Title

Chapter 12 Addressing Groundwater Fluoride Contamination Using Inexpensively Processed Bauxite

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Addressing Groundwater Fluoride Contamination Using Inexpensively Processed Bauxite

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For authorship of this work, both authors share equal credit

Abstract: Globally, 200 million people are at risk of adverse health effects from drinking groundwater contaminated with high fluoride concentrations that exceed the World Health Organization's maximum contaminant limit (WHO-MCL = 1.5 ppm F^-). Although many defluoridation technologies have been demonstrated to work in the lab, most have proven inappropriate for impoverished rural regions of developing countries because they are cost-prohibitive, require skilled labor, or are difficult to scale. The authors of this chapter submit evidence for the use of bauxite, an aluminum-rich ore, as a potentially inexpensive, effective, and scalable defluoridation technology. Specifically, we present results from experimental studies that characterize globally diverse bauxite ores, elucidate fluoride removal mechanisms, and establish proof of concept that mildly processed bauxite can cost-effectively remediate field-relevant fluoride concentrations in synthetic and real groundwater matrices at field-relevant kinetics. We discuss practical implications of these research findings and highlight remaining challenges and unknowns that need to be further studied before implementing the proposed defluoridation process in the field.

Keywords: Fluoride, bauxite, groundwater, India, adsorption, drinking water treatment

1. Introduction

1.1. Sources and Distribution of Groundwater Fluoride

More than 200 million[1] people worldwide drink groundwater containing naturally[2] occurring fluoride concentrations[3] surpassing the World Health Organization's recommended maximum contaminant level (WHO-MCL) of 1.5 ppm F^-.[4] The fluoride-affected areas shown in Figure 1 include arid regions of India, China, the East African Rift Valley, the Middle East, northern Mexico, and central Argentina.[5,6] Although fluoride can enter the environment through effluents from human activities such as industry (e.g., aluminum smelters) and application of phosphate fertilizers, its high concentration in groundwater is *primarily* due to the dissolution of fluoride-rich minerals in sedimentary (e.g., limestone) and igneous (e.g., granite) rocks (Table 1).[2,3]

The concentration of fluoride in groundwater is controlled by the solubility of these fluoride-bearing minerals and is dependent on several factors including an aquifer's geochemical composition, alkalinity, pH, total dissolved solids, hardness, temperature, residence times, and climatic conditions.[7] Evidence indicates that most surface waters and shallower hand-dug wells often do not contain high fluoride concentrations due to high rainwater infiltration/dilution and short contact times between water and fluoride-bearing minerals in rocks.[6] In parts of the world where surface waters or shallow aquifers are rare, people must rely on accessing deep aquifers using boreholes or wells that reach deeper and access older aquifers – these can have higher fluoride concentrations due to lower groundwater flow rates and longer contact time available for equilibration. Fluoride concentrations in rainfall and surface waters are typically 1-2 orders of magnitude lower (less than 0.03 and 0.3 ppb F^-, respectively)[3] than in groundwater; however in certain volcanic areas with hydrothermal activity shallower aquifers can also be contaminated with fluoride due to the increased solubility of fluoride-rich minerals at higher temperatures.[8] In general, geochemists have demonstrated that deeper/older groundwater aquifers in arid climates characterized by low calcium ("soft water"), high temperatures, high bicarbonate alkalinity (high pH), high silica content, and high salinity/ionic strength, are more likely to have higher concentrations of fluoride due to increased solubility of the fluoride bearing minerals.[6–9]

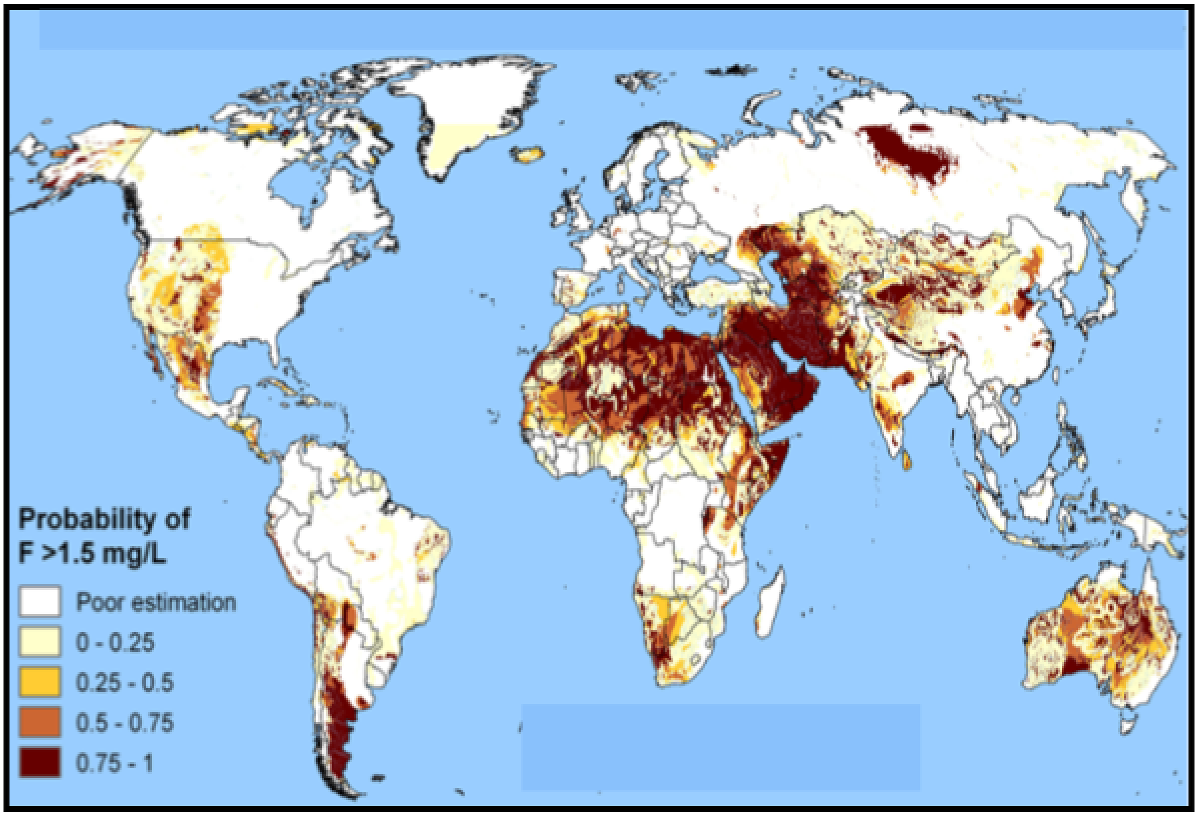
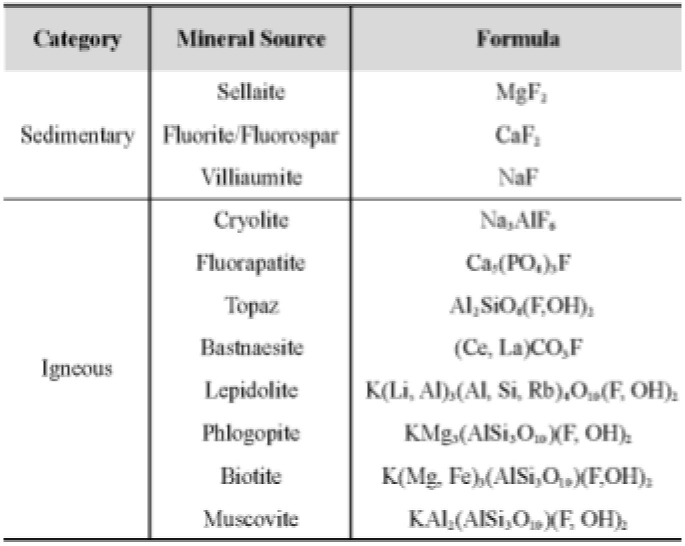


Figure 1. Probability of groundwater fluoride concentrations exceeding the WHO-MCL (1.5 mg F^-/L) according to EAWAG's predictive models from Amini et al., 2008. "Environmental Science & Technology", ""issue" : "10", "page" : "3662-3668", "title" : "Statistical Modeling of Global Geogenic Fluoride Contamination in Groundwaters", "volume" : "42"

Table 1. Mineral sources of fluoride found in sedimentary and igneous rocks. From Madhukar et al., 2014 "Journal of Water Pollution & Purification Research", "issue" : "2", "page" : "1-12", "A Review on Conventional and Alternative Methods for Defluoridation of Water", "volume" : "1"

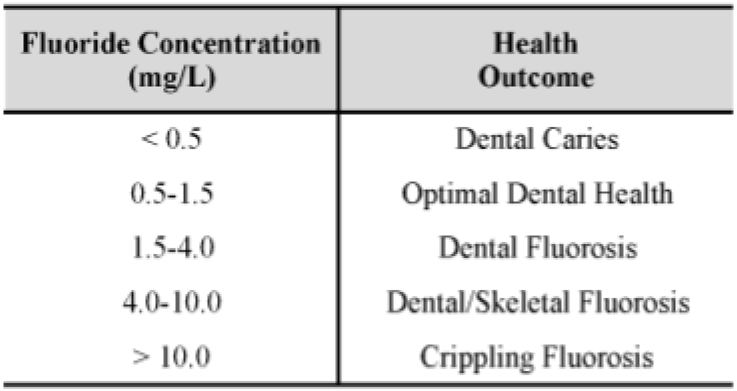


Category	Mineral Source	Formula
Sedimentary	Sellaite	MgF_2
	Fluorite/Fluorospar	CaF_2
	Villiaumite	NaF
Igneous	Cryolite	Na_3AlF_6
	Fluorapatite	$Ca_5(PO_4)_3F$
	Topaz	$Al_2SiO_4(F,OH)_2$
	Bastnaesite	$(Ce, La)CO_3F$
	Lepidolite	$K(Li, Al)_3(Al, Si, Rb)_4O_{10}(F, OH)_2$
	Phlogopite	$KMg_3(AlSi_3O_{10})(F, OH)_2$
	Biotite	$K(Mg, Fe)_3(AlSi_3O_{10})(F,OH)_2$
	Muscovite	$KAl_2(AlSi_3O_{10})(F, OH)_2$

1.2. Health Impacts of Excess Fluoride Intake

Fluoride at low concentrations (0.5-1.5 mg F^-/L) is often intentionally added to drinking water supplies to prevent dental caries by strengthening enamel through the formation of an acid resistant fluorapatite layer.[10] Owing to health concerns, the optimal level of fluoride in drinking water was lowered by the U.S. Department of Health and Human Services from 1.2 ppm (in force since 1962) to 0.7 ppm of F- (announced in 2015)[11]. However, prolonged exposure to excessive fluoride concentrations can cause anemia attributed to poor nutrient absorption, mottled enamel (dental fluorosis), and irreversible bone deformities in children at higher exposures (skeletal fluorosis) (Table 2).[5] The occurrence and intensity of fluorosis is dependent on the fluoride concentration in drinking water and additional factors including dietary habits/nutritional intake (e.g., calcium and Vitamin C) and overall physical activity. High fluoride content has been reported in major agricultural crops and edible products including various grains, vegetables, nuts, spices, meat, and beverages.[9] Figure 2 demonstrates the drastic effects of excess fluoride intake on children and adults as seen in Nalgonda District (Telangana, India), a region with endemic dental and skeletal fluorosis.

Table 2. Health effects of fluoride consumption. From Mohapatra et al., 2009. "Journal of Environmental Management", "Review of fluoride removal from drinking water", "volume" : "91"



Fluoride Concentration (mg/L)	Health Outcome
< 0.5	Dental Caries
0.5-1.5	Optimal Dental Health
1.5-4.0	Dental Fluorosis
4.0-10.0	Dental/Skeletal Fluorosis
> 10.0	Crippling Fluorosis

1.3. Defluoridation Methods: Membrane-Based, Precipitation, Adsorption, and Electrocoagulation

Membrane-based methods such as Reverse Osmosis (RO) and nanofiltration are widely used in advanced water treatment to remove minerals, pathogens, organic pollutants, total dissolved solids, and inorganic contaminants (e.g. F, Pb, etc.) found in wastewater, surface water, or groundwater. These methods are advantageous because they remove solutes larger than their pore size without extra chemical addition, work in a wide pH range, and do not have problems with ion interference.[9] However, due to their reliance on large external applied pressures to overcome the osmotic pressure and need for remineralization of product water, RO and nanofiltration have large capital and operational costs. Moreover, low water recovery rates and the generation of a concentrated salty brine waste stream create waste disposal problems, making these methods unacceptable for remote water-scarce regions.[12] Even atmospheric pressure membrane processes that do not require application of an external pressure (e.g., electrodialysis)[13] are energy-intensive because they require the use of direct current to control the selective flow of charged ions.[6,8] Membrane processes are non-selective; this implies that reducing the fluoride concentration from 6 ppm F^- to 1.5 ppm F^- also requires the removal of all other (generally harmless) ions by a factor of 4. Thus, so far as remediation of excessive levels of fluoride is the primary target concern, membrane processes result in wasted energy and wasted cost. In general, membrane processes are difficult to implement in a rural settling due to their requirement for skilled operators, prohibitively high capital cost, and need for regular replacement (or regeneration) of membranes after frequent fouling and degradation.[3,14]

