessary. A constant initial fluoride concentration of 10 mg F$^-$/L and a bauxite dose of 6 g/L (60 ± 0.1 mg/10 mL) were used in these experiments.

Experiments to determine the effect of ionic strength on fluoride removal were conducted with Guinea bauxite (dose: 10 g/L (100 ± 0.1 mg/10 mL)) in 5 mM HCO$_3^-$ + 10 mg F$^-$/L amended with increasing concentrations of NaCl (1, 10, 100 mM). The kinetics of fluoride removal were investigated in synthetic Sri Lankan groundwater with AA and milled Guinea bauxite (doses of 4 g/L (40 ± 0.1 mg/10 mL) and 10 g/L (100 ± 0.1 mg/10 mL), respectively) by monitoring fluoride concentrations after 1, 3, 5, 8, and 24 h (SI Table S2 and Figure S4). All experiments were conducted in duplicate or more.

2.4. Determination of Equilibrium pH. Suspensions of each milled bauxite ore (dose: 1 g/L) were mixed in open glass beakers containing 35 mM NaCl for 24 h and the final pH, henceforth referred to as "equilibrium pH", was measured. To understand the observed differences in equilibrium pH between the 4 bauxite ores, we conducted separate experiments with higher doses (4 g/L) of bauxite and measured the dissolved calcium and inorganic carbon (DIC) concentrations in the filtrate (0.2 μm) after overnight mixing. Calcium was measured using ion chromatography (IC, Metrohm Chromatagraph, IonPac CS12 column) and dissolved inorganic carbon was determined with a total carbon analyzer (Shimadzu TOC-V$_{CSH}$) as the difference between total carbon (TC, representing

Figure 2. Adsorption (A) Isotherms and (B) Envelopes of the four bauxite ores to showing the respective effects of equilibrium fluoride concentration and pH on fluoride removal. Adsorption isotherms were characterized in 50 mM MES + 5 mM HCO_3^-, at a constant pH of 6.0, with solid lines indicating the Freundlich model fit generated by ISOFIT (fitted model constants and BET surface area are also indicated). Adsorption envelopes were characterized in 5 mM HCO_3^- + buffers, at constant ionic strength, with dashed lines drawn to guide the eye and not to represent a model fit. We present averages from duplicate experiments and error bars are the largest of the range from duplicate tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe, Tristar II 3020).

inorganic and organic carbon) and non-purgeable organic carbon (NPOC, representing nonvolatile organic carbon).

2.5. ATR-FTIR Spectroscopy Analysis. Guinea Bauxite was analyzed by horizontal attenuated total reflection Fourier transform infrared spectroscopy (HATR-FTIR, PerkinElmer Spectrum One) before and after batch adsorption experiments to detect potential changes in hydroxyl (−OH) peaks. Samples were prepared by exposing 2 g/L of milled bauxite ore either to a solution of 500 mg F⁻/L or to a solution of 100 mg F⁻/L replaced every hour for 4 h. All samples were allowed to equilibrate for 24 h and dried overnight at 100 °C before analysis.

2.6. Estimation of Treatment Costs. We compared per capita annual material costs of remediating fluoride-contaminated groundwater with Guinea bauxite and with AA in the various synthetic and real groundwater matrices listed in SI Table S2. For these calculations, we conducted adsorption tests using each adsorbent a single time in a batch process where the adsorbent was dispersed in the water and kept well-mixed for 24 h. For AA, we made additional calculations based on conservative assumptions that AA could be used in a column filter (breakthrough at 75% capacity), regenerated (through NaOH treatment) to 70% of its previous capacity, and reused for four cycles, consistent with data from a 2014 EPA report.[13] Our estimates do not include potential material losses during treatment or the cost of treatment chemicals (e.g., acids and bases). We also made the following assumptions: volume of drinking water per capita per day = 7.5 L[33] and material costs of AA and bauxite = $1.5/kg[13] and $0.03/kg,[12] respectively, according to current market prices.