Precipitation methods rely on the addition of aluminum, calcium, or magnesium salts (e.g., $CaCl_2$, $CaSO_4$, $CaMg(CO_3)_2$, MgO, $Mg(OH)_2$) to remove fluoride through the formation of solids such as fluorite (CaF_2), fluorapatite ($Ca_5(PO_4)_3F$), and sellaite (MgF_2).[15] In particular, the Nalgonda Technique (NT) developed in 1961 by the India's NEERI (National Environmental Engineering Research Institute) involves rapid mixing of lime ($Ca(OH)_2$), alum ($Al_2(SO_4)_3$), and bleaching powder into fluoride-contaminated groundwater followed by flocculation, sedimentation, and filtration of precipitated fluorite solids.[15] Alum enhances formation and settling of floc precipitates and also generates aluminum hydroxide ($Al(OH)_3$), which further removes fluoride through adsorption.[9] Despite the apparent simplicity in its design, the following barriers have prevented the NT from being scaled-up and treating high groundwater fluoride concentrations (> 5 ppm F^-) effectively: i) reduced fluorite precipitation in the presence of phosphate ions,[14] ii) high residual concentrations of sulfate and aluminum present in the treated water[9] due to large alum doses (700-1200 ppm), and, iii) low defluoridation efficiency (< 70%) due to fluorite's solubility limit and formation of aqueous aluminofluoro complexes.[6,9,12] Although the NT has been implemented in resource constrained regions in India, Kenya, Senegal, and Tanzania[14], users have complained about the salty taste of the treated drinking water, high maintenance cost of the community plants, need for a large sludge drying bed area, requirement for additional chemicals to soften the treated water, and lack of process automation.[6,9]

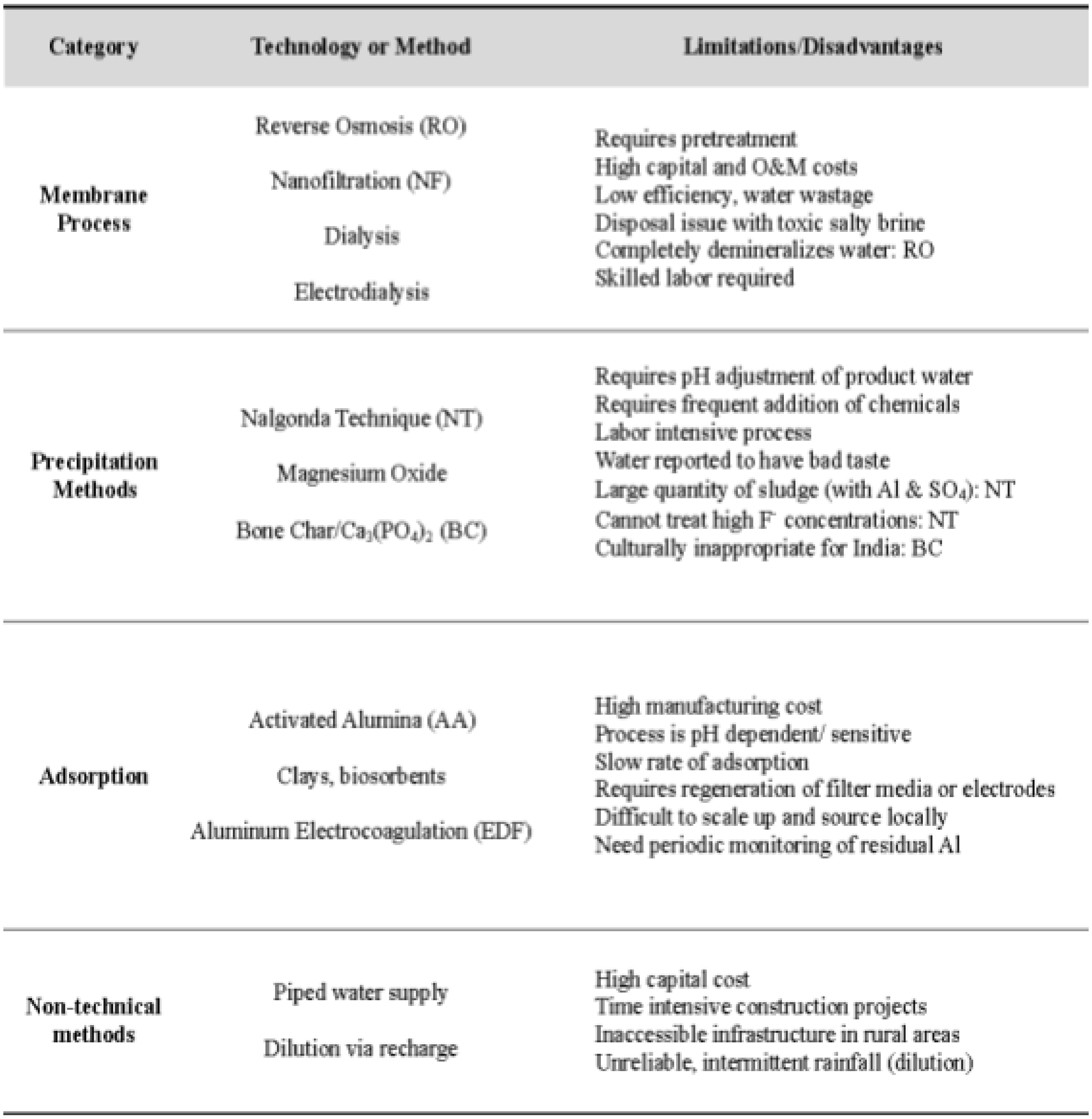
In contrast to pressure-driven membrane systems and precipitation techniques, adsorption methods are widely used due to their relative ease of operation and cost effectiveness. Adsorbent media (used in filter columns or batch systems) must be either discarded or regenerated as the active material becomes saturated.[15] Bone char (BC) is a low-cost adsorbent method used in East Africa that is prepared by heating animal bones in a furnace (at T=300-800 °C for 1-3 hours) to increase surface area and remove the organic content in the bones.[8,15] The major components of BC include the primary active component, hydroxyapatite (57-80%), calcium carbonate (6-10%), and carbon (7-10%).[8] To increase fluoride removal efficiency of the BC substrate, calcium phosphate pellets are often added to catalyze additional contact precipitation of fluorite and fluorapatite solids.[8,15] The primary issues limiting the widespread use of BC as a defluoridation technology include lack of religious/cultural acceptance, problems routinely sourcing the raw material at the required scale, and users' dislike of the taste and odor of treated water.[3,16,17] Other fluoride-specific adsorbents include ion exchange resins and various low-cost organic and inorganic materials.[6,18] Naturally-derived defluoridation adsorbents include biosorbents (e.g., moringa and tamarind seeds, carboxylated chitosan and alginate beads, citrus peels, tea ash, and egg shell powder), fly ash, clays (e.g., zeolites, bentonite, kaolinite, smectites, montmorillonite, and layered double hydroxides), and metal oxides (e.g., of Fe, Al, Ti, etc.).[3,15,19] In particular, Activated Alumina (AA) filters are widely used due to their effectiveness, relative affordability for the upper middle class,[20] and because of the strong affinity between aluminum and fluoride. AA is produced by first extracting aluminum oxides from bauxite, a composite ore that also contains oxides of iron, silicon, titanium, and other trace minerals. Industrial refining methods such as the Bayer process utilize pressurized sodium hydroxide and temperatures exceeding 1000°C to eliminate impurities, concentrate the Al fraction of bauxite, and activate alumina (Al_2O_3) through further calcination. As a result of these processing methods, AA generation is highly resource-intensive in terms of capital and operating costs, energy, and greenhouse gas emissions.[21] Additionally, AA requires caustic chemicals for regeneration[9,13] and also needs trained operators in handling of such chemicals; these are not always locally available.[3]

Another method, electrolytic defluoridation (EDF), relies on the oxidation of aluminum electrodes to generate in-situ aluminum hydroxide ($Al(OH)_3$) adsorbent, removing the need for handling caustic chemicals or establishing a supply chain of chemicals.[8] Although EDF can effectively treat fluoride contaminated groundwater, produces minimal sludge, and is based on an easily fabricated and scalable modular system,[22] it faces numerous challenges including lack of proper maintenance of plants not operated by private vendors and a potentially prohibitive capital cost for plant construction.

1.4. Long-term Sustainability of Existing Fluoride Removal Technologies

Numerous factors affect the long term success of a defluoridation technology in the field including technical parameters (e.g., fluoride removal effectiveness, added contaminants in treated water), operational elements (e.g., material sourcing, waste disposal, need for skilled labor in maintenance/operation), and social variables (e.g., cost, user adoption, community participation).[3] Table 3 outlines a summary of challenges associated with various defluoridation methods currently used in the developing world. Based on case studies from countries where these technologies have been implemented in remote rural settings (e.g., India, Kenya, and Ethiopia), a majority of these methods appear to unsustainable and ineffective due to issues including unaffordability and maintenance difficulties (e.g., for RO, AA, NT,[6] and EDF),[12] chemical and mechanical equipment supply chain challenges (e.g., for NT), taste of product water (e.g., for NT and BC), cultural/religious prohibitions (e.g., for BC)[12], and difficulty scaling up (e.g., for BC).[23]

Table 3. Limitations of existing defluoridation technologies. From Mohapatra et al., 2009. "DOI" : "10.1016/j.jenvman.2009.08.015", "Review of fluoride removal from drinking water", "volume" : "91" 2012. "Chemical Reviews", "issue" : "4", "2012", "page" : "2454-2466", "Fluoride in Drinking Water and Defluoridation of Water". "volume" : "112"



Category	Technology or Method	Limitations/Disadvantages
Membrane Process	Reverse Osmosis (RO) Nanofiltration (NF) Dialysis Electrodialysis	Requires pretreatment High capital and O&M costs Low efficiency, water wastage Disposal issue with toxic salty brine Completely demineralizes water: RO Skilled labor required
Precipitation Methods	Nalgonda Technique (NT) Magnesium Oxide Bone Char/$Ca_3(PO_4)_2$ (BC)	Requires pH adjustment of product water Requires frequent addition of chemicals Labor intensive process Water reported to have bad taste Large quantity of sludge (with Al & SO_4): NT Cannot treat high F^- concentrations: NT Culturally inappropriate for India: BC
Adsorption	Activated Alumina (AA) Clays, biosorbents Aluminum Electrocoagulation (EDF)	High manufacturing cost Process is pH dependent/ sensitive Slow rate of adsorption Requires regeneration of filter media or electrodes Difficult to scale up and source locally Need periodic monitoring of residual Al
Non-technical methods	Piped water supply Dilution via recharge	High capital cost Time intensive construction projects Inaccessible infrastructure in rural areas Unreliable, intermittent rainfall (dilution)

2. Bauxite-Based Defluoridation Process

2.1. Process Overview

The recently patented bauxite-based defluoridation process proposes the use of mildly processed (powdered) bauxite ore as a single-use dispersive batch media in a community-scale system.[24] Bauxite, a globally abundant ore of aluminum, is a viable, effective, and low-cost fluoride adsorbent alternative to AA. Raw bauxite ore is comprised of a primary aluminum oxide mineral known as gibbsite ($Al(OH)_3$)[25–27] and its material cost ($30/tonne)[28] is 50x lower than the heavily processed and purified end product, activated alumina (($1500/tonne).[29] Earlier researchers have reported bauxite's ability to adsorb fluoride[30–32] but many of them did not explore the specific dose of bauxite needed to remediate high fluoride concentrations in contaminated groundwater down to the WHO-MCL (1.5 ppm F^-). Bauxite deposits are present worldwide, including in countries with fluoride-contaminated regions (e.g., India, Ghana, Tanzania, and China). In particular, one-third of the global affected population at risk of developing fluorosis (66 million people)[1] live in India, which is also home to the 5th largest bauxite deposits (3037 million tonnes).[33]

Overall, the bauxite-based defluoridation process described in this chapter offers a potential defluoridation method that is (a) effective at remediating fluoride contaminated groundwater, (b) affordable to impoverished households, (c) easy to operate and maintain without skilled labor, (d) culturally appropriate and (e) widely available in fluoride-affected regions worldwide (Figure 3).

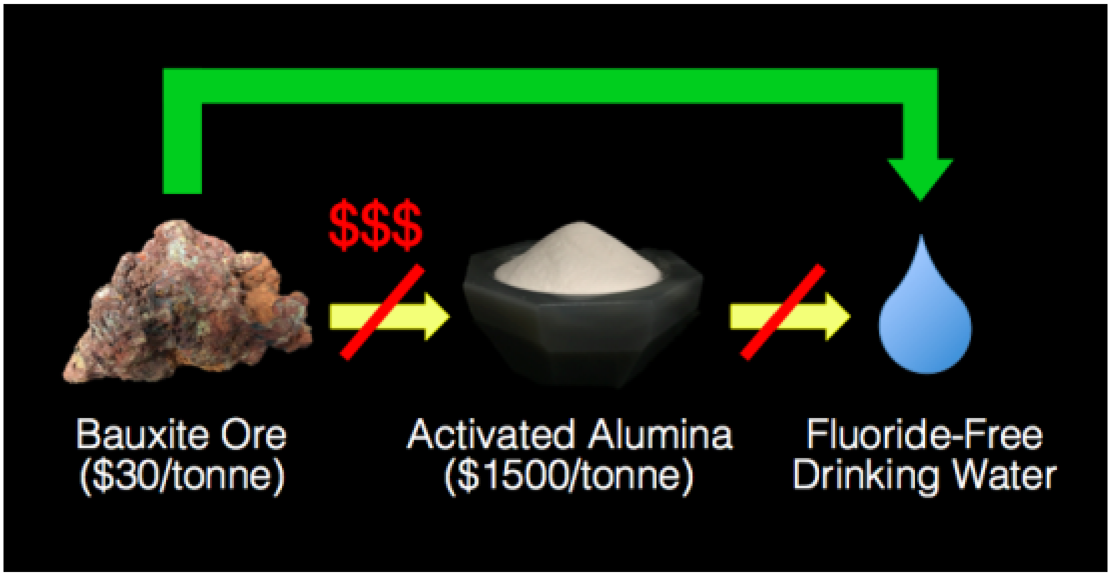


Figure 3. Flow diagram demonstrating cost savings associated with using raw bauxite as opposed to activated alumina as an adsorbent material for remediating fluoride contaminated groundwater.

In upcoming sections, we present results from batch adsorption, kinetic, mechanistic, and competition studies in synthetic and real groundwater matrices, molecular characterization of globally diverse bauxite ores, and comprehensive cost analyses comparing bauxite to AA and comparing various combinatorial bauxite processing/treatment scenarios. These results strongly suggest that bauxite-based defluoridation is a cost-competitive alternative to AA and is a potentially transformative technology to substantially improve access to safe water for tens of millions of people in fluoride-affected remote, rural, and resource-constrained communities. We conclude by highlighting some remaining technical, operational, and social challenges that must be addressed before implementing, scaling up, and commercializing bauxite-based defluoridation as an appropriate technology for fluoride remediation in rural impoverished settlings.

2.2. Material Characterization of Global Raw Bauxite Ores

Raw bauxite ores sourced from India, Guinea, Ghana, and USA were characterized and compared in terms of elemental and mineral composition, fluoride adsorption affinity and capacity, surface area, and equilibrium suspension pH[24]. Figure 4 shows images of each bauxite ore as received (before milling), after milling, and with Scanning Electron Microscopy (SEM).

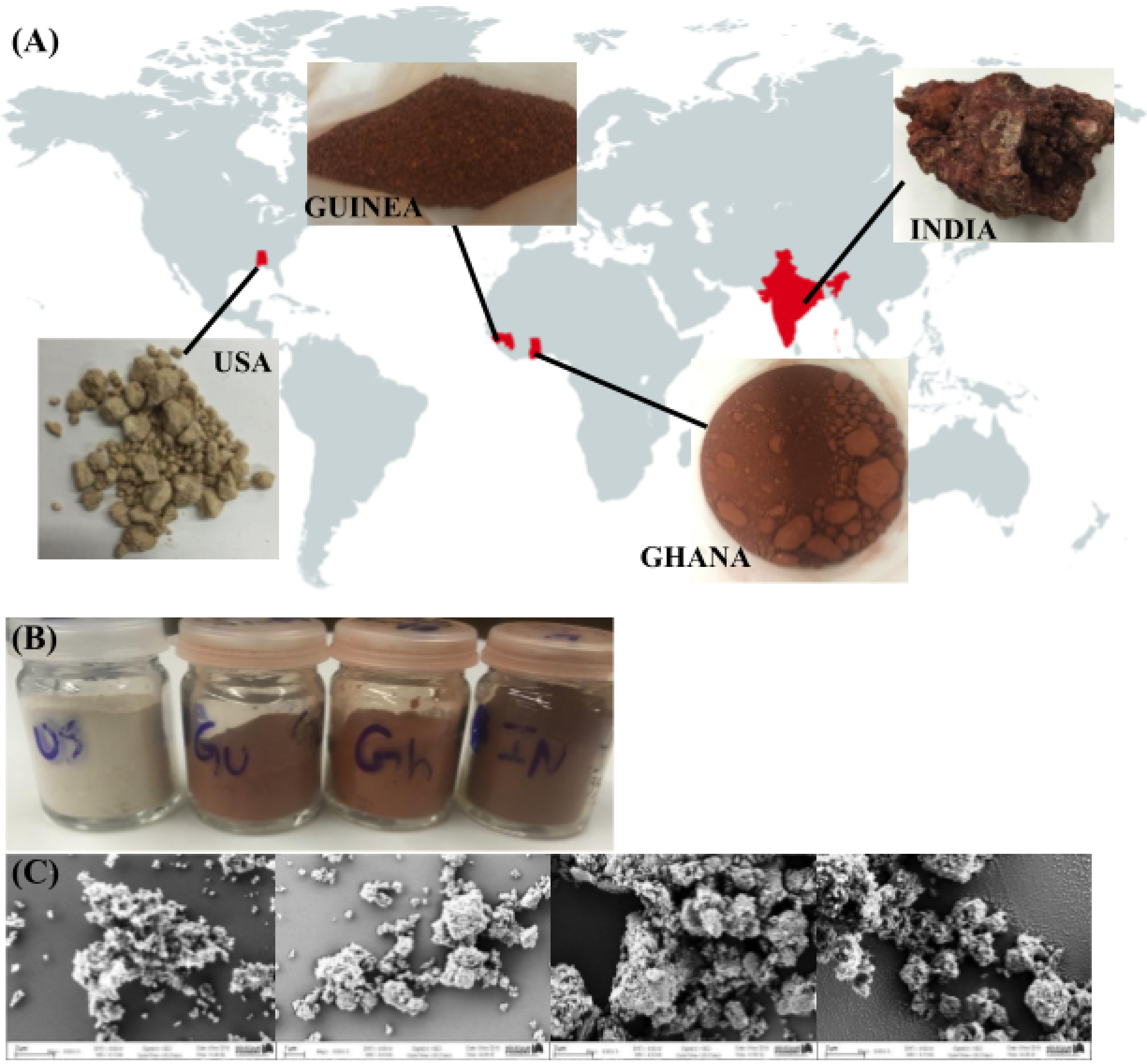


Figure 4. Images of raw bauxite ores shown **(A)** as received (before ball milling), **(B)** after ball milling and **(C)** at 8K magnification using a Scanning Electron Microscope (SEM). Geographical origin of bauxite ore samples as presented from left to right in all panels: USA, Guinea, Ghana, and India.

In terms of fluoride removal performance, experiments conducted in synthetic groundwater (prepared using recipes from the British Geologic Survey[3]) to reduce fluoride from an initial concentration of 10 mg F^-/L to below the WHO-MCL of 1.5 mg F^-/L showed that Guinea, Ghana, and USA bauxites performed similarly, with minimum required doses of approximately 9.5-10.6 ± 1.0 g/L (Figure 5A).[24] In contrast, India bauxite had a significantly lower performance, with a minimum required dose of 22.8 ± 1.0 g/L. Additional studies using different levels of processing, solution matrices, and initial fluoride concentrations indicate that a variety of bauxite ores (from Malawi, Texas, Tanzania, etc.) require higher doses the samples tested in this study, possibly due to coarser particle sizes (and hence, lower active surface area for adsorption).[31,34–41] Research indicates that differences in chemical composition of geographically diverse bauxite ores can greatly impact their specific fluoride removal performance.

X-ray Fluorescence (XRF) data shown in Figure 5B indicates that all four bauxite ores contained approximately 22-29% Al and < 2% Ti. Ghana, India, and Guinea bauxites had significant and comparable fractions of Fe (~11-14%); Si was found in all bauxite ores, and its content ranged from 0.5% in Ghana bauxite to approximately 9% in USA bauxite. The small differences (3.8-6.9%) in Al content between India bauxite and bauxite from the 3 other sites are unlikely to cause the a greater than two-fold difference in the minimum required dose in Figure 5A, as suggested by the similar fluoride removal performance of Guinea and USA bauxites despite their 3.2% difference in Al content. Similarly, the observed differences in fluoride removal performance do not appear to be correlated with the Fe, Si, and Ti contents and phases. The Ca content in most bauxite ores was below the detection limit except in India bauxite, which contained 1.8% Ca. Figure 5C 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 USA bauxite and calcium carbonate ($CaCO_3$) was found only in India bauxite.

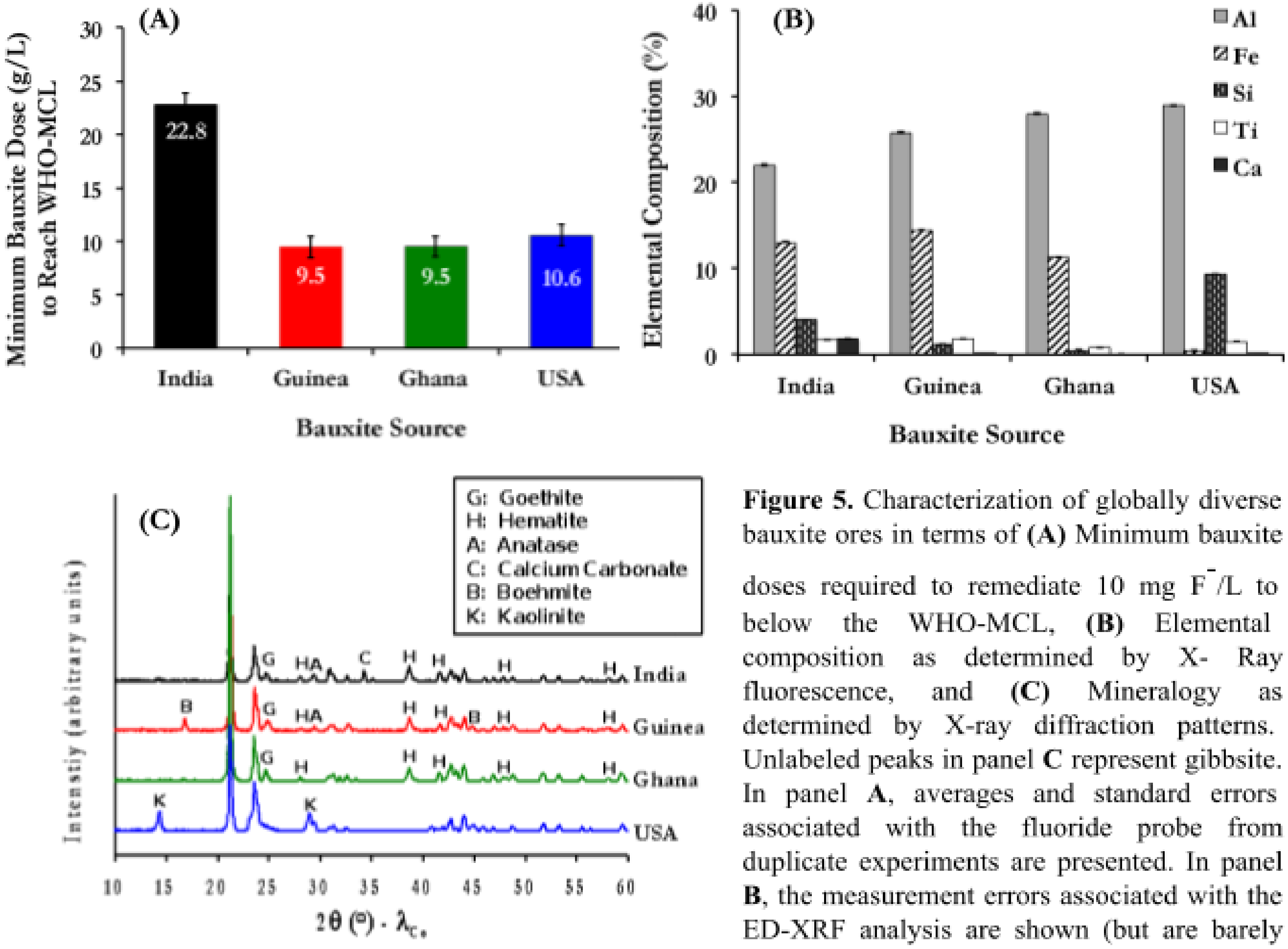
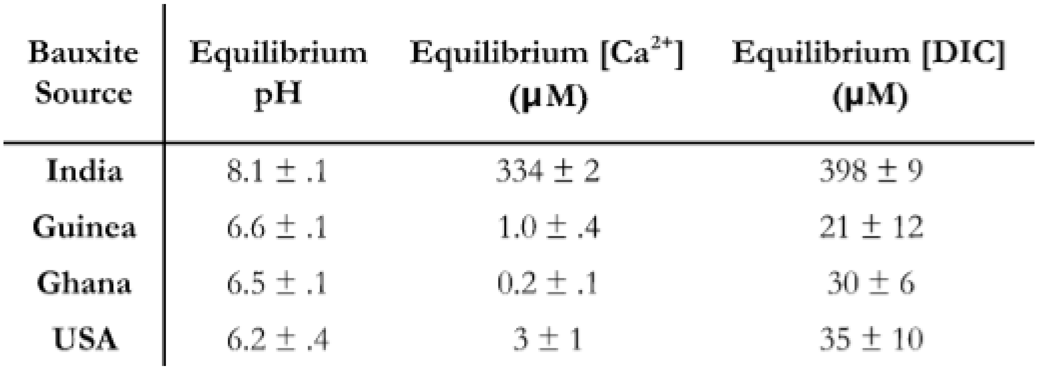


Figure 5. Characterization of globally diverse bauxite ores in terms of **(A)** Minimum bauxite doses required to remediate 10 mg F^-/L to below the WHO-MCL, **(B)** Elemental composition as determined by X- Ray fluorescence, and **(C)** Mineralogy as determined by X-ray diffraction patterns. Unlabeled peaks in panel **C** represent gibbsite. In panel **A**, averages and standard errors associated with the fluoride probe from duplicate experiments are presented. In panel **B**, the measurement errors associated with the ED-XRF analysis are shown (but are barely visible in the as-printed figure).

The equilibrium solution pH and composition (24 hours after bauxite addition) are reported in Table 4. India bauxite had a significantly higher equilibrium pH (pH 8.1 ± 0.1), compared to Guinea, Ghana, and USA bauxites (pH 6.6 ± 0.1, 6.5 ± 0.1, and 6.2 ± 0.4 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 in line with the previous XRD and XRF data (shown in Figures 5B and 5C) and are indicative of the dissolution of $CaCO_3$, which is present only in Indian bauxite and correlated with its lower fluoride removal performance.



Bauxite Source	Equilibrium pH	Equilibrium $[Ca^{2+}]$ (μM)	Equilibrium [DIC] (μM)
India	8.1 ± .1	334 ± 2	398 ± 9
Guinea	6.6 ± .1	1.0 ± .4	21 ± 12
Ghana	6.5 ± .1	0.2 ± .1	30 ± 6
USA	6.2 ± .4	3 ± 1	35 ± 10

Table 4. Characterization of a suspension (initially 35 mM NaCl) in equilibrium with each bauxite ore in terms of pH, dissolved calcium, and dissolved inorganic carbon (DIC). Averages from duplicate experiments and reported errors are presented as the larger 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).

2.3. Spectroscopic Studies

The nature of fluoride adsorption (e.g., specificity and strength of Al-F bond), formation of complexes at surface sites on bauxite, and interaction of bauxite's surface functional groups with fluoride in different conditions (e.g., pH, temperature, NOM, co-occurring ions, etc.) can be studied using spectroscopic methods. In addition to using FTIR to study –OH peaks and other functional groups at different wavelengths, the aluminum fluoride bond and overall coordination environment can be studied at multiple scales using different techniques. Some options include X-ray photoelectron spectroscopy (XPS, to quantify elemental composition of the top 10nm of the surface and determine binding energies), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), to visualize surface topography and elemental mapping).

Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectra can also be used gather detailed localized structural information around the aluminum metal centers in bauxite. Researchers have investigated the electronic structures, molecular orbitals, and coordination numbers and states of crystalline and amorphous materials by comparing measured and calculated XANES at the F K-edges of aluminum fluoride solids polymorphs (AlF_3)[42] and at the Al K-edge of transitional poorly-crystalline aluminas (Al_2O_3)[43] and other aluminum oxide minerals (e.g., gibbsite, boehmite, diaspora, kaolinite, etc.).[44] Other groups have used Nuclear Magnetic Resonance (NMR, 27Al and 19F)[45] to study the coordination geometry of aqueous fluoroaluminate complexes (AlF_4^-) or have relied on combined spectroscopic studies (e.g., XAS and IR)[46] to characterize the geometric and electronic structural characteristics of aqueous aluminum-organic complexes (e.g., Al-EDTA, Al-oxalate, $AlCl_3$, etc.)[47] and determine the impact of varying pH and NOM on aluminum speciation in soils and streams.[46]

2.4. Fluoride Removal Mechanisms

Horizontal Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy(HATR-FTIR) measurements shown in Figure 6A suggest that bauxite -similar to the pure gibbsite mineral- also forms a specific, inner-sphere complex with fluoride, and this takes place through ion exchange of F^- with –OH groups. In particular, a decrease in transmittance in –OH peaks (3650-3350 cm^{-1}) is observed upon fluoride adsorption, and previous FTIR studies confirm that the peak at ~3400 cm^{-1} is characteristic of the stretching vibration of hydroxyl groups on the surface of gibbsite. [48,49] Figure 6B corroborates that weak, outer-sphere electrostatic interactions do not play a major role in fluoride adsorption on bauxite, consistent with the primary role of inner-sphere complexation previously reported for pure gibbsite.[25,50,51] In particular, varying ionic strength over 2 orders of magnitude (1-100 mM) does not affect fluoride removal, despite increased charge screening of the adsorbent surface. A visual representation of the inner-sphere complexation mechanism is shown in Figure 6C.

3. Fluoride Removal in Synthetic and Real Groundwater

3.1. Adsorption Isotherms: Effect of Initial Fluoride Concentration on Removal

The relationships between adsorption density (in mg F^-/g bauxite) and equilibrium fluoride concentration (in mg F^-/L water) for each bauxite ore are shown in the experimental adsorption isotherms in Figure 7, obtained at a fixed pH of 6 (controlled using MES), near the pH of minimum solubility of gibbsite. Additional details of the experimental methodology (e.g., solution composition, contact time, fluoride measurement techniques etc.) can be found in the original manuscript[24]. These isotherms were best fit to and described by the Freundlich isotherm

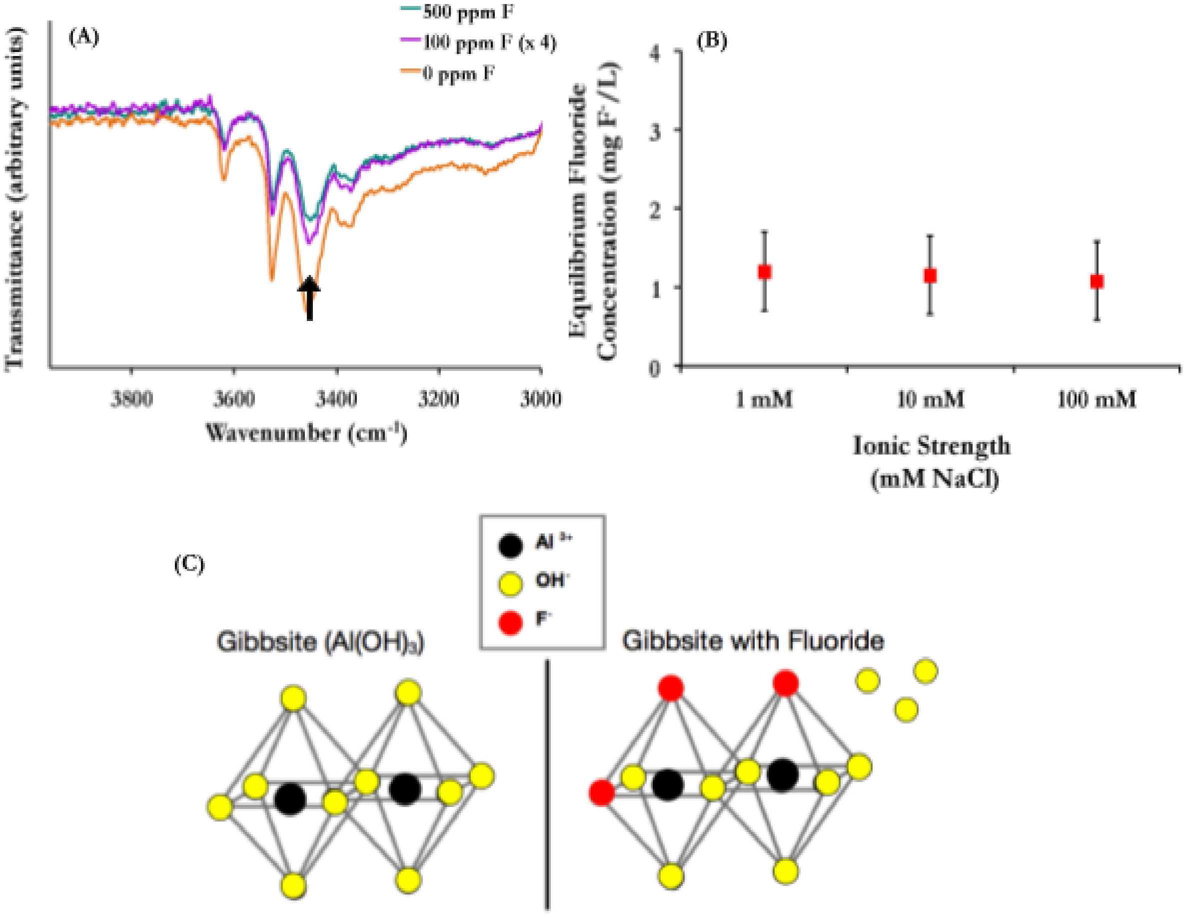
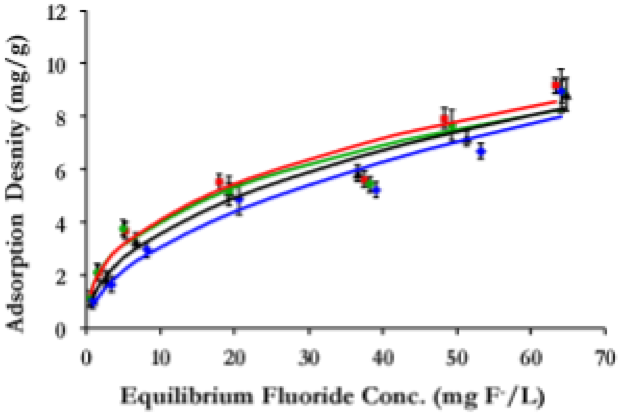


Figure 6. Investigation of fluoride removal mechanisms through **(A)** HATR-FTIR absorbance spectra for Guinea bauxite (2 g/L dose) with an initial fluoride loading of 0, 100 x 4 (replaced every hour for 4 hours), and 500 ppm F^- (loaded once), respectively, **(B)** Study on effect of ionic strength on fluoride removal using Guinea bauxite. Initial [F^-]: 10 mg F^-/L; Dose: 10g/L, and **(C)** Diagram demonstrates the removal mechanism of fluoride on gibbsite as through ion exchange between fluoride (F-) and hydroxyl groups (OH-) on the surface of gibbsite. Image adapted from Dr. Katherine Alfredo's dissertation.The University of Texas Austin,: "Drinking Water Treatment by Alum Coagulation: Competition Among Fluoride, Natural Organic Matter, and Aluminum"

model, $q=KC_e^{1/n}$, 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 shape of the Freundlich isotherm indicates potential multi-site complexation, especially given the first dip, which indicates saturation of a high-affinity site. The fitted Freundlich parameters (K and 1/n) of the 4 ores showed no statistically significant difference, which indicates that all four bauxites have a similar intrinsic capacity and affinity for fluoride (when pH is controlled). This finding, in conjunction with similar measured surface areas of all 4 bauxite ores (ranging from 14.1 ± 4.0 to 17.2 ± 2.5 m^2/g) indicates that differences in intrinsic adsorption capacity or affinity did not cause differences in fluoride removal efficiencies seen between the 4 bauxite ores in the earlier Figure 6A (e.g., a lower K value for USA bauxite compared to Guinea and Ghana bauxites did not result in significantly lower fluoride removal).



	K	1/n	Surface Area (m²/g)
▲ India	1.3	0.45	17.2 ± 1.4
■ Guinea	1.7	0.39	17.2 ± 2.5
● Ghana	1.7	0.38	14.1 ± 4.0
◆ USA	1.0	0.51	16.4 ± 1.3

Figure 7. Adsorption isotherms of the 4 bauxite ores showing the effect of equilibrium fluoride concentration on fluoride removal. Adsorption isotherms were characterized after 24 hours in 50 mM MES + 5 mM HCO_3 (ionic strength ~ 61mM), 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). Averages from duplicate experiments are presented and error bars are the larger of the range from duplicate tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe, Tristar II 3020).

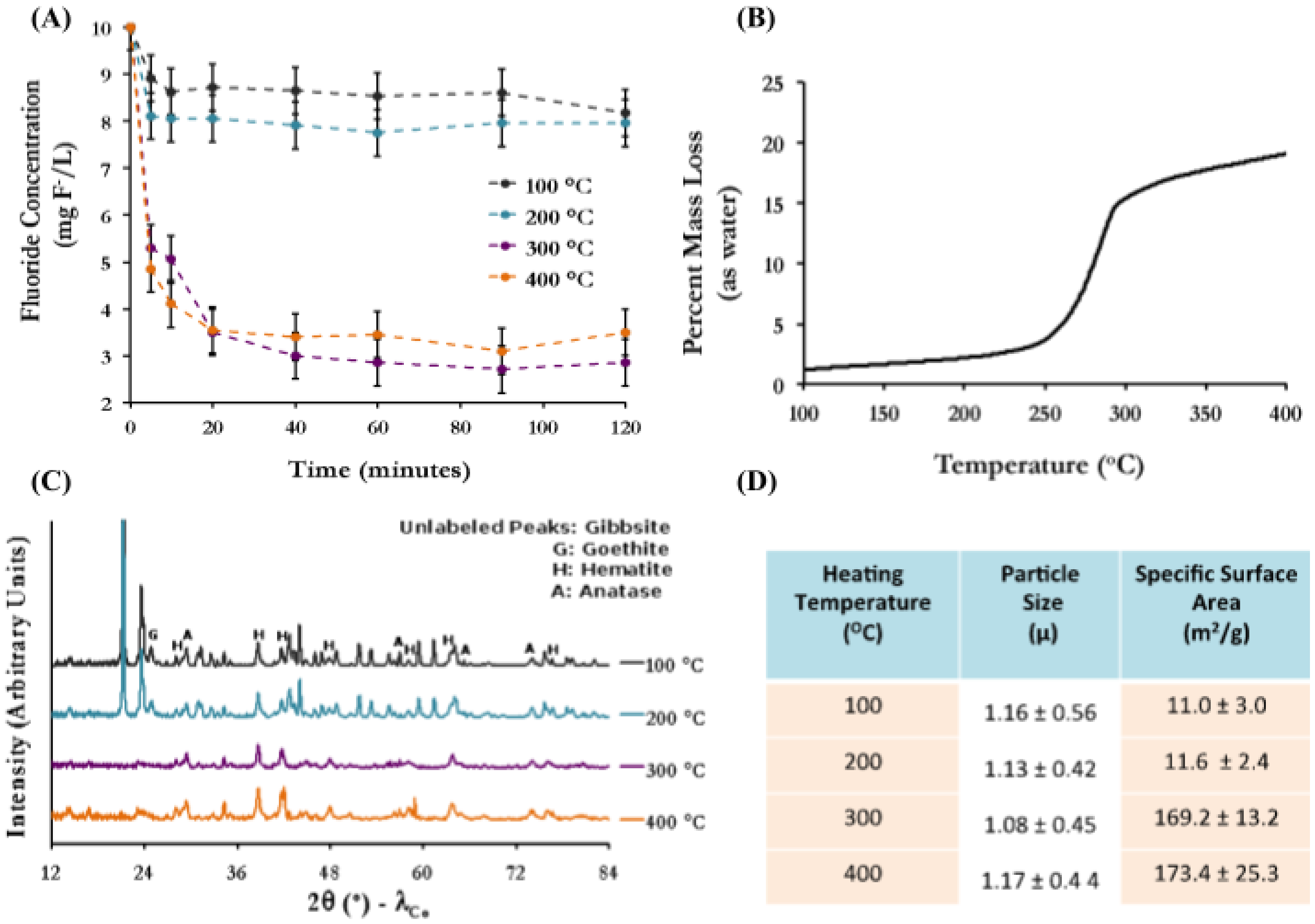
3.2. Effect of Thermal Activation on Bauxite and Fluoride Removal

India represents one-third of the global fluorosis burden (66 million people).[1,52] Excess fluoride contamination of groundwater occurs in approximately 70% of the states in the country.[53] However, India is also the fifth major global producer and exporter of bauxite[33], so there exists a promising opportunity to better utilize the abundant bauxite ore available throughout India rather than importing more efficient raw ores from other countries for affordable fluoride remediation.

Research to modify the performance of Indian bauxite through mild, low-cost thermal treatment successfully demonstrates the potential use of this locally sourced material as a practical and inexpensive route towards alleviation of a significant source of chronic human suffering.[54] In these experiments and other following studies mentioned in this chapter, the complex synthetic Sri Lankan groundwater matrix recipe provided by the British Geologic Survey was chosen to stay in line with previous work using the same Indian bauxite and to provide a conservative estimate of costs. Figure 8A shows that heating Indian bauxite samples at temperatures greater than 200°C produces a substantial improvement in fluoride removal performance in batch adsorption studies using bauxite as a one-time-use dispersive media. Fluoride adsorption using bauxite was rapid; within 20 minutes the system was close to reaching equilibrium; fluoride concentrations did not vary greatly between 20 min. and 2 hr. This initial rapid uptake is likely due to surface adsorption and the flattening of the curve after 20 minutes represents diffusion of fluoride into interior pores of the micron-sized bauxite particles. Researchers studying other aluminum-based adsorbents used for fluoride removal have reported similar kinetic trends [55–57].