3. RESULTS AND DISCUSSION

3.1. Differences in Bauxite Ore Performance. Figure 1a shows the minimum dose of each bauxite ore required to reduce fluoride from an initial concentration of 10 mg F⁻/L in synthetic Sri Lankan groundwater to below the WHO-MCL of 1.5 mg F⁻/L. We found that Guinea, Ghana, and U.S. bauxites performed similarly, with minimum required doses of 9.5−10.6 ± 1.0 g/L, while India bauxite had a significantly lower performance, with a minimum required dose of 22.8 ± 1.0 g/L. This result shows that the geographical source of bauxite ore can greatly impact its fluoride removal performance, and suggests that the chemical composition of the ore may affect

fluoride removal. Compared to previous studies, which used different bauxite ores (e.g., from Malawi, Texas, Tanzania, etc.), levels of processing, solution matrices, and initial fluoride concentrations, our measured minimum required doses are lower (possibly due to our finer particle size).[20−28]

3.2. Chemical Characterization of Bauxite Ores. Figure 1b shows the chemical composition of the four bauxite ores as determined by XRF. All bauxites contained approximately 22−29% Al and <2% Ti (LOD_{Al}= 0.1%, LOD_{Ti} = 0.01%). Ghana, India, and Guinea bauxites had significant and comparable fractions of Fe (∼11−14%) (LOD_{Fe} = 0.005%). Si was found in all bauxite ores, and its content ranged from 0.5% in Ghana bauxite to approximately 9% in U.S. bauxite (LOD_{Si} = 0.1%). The Ca content in most bauxite ores was below the detection limit (LOD_{Ca} = 0.02%) except in India bauxite, which contained 1.8% Ca. Figure 1c shows the XRD patterns of the 4 bauxite ores. The main crystalline Al phase in all bauxites was gibbsite, and an additional crystalline Fe phase, hematite, was detected in Ghana, India, and Guinea bauxites. Consistent with XRF results, kaolinite was found only in U.S. bauxite and calcium carbonate ($CaCO_3$) was found only in India bauxite.

Taken together, the results in Figures 1b and c show that Al content and phase cannot explain the lower fluoride removal performance of India bauxite. The small difference in Al content between India bauxite and the three other ores (3.8−6.9%) would not likely result in a greater than 2-fold difference in the minimum required dose (as suggested by the similar fluoride removal performance of Guinea and U.S. bauxites despite their 3.2% difference in Al content) (Figure 1a and c). Similarly, the observed differences in fluoride removal performance do not appear to be correlated with the Fe, Si, and Ti contents and phases. In contrast, the presence of $CaCO_3$ in India bauxite might be correlated with its poorer fluoride removal performance. Regardless of the bauxite ore used, ICP-OES results demonstrated minimal leaching of Al and Fe ions (final concentrations were below the detection limit; <0.01 ppm), resulting in treated water in conformity with WHO standards for Al and Fe (<0.1 and <0.3 ppm respectively).

3.3. Adsorption Isotherms and Envelopes. Figure 2a shows the relationship between adsorption density and equilibrium solute concentration for each bauxite ore. Our experimental isotherms were best fitted to the Freundlich model described by $q = KC_e^{1/n}$ where q (mg/g) is the

adsorption density, C_e (mg/L) is the equilibrium adsorbate (fluoride) concentration, and K (adsorption capacity) and n (adsorption strength) are constants. The fitted Freundlich parameters (K and $1/n$) of the four ores, specified in Figure 2a, showed no statistically significant difference (overlapping 95% confidence intervals), which indicates that all four bauxites have a similar intrinsic capacity and affinity for fluoride. This finding suggests that differences in fluoride removal efficiencies observed between the four bauxite ores in Figure 1a are not caused by differences in intrinsic adsorption capacity or affinity (e.g., a lower K value for USA bauxite compared to Guinea and Ghana bauxites did not result in significantly lower fluoride removal). Consistent with the virtually identical adsorption isotherms, the BET surface areas of the four milled bauxite ores were not significantly different, ranging from 14.1 ± 4.0 to 17.2 ± 2.5 m^2/g, indicating comparable adsorption capacities (Figure 2a).