Thermogravimetric Analysis (TGA) of the Indian bauxite ore shows that the majority of mass loss (approximately 15%, due to dehydroxylation) occurred at temperatures between 250°C and 300°C, and the compound given off was confirmed via mass spectrometry (MS) to be water (Figure 8B).

The X-ray Diffraction (XRD) patterns of Indian bauxite heated at four temperatures (100°C, 200°C, 300°C, and 400°C) as shown in Figure 8C indicate that the main crystalline Al phase is gibbsite, and additional crystalline Fe oxide phases (goethite and hematite) and Ti oxide phase (anatase) were detected. The diffraction patterns for crystalline gibbsite in bauxite samples heated at 100°C and 200°C are indistinguishable (Figure 8C truncates the 100°C peaks for convenient display) and these same major peaks are absent when the bauxite is heated at 300°C or 400°C. The iron and titanium oxide phases present in bauxite do not show the same structural deformations or changes in crystallinity at 300°C or 400°C. Figure 8D demonstrates that although the particle size remains constant across Indian bauxite samples heated between 100°C and 400°C, the surface area increases dramatically (> 15X) from approximately 11 m^2/g at 100°C to 170 m^2/g at 300°C.



Heating Temperature (°C)	Particle Size (μ)	Specific Surface Area (m^2/g)
100	1.16 ± 0.56	11.0 ± 3.0
200	1.13 ± 0.42	11.6 ± 2.4
300	1.08 ± 0.45	169.2 ± 13.2
400	1.17 ± 0.44	173.4 ± 25.3

Figure 8. Characterization of thermally-activated Indian bauxite in terms of **(A)** Fluoride removal kinetics (raw dose 10 g/L, synthetic Sri Lankan groundwater of initial pH 8.7), **(B)** Mass loss measured using Thermogravimetric Analysis and Mass Spectrometry (TGA-MS), **(C)** Mineralogy as determined by X-ray diffraction patterns, and **(D)** Particle size and specific surface area measurements. In panels **A** and **D**, averages from duplicate experiments are presented and errors are the largest of the range from duplicate tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe, DLS, Tristar II 3020).

Taken together, the results in Figure 8 show that the major impacts of heating Indian bauxite occur between 200°C and 300°C, indicated by the decrease in crystallinity and increase in surface area due to loss of structural waters of hydration. Other studies have reported a similar structural deformation of crystalline gibbsite minerals present in bauxite when heated between 200°C and 300°C, as it transforms to the more amorphous boehmite phase through partial dehydroxylation (e.g., loss of two waters of hydration).[30,32,50,58] Figure 9 shows SEM images of Indian bauxite samples heated at 100°C and 300°C.

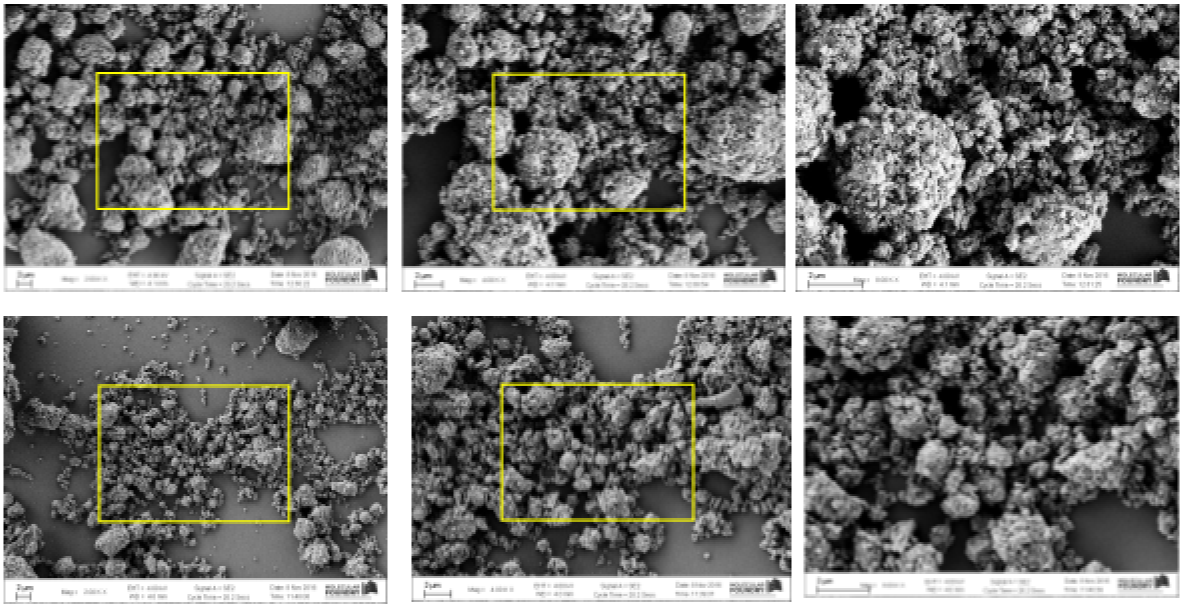


Figure 9. Images of milled Indian bauxite ores heated at 100°C (top row) and 300°C (bottom row) at 2K, 4K, and 8K magnification (left to right) using a Scanning Electron Microscope (SEM). Yellow boxes highlight the region being magnified and shown in the subsequent magnification.

3.3. Effect of Solution pH on Fluoride Removal/Desorption and Leaching of Metals

In addition to mild thermal activation of Indian bauxite ore to improve its performance, researchers also report a straightforward route to enhance its fluoride removal performance through the acidification of fluoride-contaminated groundwater using readily available mineral acids (HCl) or carbon dioxide gas (CO_2)[54].

Adsorption envelopes presented in Figure 10 demonstrate that solution 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. In particular, bauxite ores from Guinea, Ghana, USA, and India all had an optimal adsorption pH of 5.0-6.0. Furthermore, the adsorption envelopes of all 4 bauxite ores were close to identical, indicating a similar fluoride adsorption behavior throughout a wide pH range (4-8). More generally, 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.[25]

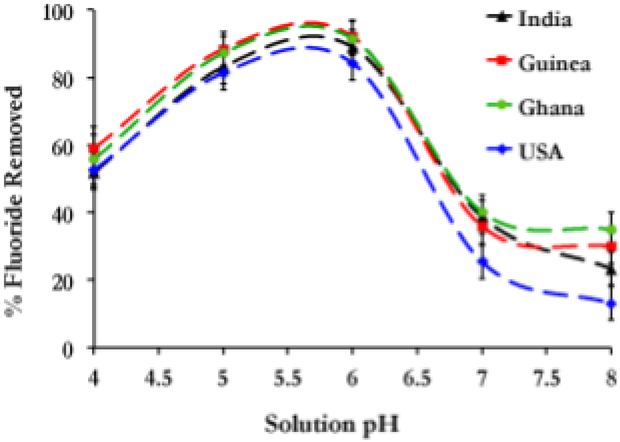


Figure 10. Adsorption envelopes of the 4 bauxite ores showing the effect of solution pH on fluoride removal. Adsorption envelopes were characterized in 5 mM HCO_3^- + buffers, at constant ionic strength, with dashed lines drawn to guide the eye and not to represent a model fit. Averages from duplicate experiments are presented and error bars are the larger of the range from duplicate tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

Figure 11 shows the enhancement of fluoride removal performance of Indian bauxite a result of lowering the alkaline initial pH of Sri Lankan groundwater (pH ~ 8.7) down to 6.0 ±0.1 through addition of HCl or bubbling of CO_2 gas. In all the experiments summarized in Figure 11, a dose of 10 g/L (=0.169 g/20 mL) of raw Indian bauxite (with or without heating) was added to synthetic Sri Lankan groundwater containing an initial fluoride concentration of 10 mg F^-/L. Regardless of the source of acidification or whether the acid source was added continually over the duration of the experiment or initially in bulk, the improvement in fluoride removal due to groundwater acidification is consistent. At a dose of 10 g/L, bauxite heated to 300°C and added to acidified water is close to nearing the WHO-MCl for fluoride, but a much larger dose of 100°C bauxite is required to remediate an initial concentration of 10 mg F^-/L.

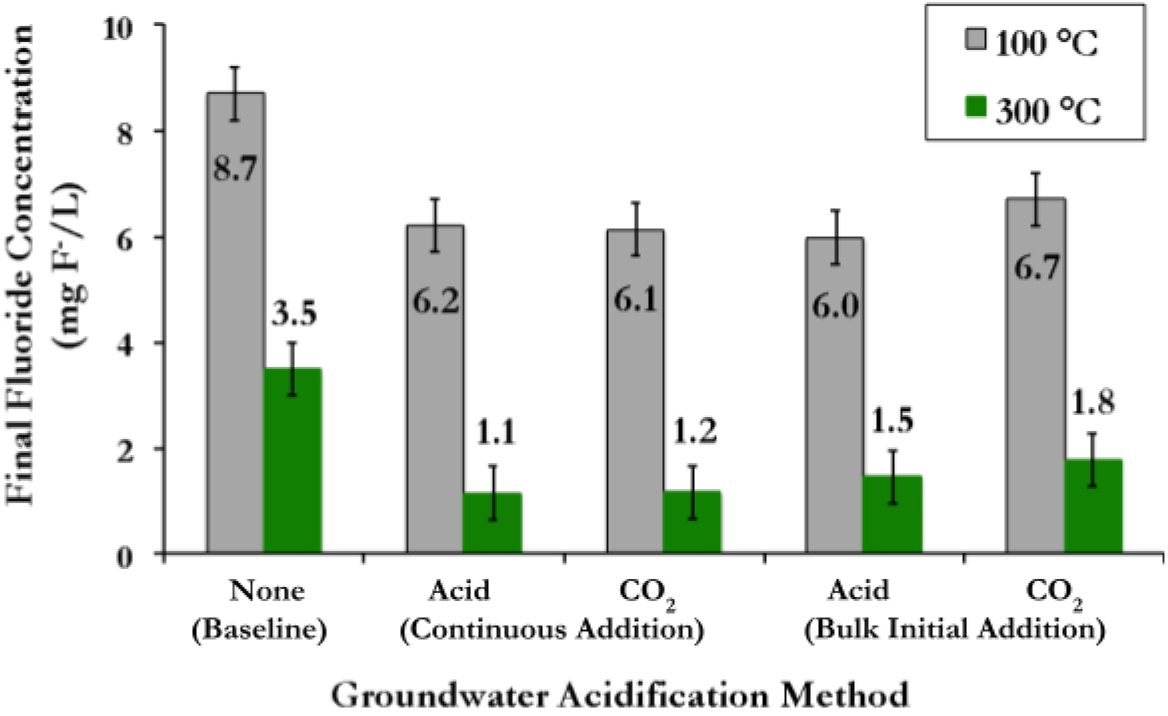


Figure 11. Effect of various groundwater acidification methods on fluoride removal (initial concentration 10 mg F⁻/L). Batch adsorption experiments were conducted for 20 minutes in synthetic Sri Lankan groundwater using Indian bauxite (raw dose 10 g/L) heated at 100 °C or 300 °C. Solution pH was maintained at 6.0 ± 0.5 through either continuous or bulk initial addition of acid (1.1 M HCl) or CO_2 (rate 0.25 L/min). Averages are presented and error bars are the larger of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

Regardless of the source of acid (mineral acid or carbonic acid), fluoride desorption was not observed during a 1-hour (no mixing) settling period (Figure 12). Even in cases where groundwater was acidified with CO_2 and solution pH rose slightly (from pH 6.0 to pH 6.2) during the settling period due to CO_2 evolution, adsorbed fluoride did not return to the groundwater matrix. This finding that fluoride remains adsorbed after 1 hour of post-adsorption settling is promising support for testing the performance of this defluoridation process in the field.