Figure 2b shows that the adsorption envelopes of the four bauxite ores were close to identical, indicating a similar adsorption behavior throughout a wide pH range (4−8). In addition, all ores had an optimal adsorption pH of 5.0−6.0. The adsorption envelopes demonstrate that pH has a substantial influence on fluoride removal, with a unit pH increase above the optimum pH leading to a 50−59% decrease in fluoride adsorption. These adsorption envelopes are characteristic of anion sorption, with a decrease in removal both at lower and higher pH, due to competing reactions of surface protonation and OH$^-$ complexation, respectively. At acidic pH, the ligand-promoted dissolution of gibbsite and the formation of aqueous fluoride complexes (e.g., HF, AlF^{2+} AlF_2^+, AlF_3, AlF_4^-, AlF_5^{2-}, or AlF_6^{3-}) might also contribute to the decrease in fluoride removal.[15]

3.4. Influence of Equilibrium pH on Fluoride Removal.
In batch adsorption experiments in Sri Lankan groundwater with an initial pH of 6.0 ± 0.1 (Figure 1a), we observed that the final solution pH after 24 h was significantly higher for India bauxite (average final pH 7.5 ± 0.1) compared to the 3 other ores (average final pH 6.4 ± 0.1, 6.3 ± 0.1, and 6.5 ± 0.1 for U.S., Guinea, and Ghana bauxites, respectively). Although a minor pH increase is expected upon fluoride adsorption due to the replacement of OH$^-$ groups on the surface of gibbsite,[15,29,34] this ion exchange process cannot account for the observed differences in final pH between India bauxite and the other three ores.

To further understand the effect of bauxite addition on solution pH, we conducted experiments in a simpler electrolyte (35 mM NaCl) in the absence of fluoride and characterized the equilibrium pH and composition of the suspension after 24 h. As summarized in Table 1, we found a significantly higher equilibrium pH for India bauxite (pH 8.1 ± 0.1, compared to pH 6.6 ± 0.1, 6.5 ± 0.1, and 6.2 ± 0.4 for Guinea, Ghana, and U.S. bauxites, respectively), which coincided with substantially higher concentrations of Ca and inorganic carbon (334 ± 2 μM Ca and 398 ± 9 μM C, respectively, for India bauxite, compared to ≤ 3 μM Ca and ≤ 35 μM C, respectively, for the other bauxites). These results are indicative of the dissolution of CaCO$_3$ (only present in India bauxite, Figure 1b and c), and the observed increase in pH corresponds to the increase theoretically expected from the dissolution of ~0.3 mM CaCO$_3$ (see SI, Section 7).

We concluded that the substantially higher equilibrium pH of India bauxite compared to the other ores is due to the presence and partial dissolution of CaCO$_3$. Because an alkaline pH (i.e., a

Table 1. Characterization of pH, Dissolved Calcium, and Dissolved Inorganic Carbon (DIC) of Each Bauxite Ore in Equilibrium with a Suspension (35 mM NaCl)[a]

bauxite source	equilibrium pH	equilibrium [Ca^{2+}] (μM)	equilibrium [DIC] (μM)
India	8.1 ± 0.1	334 ± 2	398 ± 9
Guinea	6.6 ± 0.1	1.0 ± 0.4	21 ± 12
Ghana	6.5 ± 0.1	0.2 ± 0.1	30 ± 6
U.S.	6.2 ± 0.4	3 ± 1	35 ± 10

[a]We present averages from duplicate experiments and reported errors are the largest of the range from duplicate tests and measurement errors associated with the analytical equipment used (e.g., pH probe, Ion Chromatograph, and Total Carbon Analyzer).

pH ≫ PZC) is unfavorable for fluoride adsorption (Figure 2b), the dissolution of CaCO$_3$ is likely responsible for the lower performance of India bauxite (Figure 1a, SI Figure S2). This finding is also consistent with the adsorption isotherms of the globally diverse bauxite ores being similar under constant pH conditions (Figure 2a). Taken together, our results suggest that when surface capacities and affinities are comparable, fluoride removal is primarily influenced by the presence of trace alkaline minerals such as CaCO$_3$, which alter the equilibrium solution pH.

3.5. Fluoride Adsorption Mechanism.
HATR-FTIR measurements showed a decrease in transmittance in −OH peaks (3650−3350 cm^{-1}) upon fluoride adsorption, independent of the loading method (Figure 3a). Previous FTIR studies have shown that the peak at ~3400 cm^{-1} is characteristic of the stretching vibration of hydroxyl groups on the surface of gibbsite.[30,35] Therefore, our results suggest that similar to pure gibbsite, bauxite also forms a specific, inner-sphere complex with fluoride through ion exchange with − OH groups. Figure 3b shows that varying ionic strength over 2 orders of magnitude (1−100 mM) did not affect fluoride removal with Guinea bauxite, despite increased charge screening of the adsorbent surface. This finding (along with the PZC data presented in SI Figure S2) indicates that weak, outer-sphere electrostatic interactions do not play a major role in fluoride adsorption on bauxite in our pH range of interest, consistent with the primary role of inner-sphere complexation previously reported for pure gibbsite.[15,29,34]

3.6. Comparison between AA and Guinea Bauxite.
Figure 4 compares the minimum required doses and materials costs for remediating a simple binary-solute electrolyte and several synthetic and real groundwater matrices (SI Table S2) with AA and Guinea bauxite (the best performing bauxite ore, Figure 1a). Our cost estimates are based on experimentally determined minimum required doses, which demonstrate that on average, Guinea bauxite requires 1.5−2.3 times the dose of AA (depending on groundwater composition) to remediate an initial fluoride concentration of 10 mg F$^-$/L to the WHO-MCL (Figure 4a). Larger doses required for bauxite are consistent with its lower specific surface area and thus lower adsorption capacity (Figure 2a). We found that for both AA and bauxite, the minimum dose required to reach the WHO-MCL is higher in synthetic and real groundwater than in the simple binary-solute electrolyte (NaCl + NaHCO$_3$). This trend is likely due to the presence of potentially competitive species such as oxyanions (e.g., SiO_4^{4-}, HCO_3^-, SO_4^{2-}, NO_3^-),[27,32,36] as well as natural organic matter (likely to be present in real groundwater).[32,37]