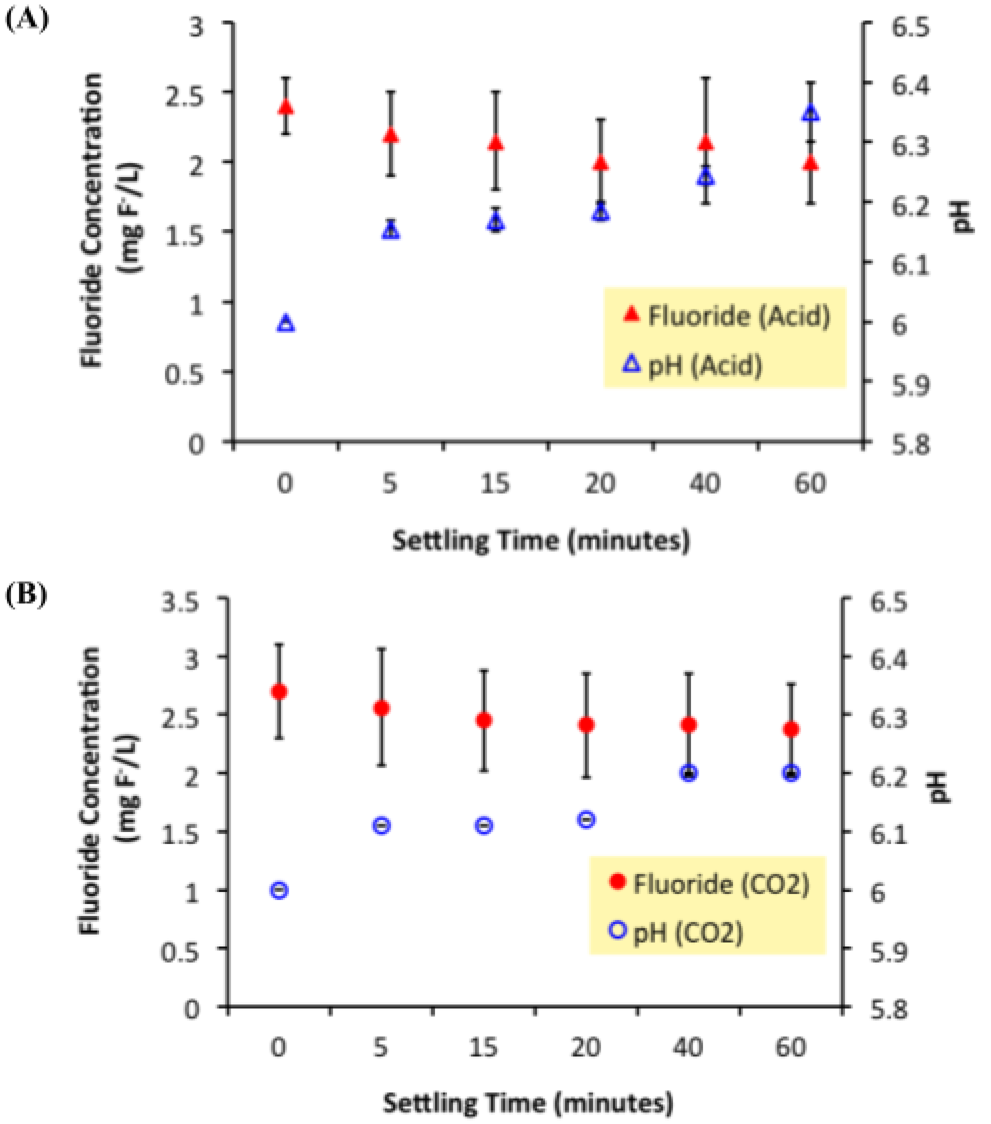
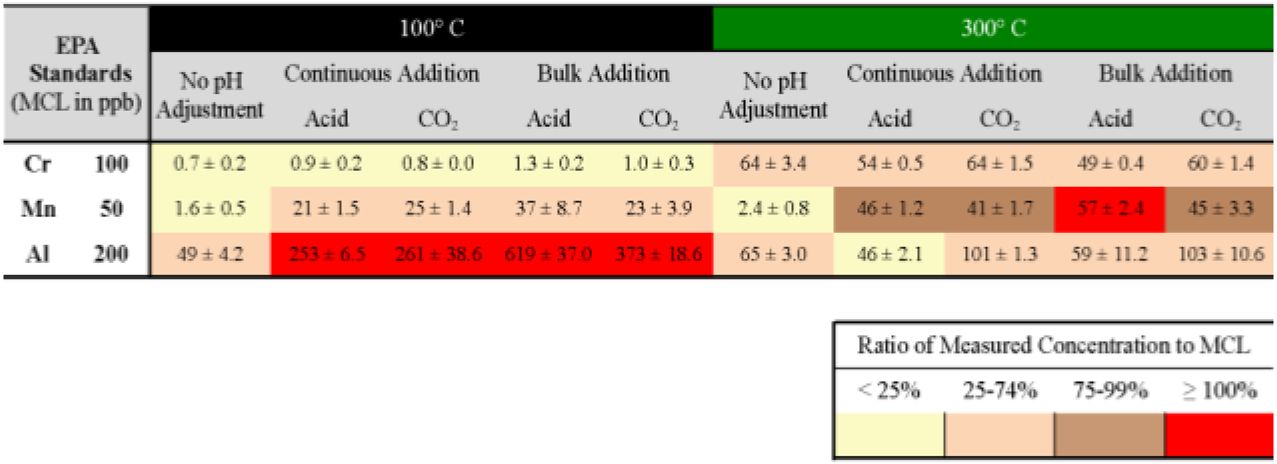


Figure 12. Tracking changes in fluoride concentration and solution pH during 1 hour of settling after 20-minutes of batch adsorption in Sri Lankan groundwater using **(A)** Acid (HCl) and **(B)** CO_2 for pH adjustment. Averages are presented and error bars are the largest of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

Product water resulting from the treatment scenarios in Figure 11 is compliant with EPA guidelines for contaminants regulated in drinking water for some scenarios but not for others. In all scenarios, the aqueous concentrations of Ag, As, Cd, Cu, Fe, Pb, Se, and Zn were below 25% of the EPA-MCL or Secondary MCL (SMCL). Table 5 highlights three elements of concern (e.g., Cr, Mn, and Al) that approached or exceeded the EPA limit in the product water for some of the scenarios outlined in Fig. 5. Our data indicate that Cr dissolution was more prominent in treatment scenarios using 300°C bauxite, perhaps due to a temperature-dependent increase in oxidation rate of insoluble Cr (III) to its more soluble Cr (VI) form. Although the Cr concentrations in our product water were below 75% of the current national EPA-MCL (100 ppb total Cr), the primary drinking water standard for Cr (VI) is being revisited by the US-EPA and has recently been lowered in particular states (e.g., CA, where the EPA-MCL for total Cr is 50 ppb).

In scenarios where 300°C bauxite is added to acidified groundwater, Mn concentrations tend to be higher and the concentration of Mn exceeds the EPA-MCL (50 ppb Mn) for one particular treatment scenario where 300°C bauxite is used in groundwater acidified through bulk acid addition. It is also noted that for all treatment scenarios where 100°C bauxite is added to acidified groundwater, the concentration of Al in the product water exceeds the EPA-MCL (200 ppb Al). One explanation for why Al dissolution is less prominent in 300°C bauxite is that bauxite dehydroxylates to boehmite in that temperature range and boehmite is generally less soluble than gibbsite, as reported by other theoretical studies.[59,60]

Table 5. Concentrations (in ppb) of metals of concern in product water from batch experiments outlined in Figure 11 measured using ICP-MS. Averages and the range from duplicate batch adsorption tests are presented.



EPA Standards (MCL in ppb)		100° C					300° C				
		No pH Adjustment	Continuous Addition		Bulk Addition		No pH Adjustment	Continuous Addition		Bulk Addition	
			Acid	CO_2	Acid	CO_2		Acid	CO_2	Acid	CO_2
Cr	**100**	0.7 ± 0.2	0.9 ± 0.2	0.8 ± 0.0	1.3 ± 0.2	1.0 ± 0.3	64 ± 3.4	54 ± 0.5	64 ± 1.5	49 ± 0.4	60 ± 1.4
Mn	**50**	1.6 ± 0.5	21 ± 1.5	25 ± 1.4	37 ± 8.7	23 ± 3.9	2.4 ± 0.8	46 ± 1.2	41 ± 1.7	57 ± 2.4	45 ± 3.3
Al	**200**	49 ± 4.2	253 ± 6.5	261 ± 38.6	619 ± 37.0	373 ± 18.6	65 ± 3.0	46 ± 2.1	101 ± 1.3	59 ± 11.2	103 ± 10.6

Ratio of Measured Concentration to MCL			
< 25%	25-74%	75-99%	≥ 100%
🟨	🟧	🟫	🟥

Further research must be conducted to measure the concentration of total dissolved solids (TDS) of product water in the scenarios where groundwater acidification is with HCl, because the addition of HCl could increase the TDS and adversely affect the taste of the product water.

An additional "extreme stress-test" conducted following the US EPA's Toxicity Characteristic Leaching Procedure (TCLP) to expose the bauxite-based defluoridation adsorbent material to harsher conditions (e.g., drastic pH range, higher doses, longer contact times) detected As and Mn (17 ppb and 2 ppm, respectively) above their WHO-MCL and EPA-SMCL (10 ppb and 0.05 ppm, respectively). Measurements of toxic metals (Cd, Cr, Pb, Hg) along with numerous other contaminants were all below the detection limit in the leachate (to be published, Buckley et. al 2018).

4. Cost Analyses

4.1. Schematic Process Flow in Bauxite Processing and Water Treatment Plants

To evaluate the cost tradeoffs of different combinatorial treatment methods for implementing community-scale bauxite-based defluoridation in India, we explored one particular supply chain model for providing processed bauxite to water treatment plants. As schematically shown in Figure 13A, the model assumes that raw bauxite ore is first transported from a mine to a central processing plant (CPP) located 500 km away, the average estimated distance between bauxite-producing mines and Indian districts with endemic skeletal fluorosis[61]. The CPP in this analysis was designed to have appropriate infrastructure to process (e.g., crush, mill, and heat-treat) enough raw bauxite for 500 villages of 1,000 people each. Each village is modeled to have a separate community-scale water treatment plant (WTP) and be located at an average of approximately 25 km from the CPP. The average village population was chosen based on a previous publication[62] and the population density for the circular area covered by the CPP was calculated (~300 people/km^2) using Indian Census data[63] for the three most heavily affected states with endemic fluorosis (i.e., Gujarat, Rajasthan, and Madhya Pradesh).

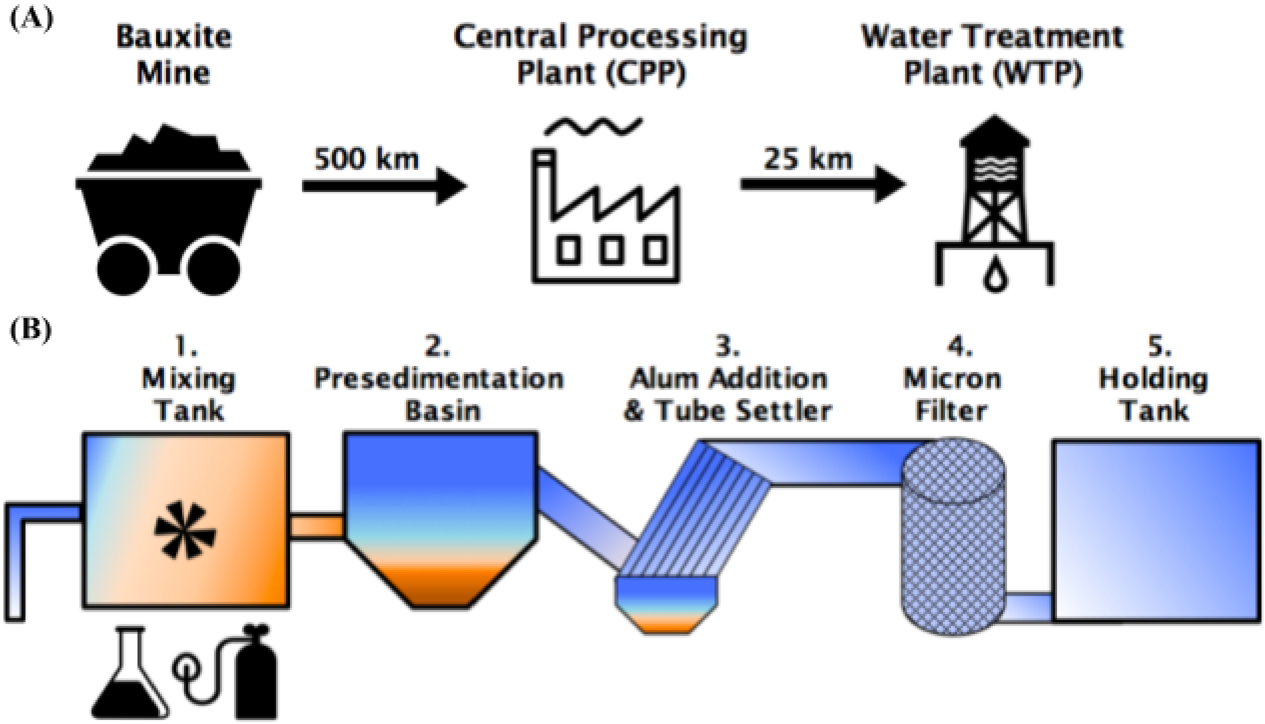


Figure 13. Schematic representation of **(A)** Flow of mined bauxite ore to central processing plants and water treatment plants and **(B)** Treatment processes at a village-scale community water treatment plant. Bauxite is injected and mixed into pumped groundwater for 20 minutes after which it enters a presedimentation basin. The supernatant water is then dosed with 30 mg/L alum and run through a tube settler and final micron filter for additional particle removal to ensure WHO turbidity standards are met (< 1 NTU). Treated water is stored in a holding tank, which can be connected to automated dispensing machines or kiosks for sale of water. Icons for the bauxite mine, central processing plant, water treatment plant, acid beaker, and CO_2 cylinder were sourced from the Noun Project and respectively created by Georgiana Ionescu, Ralf Schmitzer, and Dan Hetteix, Gabor Fulop and Arosh Khan.

The field-pilot WTP shown in Figure 13B is designed operate at a minimum capacity of 5000 L water/day to meet the daily need for the village, assuming a per capita use of 5 L/person. This value was selected as a field-relevant compromise between anecdotal reports of daily per capita water purchase value in rural regions (2 L/person) from small commercial water providers in India (e.g., WaterLife, and WaterHealth (India)) and the WHO's recommendation for daily per capita drinking and cooking water needs (7.5 L/person).[64] The WTP was modeled to have a mixing tank (for addition and mixing of treated bauxite and acid/CO_2 to fluoride-contaminated groundwater), a presedimentation basin (for initial clarification), alum addition prior to running water through a tube settler and micron filter (to reduce water turbidity to < 1 NTU), and a holding tank (for storing treated water).

Machinery in the CPP and WTPs are assumed to have a lifetime of 10 years, a conservative estimate that also accounts for the possibility of premature obsolescence due to up-scaling and growth. For each piece of equipment (e.g., tanks), consumables (e.g., bauxite ore, alum, acid, and CO_2), and reasonable values for shipping, cost estimates were solicited for products currently available in (or for delivery to) India. The costs of specific portions of the WTP (namely the pumps, tube settler, micron filter, and power supply) were obtained from actual fabrication cost estimates of a 10,000 L/day field implementation of an electrochemical arsenic remediation technology in operation since April 2016 in West Bengal, India.[65] This large 10,000L pilot demonstration plant[66] involves daily processing twice the amount of water as the model WTP (5000L), so these estimates are especially conservative.