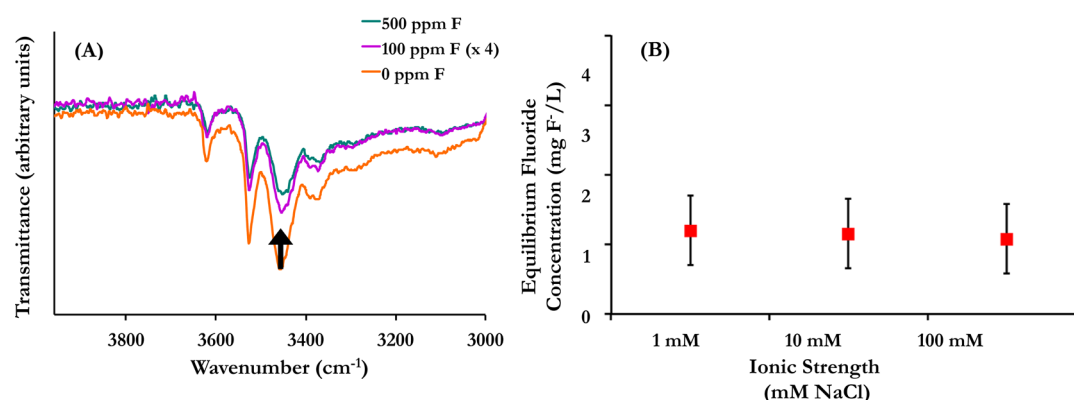
Figure 3. Investigation of fluoride removal mechanisms through (A) HATR-FTIR absorbance spectra for Guinea bauxite (2 g/L dose) with an initial fluoride loading of 0, 100 × 4 (replaced every hour for 4 h), and 500 ppm F⁻, respectively, and (B) Study on effect of ionic strength on fluoride removal using Guinea bauxite. Initial [F⁻]: 10 mg F⁻/L; Dose: 10g/L.
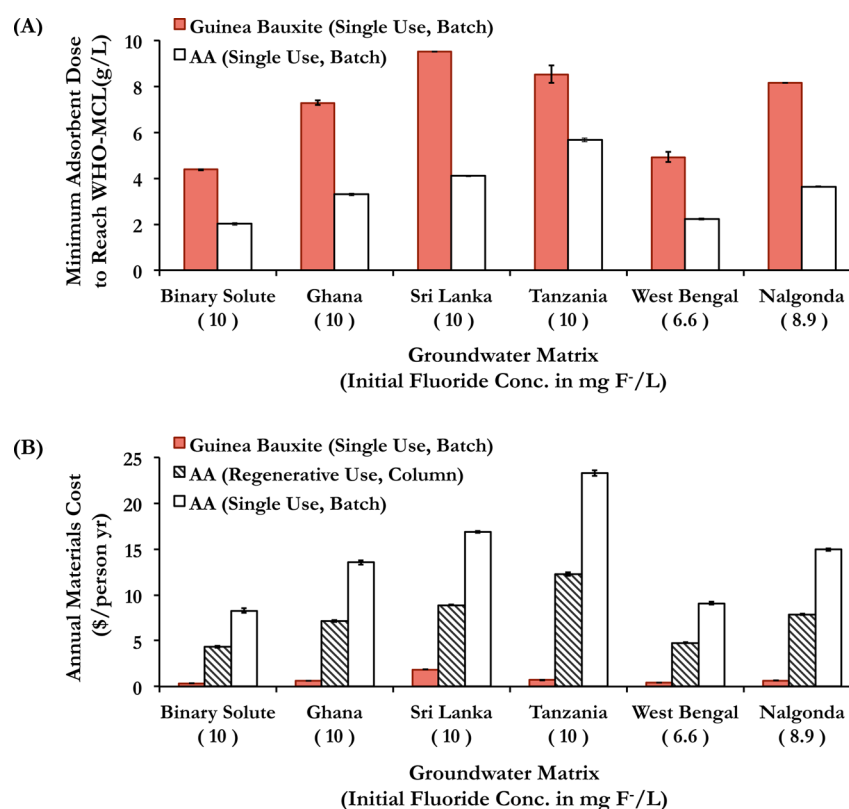

Figure 4. Comparison of (A) Minimum required doses and (B) Annual per capita material costs for remediating several synthetic groundwater matrices containing 10 mg F⁻/L and two real groundwater matrices (West Bengal and Nalgonda) to the WHO-MCL (1.5 mg F⁻/L) using milled Guinea bauxite (single-use batch process) and unmodified AA (both in single-use batch process and in column process with media regeneration). We present averages and error bars represent the larger of the range from duplicate tests and measurement errors associated with the fluoride probe. Cost calculations are described in section 2.6 and recipes for the groundwater matrices are given in SI Table S2.

Figure 4b shows that the material cost of fluoride remediation with Guinea bauxite is consistently and substantially lower than with AA across all tested groundwater matrices: ∼23−33× lower if AA is assumed to be used in a single-use batch process and ∼11−18× if AA is assumed to be used in a column process with media regeneration. Even when using regenerated AA (which is ∼50% cheaper than single-use AA), treatment with AA is still significantly more expensive than with Guinea bauxite as single-use batch media. When considering the worst performing ore (India bauxite, which requires 2.4× the minimum dose of Guinea bauxite to

remediate Sri Lankan groundwater, as shown in Figure 1a), the material cost of using bauxite remains 4.7−8.8× lower than AA.

In addition to the cost advantage, another benefit of using mildly processed bauxite as single-use batch media is that in contrast to AA, the preparation of the bauxite adsorbent does not involve any activation or regeneration with hazardous chemicals that can increase the leaching of metals in the product water. Finally, we note that Guinea bauxite has fluoride removal kinetics comparable to AA, with approximately 80% of total fluoride removal occurring in the first hour in synthetic Sri

Lankan groundwater, confirming that bauxite can realistically be used in field applications (SI Figure S4).

3.7. Implications for Groundwater Treatment. Overall, our study demonstrates that mildly processed bauxite ore is an effective fluoride removal adsorbent capable of remediating high fluoride levels (up to 10 mg F^-/L) to below the WHO-MCL in groundwater characteristic of affected regions, and is a cost-competitive alternative to AA. When considering fluoride removal on a per unit surface area basis, our results suggest that bauxite has a stronger affinity for fluoride adsorption than AA (i.e., bauxite requires only ∼2× the dose despite having 7× lower SSA than AA).

Our results showed that the chemical composition, and therefore the geographical origin of the bauxite ore, could substantially impact its fluoride removal performance. Specifically, we found that the presence of trace minerals such as $CaCO_3$ can reduce the affinity of bauxite ore for fluoride by modifying the equilibrium suspension pH. Similarly, other alkaline (e.g., $MgCO_3$, $CaMg(CO_3)_2$, etc.) or acidic (e.g., humic materials, silicates) minerals often present in bauxite ores[31] may affect their fluoride removal performance. Of the four ores we tested, India bauxite was the least efficient, but it is geographically closest to $^1/_3$ of the fluoride-affected population,[18] which highlights the need to analyze the trade-offs between transportation costs and adsorption efficiency. Future research will (i) investigate nonhazardous and locally appropriate activation methods to potentially enhance India bauxite's performance and cost-competitiveness; and (ii) will determine if any nonalkaline bauxite deposits are present in India. We also found that fluoride adsorbs to bauxite through an ion-exchange process; therefore future work should focus on the effect of potential competitors commonly found in groundwater (e.g., Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, NOM), which may significantly impact the efficiency of fluoride removal by bauxite in the field.

Finally, prior to implementing this water treatment process in the field, additional research must be conducted to (1) identify potential low-cost solid-separation methods and (2) test the efficiency of different reactor designs such as a sequential batch reactor (to saturate/reuse bauxite media) and a column filter with regeneration (using larger particle size to avoid clogging).

■ ASSOCIATED CONTENT

ⓢ Supporting Information
The SI is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b04601.