All current market prices are outlined in a spreadsheet found at https://tinyurl.com/cpp-wtp-cost-analysis. This spreadsheet is divided into four primary sections reflecting the stages of processing: mining (raw bauxite costs); transportation; central processing plant; and water treatment plant costs and contains references and information relating to the capital costs and electricity consumption of each piece of equipment (including equipment model numbers, commercial supplier companies, lifetime, duration, and usage assumptions). Electricity costs were based on the power rating of the machinery; the number of hours of use based on laboratory tests; and an assumed electricity tariff of $0.07/kWh. The WTP was assumed to be able to operate up to 16 hours per day.

Since the primary purpose of the cost estimate is to compare processing options, the analysis ignores the time value of money and uncertainties around the exchange rate between U.S. dollars and Indian rupees. All estimates are given in recent (2017) USD assuming an exchange rate of 67 rupees to the dollar. Overall, estimates include core technology costs and exclude costs of land, operator salaries, building infrastructure, quality control, public education, marketing, and outreach to target populations These latter costs were excluded as they contain greater uncertainty and since they are common to all treatment options, they do not contribute to differentiating between the different treatment options.

4.2. Potential Application Scenario: India

A hypothetical case study to apply the model described in Section 4.1 presents a map of districts in India with reported endemic fluorosis, excess groundwater fluoride contamination, and locations of bauxite mines (Figure 14A). The map was generated using data outlined and sourced in the following spreadsheet: https://tinyurl.com/fluoride-bauxite-locations. Polygon shape files were sourced from the GADM database of Global Administrative Areas (http://gadm.org) and the map data was visualized using R libraries (raster, sp, maptools, and ggplot2). Details regarding distances between locations and population densities are also provided in the spreadsheet above. The example in Figure 14B demonstrates the feasibility of the assumptions used in the general cost model by showing that the bauxite used in this study (from

Visakhapatnam) could realistically be transported to a CPP in Nalgonda District (a fluorosis affected region located approximately 500km away).

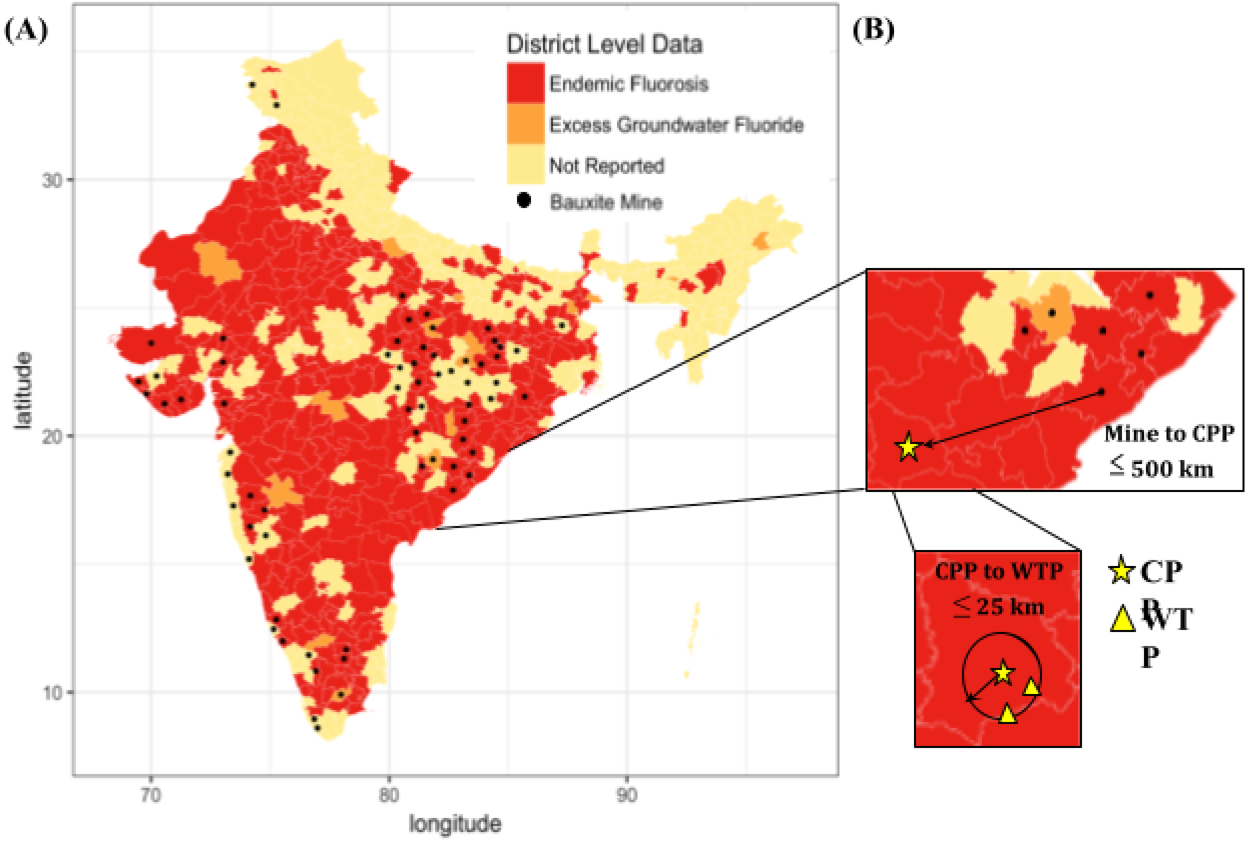


Figure 14. Maps of **A)** districts in India with endemic fluorosis (red), excess groundwater fluoride (orange), and bauxite mines locations (black dots), and **B)** A realistic example of the relative locations of a bauxite mine in Visakhapatnam, a central processing plant (CPP, shown as a yellow star) in Nalgonda District, and water treatment plants (WTP, shown as yellow triangles). This figure was generated using R visualization packages. Map boundaries are per data in the following spreadsheet (https://tinyurl.com/fluoride-bauxite-locations) and may be inaccurate. Polygon shapefiles were sourced from the GADM database of Global Administrative Areas (http://gadm.org) and the map data was visualized using R libraries (raster, sp, maptools, and ggplot2).

4.3. Comparing Combinatorial Treatment Scenarios

To provide empirical inputs for calculating the raw material cost of bauxite, consumables, and electrical equipment used in the bauxite processing and water treatment plants, batch adsorption experimen ts were conducted for the different combinatorial treatment methods (e.g., heating bauxite and acidifying groundwater with acid/CO_2). Figure 15 presents the minimum bauxite doses required to remediate 10 mg F^-/L down to the WHO-MCL in synthetic groundwater. For the baseline (no acidification) scenario, the minimum required dose for 100°C bauxite (~287 g/L) is impractically large, approximately 13.5x larger than that for 300°C bauxite (~21 g/L). Groundwater acidification by mineral acid or CO_2, reduces the required doses, but not in the same proportion; the resulting average minimum required dose for 100°C bauxite (~77 g/L) is approximately 6.4x larger than that for 300°C bauxite (~12 g/L). As a result, based on doses alone, the most practically feasible options for defluoridation with manageable material transport and handling requirements appear to be any of the scenarios using heat-activated bauxite (T=300°C).

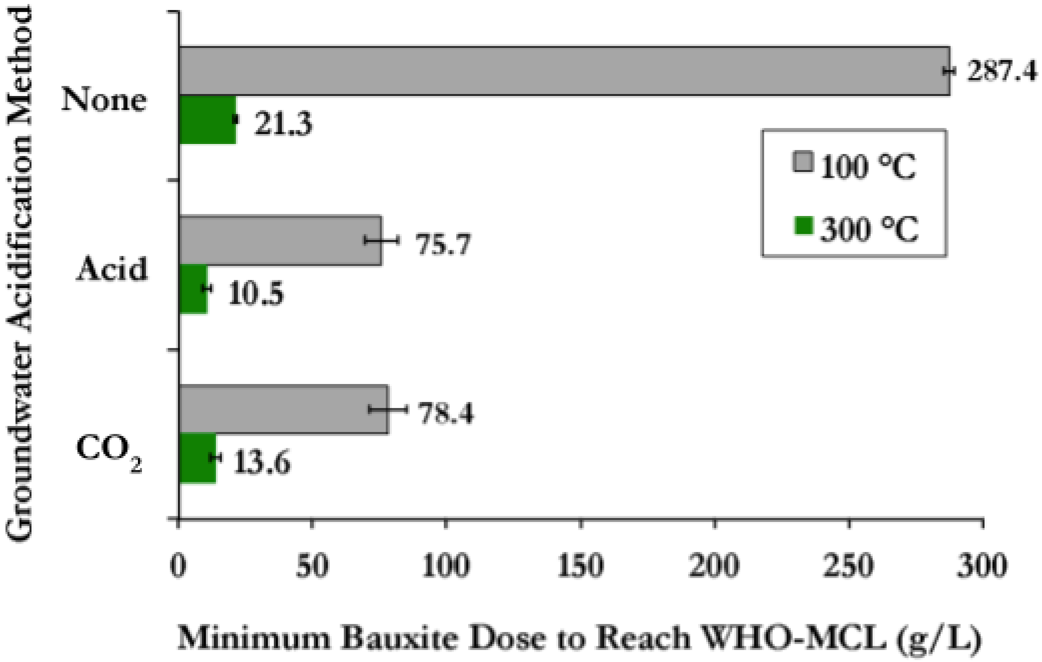
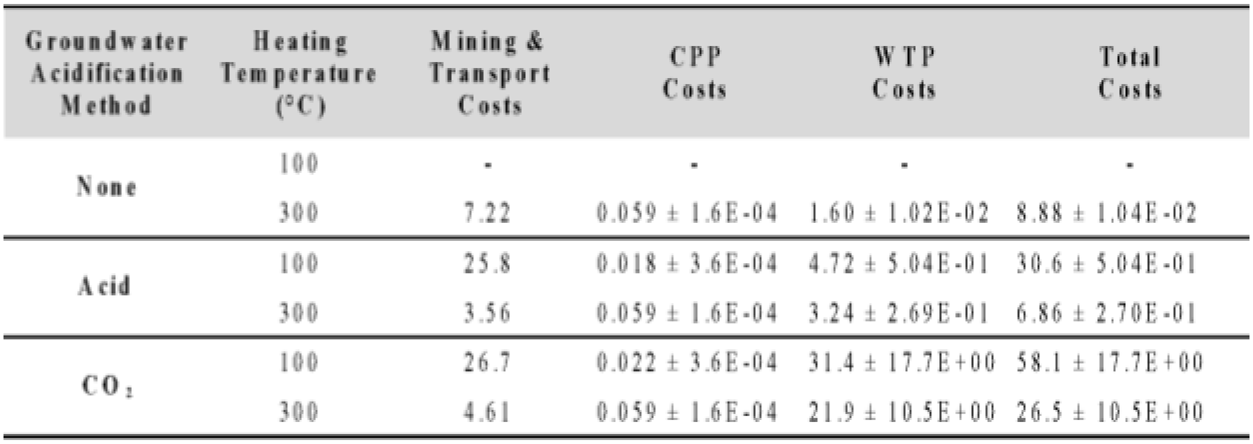


Figure 15. Comparison of minimum required doses to remediate an initial fluoride concentration of 10 ppm F^- to the WHO-MCL (1.5 ppm F^-) for various combinatorial treatment scenarios. Batch experiments run for 20 minutes in Sri Lanka groundwater. In certain scenarios, groundwater pH was maintained at 6.0 ± 0.5 through addition of acid (1.1 M HCl) or CO_2 (rate 0.25 L/min). Averages are presented and error bars are the larger of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

In addition, Table 6 presents the total cost for treating water for each of the possible processing methods. This analysis takes into account the capital and operational costs of the entire bauxite processing and water treatment process. Numbers are reported in USD per person per year and where multiple cost estimates were obtained, the median value is reported plus/minus the low-end range. The results indicate that the total cost of the unheated bauxite is up to an order of magnitude higher than for the heated bauxite. This implies that the additional cost of purchasing and operating an oven is offset by the substantially higher material and transportation costs associated with using the much larger required doses of raw unheated bauxite. The general trends were as expected; the raw material and transportation costs were significantly higher for the processes requiring additional bauxite. On the other hand, the cost of the CPP step was lower for the unheated bauxite since no oven would be required. The costs at the WTP were highly dependent on the costs of hydrochloric acid and CO_2 for the cases where they are used.

We found that using (300°C) heated bauxite in groundwater acidified with hydrochloric acid ("300-acid") was the cheapest option at \$6.86 per person per year. This option benefits from significantly reduced raw material and transportation costs relative to the other options, though it makes the WTP process more expensive due to the cost of the acid. The second cheapest option was using heated bauxite without the additional groundwater acidification step ("300-only"); the total cost of this process was \$8.88 per person per year. The other three options (300-CO_2, 100-acid, and 100-CO_2) were significantly more expensive than the cheapest option. However, the empirically calculated mass of CO_2 used in this cost estimate is likely much higher than the actual amount of CO_2 that would be needed, in practice, to adjust the groundwater pH to 6.0. This big difference between the calculated empirical and theoretical CO_2 requirements is likely due to inefficiencies in the small-scale lab study, which was set up primarily to explore whether CO_2 could be used in this treatment scenario, rather than to achieve the minimal amount of CO_2 that would be needed. In a well-engineered full-scale reactor where external CO_2 is delivered for acidification, one would dissolve CO_2 under pressure in an aliquot of water that is then delivered to the reactor and well-mixed rapidly, rather than directly bubbling gas into the water. Annual pre-capita treatment cost estimates recalculated using the theoretical values of CO_2 indicate that although the CO_2 treatment options become notably cheaper (i.e., \$32 vs. \$58 for the 100C-CO_2 scenario and \$9.5 vs. \$27 for the 300-CO_2 scenario), both options are still more expensive than the 300-acid (\$6.86) and 300-only (\$ 8.88) scenarios.

Table 6. Treatment costs (in $ per person per year) of combinatorial treatment scenarios including heating Indian bauxite and acidifying groundwater using acid or CO_2. Costs for the baseline treatment scenario (no heating or groundwater acidification) are not reported because the minimum required dose (Figure 14) is unrealistically high for field operation. The values and errors presented in this table reflect the median cost estimate ± the low-end range based on three cost estimates obtained from quotes given by the manufacturing companies of the machinery and items (exceptions were instances where machinery was custom designed and estimated for this process). This reporting method avoids presenting potentially unrealistic extreme low and high cost estimates.