> Details of methodology including experimental parameters, electrolyte and sample preparation, and calculations for minimum required dose and calcite dissolution are provided in the SI in addition to supporting tables and figures referenced in the text (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*Phone: 407-529-9943; e-mail: katyacherukumilli@gmail.com.
ORCID ⓘ
Katya Cherukumilli: 0000-0002-8606-1845
Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Saxena, V.; Ahmed, S. Inferring the chemical parameters for the dissolution of fluoride in groundwater. *Environ. Geol.* **2003**, *43* (6), 731−736.
(2) Edmunds, M.; Smedley, P. Chapter 12: Fluoride in Natural Waters. In *Essentials of Medical Geology*; Selinus, O., Ed.; Springer: Netherlands: Dordrecht, 2013; pp 311−336.
(3) Chilton, J. Dahi, Lennon, E.; Jackson, M.; P., Fawell; J., Bailey *WHO Water Series: Fluoride in Drinking Water*; Fawell, J. K., Bailey, K., Eds.; World Health Organization: Geneva, 2006; http://www.who.int/water_sanitation_health/publications/fluoride_drinking_water_full.pdf.
(4) Featherstone, J. D. Prevention and reversal of dental caries: role of low level fluoride. *Community Dent. Oral Epidemiol.* **1999**, *27* (1), 31−40.
(5) Rocha-Amador, D.; Navarro, M. E.; Carrizales, L.; Morales, R.; Calderón, J. Decreased intelligence in children and exposure to fluoride and arsenic in drinking water. *Cad. Saude Publica* **2007**, *23* (4), S579−S587.
(6) Ozsvath, D. L. Fluoride and environmental health: A review. *Rev. Environ. Sci. Bio/Technol.* **2009**, *8* (1), 59−79.
(7) Jagtap, S.; Yenkie, M. K.; Labhsetwar, N.; Rayalu, S. Fluoride in Drinking Water and Defluoridation of Water. *Chem. Rev.* **2012**, *112* (4), 2454−2466.
(8) Osterwalder, L.; Johnson, C. A.; Yang, H.; Johnston, R. B. Multi-criteria assessment of community-based fluoride-removal technologies for rural Ethiopia. *Sci. Total Environ.* **2014**, *488−489* (1), 532−538.
(9) Mwenge Kahinda, J.; Taigbenu, A. E.; Boroto, J. R. Domestic rainwater harvesting to improve water supply in rural South Africa. *Phys. Chem. Earth, Parts A/B/C* **2007**, *32* (15−18), 1050−1057.
(10) Dahi, E. The State of Art of Small Community Defluoridation of Drinking Water. In *Proceedings of the 3rd International Workshop on Fluorosis Prevention and Defluoridation of Water*; Chiang Mai, Thailand, November 20−24, **2000**.
(11) Chen, W.-Q.; Graedel, T. E. Dynamic analysis of aluminum stocks and flows in the United States: 1900−2009. *Ecol. Econ.* **2012**, *81*, 92−102.
(12) Bray, L. *USGS Mineral Commodities Summaries 2015: Bauxite and Alumina*; United States Geologic Survey: Reston, VA, 2016; http://minerals.usgs.gov/minerals/pubs/commodity/bauxite/mcs-2015-bauxi.pdf.
(13) Sorg, T. *Removal of Fluoride from Drinking Water Supplies by Activated Alumina*; US EPA: Cincinnati, OH, 2014; https://nepis.epa.gov/Adobe/PDF/P100KFZQ.pdf.

(14) Choi, W.-W.; Chen, K. Y. The Removal of Fluoride From Waters by Adsorption. *J. Am. Water Works Assoc.* **2012**, *71* (10), 562−570.

(15) Farrah, H.; Slavek, J.; Pickering, W. Fluoride interactions with hydrous aluminium oxides and alumina. *Aust. J. Soil Res.* **1987**, *25* (1), 55−69.

(16) Vithanage, M.; Rajapaksha, A. U.; Bootharaju, M. S.; Pradeep, T. Surface complexation of fluoride at the activated nano-gibbsite water interface. *Colloids Surf., A* **2014**, *462*, 124−130.

(17) Gomoro, K.; Zewge, F.; Hundhammer, B.; Megersa, N. Fluoride removal by adsorption on thermally treated lateritic soils. *Bull. Chem. Soc. Ethiop.* **2012**, *26* (3), 361−372.

(18) UNICEF. *State of Art Report on Extent of Fluoride In Drinking Water and the Resulting Endemicty in India*; Fluorosis Resarch and Rural Development Foundation: New Delhi, India, 1999.

(19) *Detailed Information of Bauxite in India*; Geologic Survey of India: Hyderabad, India, 1994; Vol.,*211*; http://www.portal.gsi.gov.in/gsiDoc/pub/DID_Bauxite_WM.pdf.

(20) Buamah, R.; Mensah, R. A.; Salifu, A. Adsorption of fluoride from aqueous solution using low cost adsorbent. *Water Sci. Technol.: Water Supply* **2013**, *13* (2), 238−248.

(21) Craig, L.; Stillings, L.; Decker, D.; Thomas, M. J. Comparing activated alumina with indigenous laterite and bauxite as potential sorbents for removing fluoride from drinking water in Ghana. *Appl. Geochem.* **2015**, *56*, 50−66.

(22) Kalista, P. H. Defluoridation of High Fluoride Waters from Natural Water Sources by Using Soils Rich in Bauxite and Kaolinite. *J. Eng. Appl. Sci.* **2009**, *4* (4), 240−246.

(23) Kayira, C.; Sajidu, S.; Masamba, W.; Mwatseteza, J. Defluoridation of Groundwater Using Raw Bauxite: Kinetics and Thermodynamics. *Clean: Soil, Air, Water* **2014**, *42* (5), 546−551.

(24) Lavecchia, R.; Medici, F.; Piga, L.; Rinaldi, G.; Zuorro, A. Fluoride removal from water by adsorption on a high alumina content bauxite. *Chem. Eng. Trans.* **2012**, *26*, 225−230.

(25) Mohapatra, D.; Mishra, D.; Mishra, S. P.; Chaudhury, G. R.; Das, R. P. Use of oxide minerals to abate fluoride from water. *J. Colloid Interface Sci.* **2004**, *275* (2), 355−359.

(26) Sajidu, S.; Kayira, C.; Masamba, W.; Mwatseteza, J. Defluoridation of Groundwater Using Raw Bauxite: Rural Domestic Defluoridation Technology. *Environ. Nat. Resour. Res.* **2012**, *2* (3), 1−9.

(27) Sujana, M. G. G.; Anand, S. Fluoride removal studies from contaminated ground water by using bauxite. *Desalination* **2011**, *267* (2−3), 222−227.

(28) Thole, B.; Mtalo, F.; Masamba, W. Groundwater Defluoridation with Raw Bauxite, Gypsum, Magnesite, and Their Composites. *Clean: Soil, Air, Water* **2012**, *40* (11), 1222−1228.

(29) Dzomback, D. A.; Karamalidis, A. K. *Surface Complexation Modeling: Gibbsite*; Wiley: New York, 2010.

(30) Dodoo-Arhin, D.; Konadu, D. S.; Annan, E.; Buabeng, F. P.; Yaya, A. Fabrication and Characterisation of Ghanaian Bauxite Red Mud-Clay Composite Bricks for Construction Applications. *Am. J. Mater. Sci.* **2013**, *3* (5), 110−119.

(31) Authier-Martin, M.; Forte, G.; Ostap, S.; See, J. The mineralogy of bauxite for producing smelter-grade alumina. *JOM* **2001**, *53* (12), 36−40.

(32) Habuda-Stanić, M.; Ravančić, M. E.; Flanagan, A. A Review on Adsorption of Fluoride from Aqueous Solution. *Materials* **2014**, *7* (9), 6317−6366.

(33) Gorchev, H. G.; Ozolins, G.; World Health Organization. *Guidelines for Drinking-Water Quality*, 4th ed.; World Health Organization: Geneva, 2011; Vol. *38*; http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf.

(34) Phillips, B. L.; Tossell, J. A.; Casey, W. H. Experimental and theoretical treatment of elementary ligand exchange reactions in aluminum complexes. *Environ. Sci. Technol.* **1998**, *32* (19), 2865−2870.

(35) Prakash, S.; Das, B.; Venugopal, R. Surface Properties of Indian Hematite and Bauxite and Their Coating Mechanism with Colloidal Magnetite. *J. Sci. Ind. Res. (India).* **1999**, *58* (6), 436−442.

(36) Shrivastava, B. K.; Vani, A. Comparative Study of Defluoridation Technologies in India. *Asian J. Exp. Sci.* **2009**, *23* (1), 269−274.

(37) Hagvall, K.; Persson, P.; Karlsson, T. T. T. Speciation of aluminum in soils and stream waters: The importance of organic matter. *Chem. Geol.* **2015**, *417*, 32−43.