Groundwater Acidification Method	Heating Temperature (°C)	Mining & Transport Costs	CPP Costs	WTP Costs	Total Costs
None	100	-	-	-	-
	300	7.22	0.059 ± 1.6E-04	1.60 ± 1.02E-02	8.88 ± 1.04E-02
Acid	100	25.8	0.018 ± 3.6E-04	4.72 ± 5.04E-01	30.6 ± 5.04E-01
	300	3.56	0.059 ± 1.6E-04	3.24 ± 2.69E-01	6.86 ± 2.70E-01
CO_2	100	26.7	0.022 ± 3.6E-04	31.4 ± 17.7E+00	58.1 ± 17.7E+00
	300	4.61	0.059 ± 1.6E-04	21.9 ± 10.5E+00	26.5 ± 10.5E+00

We again emphasize that we have ignored important large costs such as labor, land and building infrastructure, management, marketing, and quality control. These are additive, thus comparing the costs in Table 6 *as ratios* would falsely exaggerate the cheapness of the cheaper option, because a common additive amount has been ignored. Within the range considered here, the estimates suggest that the most field-relevant and favorable processing option (within the range considered here) is likely to be to use 300°C heat-treated bauxite without groundwater acidification because this treatment scenario balances the benefits of lower bauxite doses (Figure 15) with increased logistical simplicity. Moreover, pH reduction using mineral acids and the Cr/Mn/Al data reported in Table 5 requires additional safety constraints, the costs of which are not included in this cost analysis but would certainly increase labor and operational costs. Therefore, heating without any acidification appears for now to be the most optimal and practical treatment scenario to follow in field operation. It is worth noting that the low-end ranges reported in Table 6 are lower than the median total cost estimates, and the overall conclusion of the analysis remains unchanged. Therefore, the uncertainty in the costs that were included is not a major source of error.

4.4. Comparing Bauxite to Activated Alumina

Another rigorous and controlled analysis was conducted to compare the performance and cost of treating fluoride-contaminated groundwater with bauxite to activated alumina (AA), a widely used fluoride adsorbent. Figure 16A shows that bauxite sourced from Guinea 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 (however, enough bauxite was not dosed in this experiment to reach the WHO-MCl). Panels B and C in Figure 16 compare the minimum required doses and materials costs for remediating several synthetic and real fluoride-contaminated groundwater matrices down to the WHO-MCL with AA and Guinea bauxite (the best performing bauxite ore, Figure 5A). The cost estimates are based on experimentally determined minimum required doses (shown in Figure 16B), which indicate 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. Larger doses required for bauxite are consistent with its lower specific surface area and thus lower adsorption capacity. Regardless, the material cost of fluoride remediation with Guinea bauxite is consistently and substantially lower than with AA across all tested groundwater matrices: ~23-33 times lower if AA is assumed to be used in a single-use batch process and ~ 11-18 times lower if AA is assumed to be used in a column process with media regeneration (Figure 16B). 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. A more extensive cost analysis to compare fluoride removal using the worst performing ore (Indian bauxite) with AA will need to be conducted in future research. As a first estimate, one can use the data in Figure 5A, which indicates that Indian bauxite requires 2.4x the minimum dose of Guinea bauxite to remediate Sri Lankan groundwater, to infer that the material cost of using bauxite would remain 4.7-8.8 times lower than AA.

For both AA and Guinea 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., $Si(OH)_4$, HCO_3^-, SO_4^{2-}, NO_3^-),[7,31,67] as well as natural organic matter likely to be present in real groundwater.[7,46] Numerous studies evaluating the competition between fluoride and commonly occurring groundwater ions and species (e.g., sulfate, nitrate, chloride, phosphate, silicic acid) conclude that phosphate negatively impacts fluoride removal by bauxite, gibbsite, or alumina[29,31,56,68]. Due to the fact that infiltration of surface fertilizer runoff could potentially introduce phosphate into groundwater in agricultural regions, it is important to consider the need for additional remediation technologies to appropriately address the effects of phosphate on fluoride removal efficiency and overall product water quality.

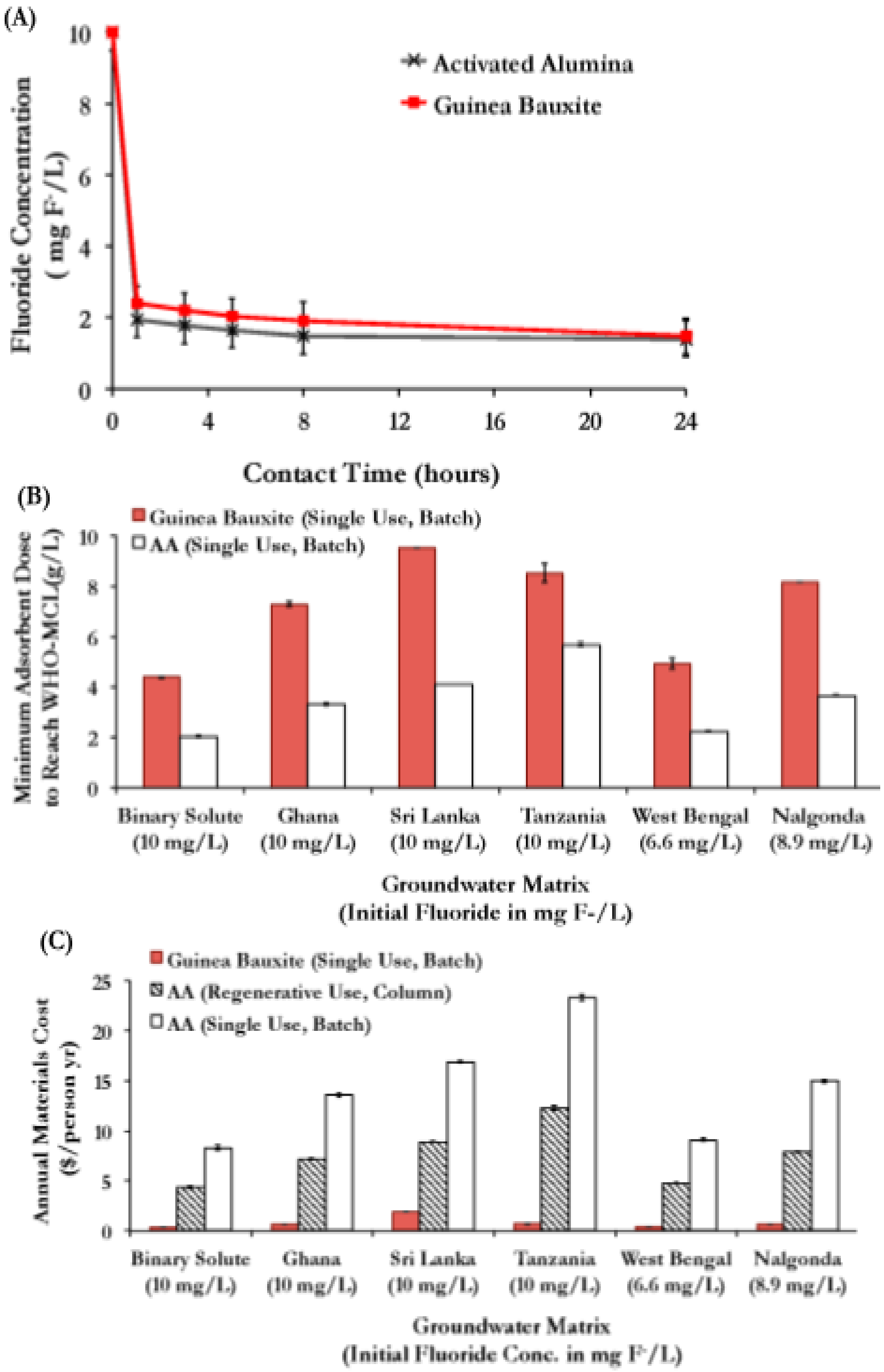


Figure 16. Comparison of **(A)** Fluoride concentration as a function of contact time for Activated Alumina and Guinea Bauxite (respective doses: 4 and 10 g/L) in synthetic Sri Lankan groundwater and (B) Minimum required doses and **(C)** Annual per capita material costs for remediating several synthetic groundwater matrices containing 10 mg F$^-$/L and two real groundwater matrices (West Bengal and Nalgonda) to the WHO-MCL using milled Guinea bauxite (single-use batch process) and unmodified AA (both in single-use batch process and in column process with media regeneration). Averages are presented and error bars represent the larger of the range from duplicate tests and measurement errors associated with the fluoride probe.

5. Conclusions and Ongoing Work

5.1. Field Reactor Designs

In order for the proposed bauxite-based defluoridation process to become a mature technology, several remaining unknowns must still be addressed. Prior to implementing this water treatment process in the field, a rigorous demonstration of the entire bauxite-based defluoridation process (from processing raw bauxite ore to producing potable water) must be conducted. To achieve this goal, low-cost solid-separation methods (e.g., (e.g., addition of a coagulant such as alum or polyaluminum chloride, while using a rapid sand filter, micron filter, and/or tube settler) can be tested to reduce the post-settling turbidity to drinking water standards.

To design an optimal reactor that utilizes bauxite's maximum adsoprtion capacity and that remains easy to operate and maintain in a rural setting, one can first refer to existing applications of common adsorbents such as activated carbon or activated alumina. These adsorbents are typically deployed as either granular filter bed media (particle size ~ 1mm) or powdered batch dispersive media (particle size < 50 μm).[69] Studies have demonstrated the successful use of bauxite as powdered dispersive batch media (particle sizes 1 μm < 250 μm). Despite working well with a finely powdered media, a continuous flow stirred tank reactor (CFSTR) design may be challenging to operate in a rural setting with intermittent power and unreliable groundwater sources. Alternatively, bauxite could also be tested as a dispersive batch media in a sequential countercurrent batch reactor to progressively treat multiple batches of fluoride contaminated water until the bauxite media has been saturated. However, it is noted that although countercurrent batch reactors will use bauxite more efficiently and reduce operating costs, they will come with increased costs in capital and labor so these tradeoffs need to be further evaluated.

Another option is to use bauxite as a coarser granular media in a plug flow reactor (PFR) where the adsorbent interacts and equilibrates with a higher influent contaminant concentration rather than with a lower effluent concentration (which in the typical case would be set at < 1.5 ppm F) as in a CFSTR. It is expected that bauxite's adsorption density (mg F^-/g adsorbent) described by the adsorption isotherms in Section 3.1 will be greater in the more efficient PFR filter reactor design. Furthermore, the use of bauxite in a column filter bed could also be studied by using larger grain sizes to avoid clogging of the filter media and to reduce the large energy requirement of pushing water through packed media. However, it is important to keep in mind that using bauxite as a coarser granular medium could also decrease the available surface area for adsorption and reduce its effectiveness as a fluoride adsorbent. Exploring whether the bauxite media could be reused till saturation or regenerated chemically is important because it would alter the cost (and perhaps complexity) of the overall treatment process. Researchers have successfully regenerated other defluoridation adsorbents (e.g., magnesium incorporated bentonite clay[70] and nano-magnesium oxide[71]) with 95-97% recovery using 1M NaOH or 1M HCl.

5.2. Waste Disposal and Resource Recovery

To address potential disposal problems and to lower operational costs, resource recovery applications for solid waste generated in the bauxite-based defluoridation process should also be investigated. It would be worthwhile to explore the potential resale of fluoride-laden bauxite sludge to aluminum manufacturing companies to further reduce the fiscal and environmental impact of implementing this technology. Studies attempting to recycle red mud, the toxic, highly alkaline (pH 10.5-12.5)[72], metal-laden waste byproduct of the Bayer process used to extract aluminum from bauxite, can shed light on potential options for reuse of bauxite in various industries (e.g., metallurgy, construction, glass/ceramics, chemical, agriculture, and water/wastewater treatment).[73] The Aluminum Company of America (more commonly known as ALCOA) proposed that carbonating the highly alkaline red mud using industrial CO_2 streams can allow for easier storage and handling so red mud residue can later be reused for a variety of useful purposes including cement and concrete manufacturing, brick and tile making[49,72–74], road construction[75], and as a soil amendment or fertilizer[73]. Other researchers have demonstrated that sulfidizing red mud (i.e., treating it with Na_2S, $(NH_4)_2S$, or H_2S to bind sulfur to metal atoms to prevent leaching) enables its use as an adsorbent for heavy metals (e.g., Cd, Cr, Pb, Hg, As, Mn, Sr) and other inorganic and organic contaminants (e.g., P, bacteria, dissolved organic carbon (tannin, lignin)).[75] Given the many proposed uses of red mud (a waste product from activated alumina and aluminum production), the fluoride-laden bauxite sludge produced by the proposed defluoridation process could also be used for similar purposes.

5.3. Technology Adoption and User behavior

Engineers and scientists have long suggested the implementation of a myriad of technical solutions to address societal problems in resource-constrained regions. Academic, corporate, and nonprofit groups have innovated numerous technologies with the intention of providing disaster relief, adequate healthcare, education, and water and sanitation in developing countries. However, as discussed by Bellman[76], the authors agree that communities are often left with failed technological interventions because lasting solutions to these deep-rooted issues must be accompanied by parallel infrastructural and institutional changes. Some infamous examples of such failed technologies implemented in some locations without institutional support include the PlayPump, LifeStraw, Unmanned-Aerial-Vehicles (volunteer drone pilots in Nepal)[76], One-Laptop-Per-Child[77], and malaria bed nets.[78] There are various lessons to be learned from the challenges faced by these entities.

Several publications[76–83] about failures of water technology and solution implementation highlight the importance of conducting field trials, needs assessments, and baseline social surveys prior to scaling up and widely implementing a new technology. Furthermore, understanding key social factors influencing adoption and retention of a technology including the local cultural context, user behavior, peoples' willingness to pay for water, peoples' preferences for water taste, and potential unintended consequences is pertinent to the long-term success of an intervention like bauxite-based defluoridation in a community.

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