

UC Berkeley

UC Berkeley Previously Published Works

Title

Effective Remediation of Groundwater Fluoride with Inexpensively Processed Indian Bauxite

Permalink

<https://escholarship.org/uc/item/0pm4f6h4>

Journal

Environmental Science and Technology, 52(8)

ISSN

0013-936X

Authors

Cherukumilli, Katya
Maurer, Tessa
Hohman, J Nathan
[et al.](#)

Publication Date

2018-04-17

DOI

10.1021/acs.est.7b05539

Peer reviewed

Effective Remediation of Groundwater Fluoride with Inexpensively Processed Indian Bauxite

Aruna Kirani Katyayani Cherukumilli, Tessa Maurer, J. Nathan Hohman, Yash Mehta, and Ashok J. Gadgil

Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.7b05539 • Publication Date (Web): 22 Mar 2018

Downloaded from <http://pubs.acs.org> on March 26, 2018

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

1 Effective Remediation of Groundwater Fluoride with Inexpensively Processed Indian Bauxite

2 Katya Cherukumilli ^{*,†}, Tessa Maurer [†], J. Nathan Hohman ^λ, Yash Mehta ^Ω, Ashok J. Gadgil ^{†,Ψ}

3 [†] Department of Civil and Environmental Engineering, UC Berkeley, California 94720-1710,

4 United States

5 ^λ Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720,

6 United States

7 ^Ω Departments of Material Sciences and Engineering and Mechanical Engineering, UC Berkeley,

8 California 94720-1710, United States

9 ^Ψ Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California

10 94720, United States

11 * **Corresponding Author.** Katya Cherukumilli, E-mail: katyacherukumilli@gmail.com; Phone:

12 407-529-9943; Address: 410 O'Brien Hall, Berkeley, CA 94720.

13 **ABSTRACT**

14 India represents one-third of the world's fluorosis burden and is the fifth global producer of

15 bauxite ore, which has previously been identified as a potential resource for remediating

16 fluoride-contaminated groundwater in impoverished communities. Here, we use thermal

17 activation and/or groundwater acidification to enhance fluoride adsorption by Indian bauxite

18 obtained from Visakhapatnam, an area proximate to endemic fluorosis regions. We compare

19 combinatorial water treatment and bauxite-processing scenarios through batch adsorption

20 experiments, material characterization, and detailed cost analyses. Heating Indian bauxite above

21 300°C increases available surface area by 15x (to ~170 m²/g) through gibbsite dehydroxylation

22 and reduces the bauxite dose for remediating 10 ppm F⁻ to 1.5 ppm F⁻ by ~93% to 21 g/L.

23 Additionally, lowering groundwater pH to 6.0 with HCl or CO₂ further reduces the average

24 required bauxite doses by 43-73% for ores heated at 100°C (~77 g/L) and 300°C (~12 g/L).
25 Product water in most examined treatment scenarios complies with EPA standards for drinking
26 water (e.g., As, Cd, Pb, etc.) but potential leaching of Al, Mn, and Cr is of concern for some
27 scenarios. Among the defluoridation options explored here, bauxite heated at 300°C in acidified
28 groundwater has the lowest direct costs (\$6.86 per person per year) and material-intensity.

29 **1. INTRODUCTION**

30 Chronic ingestion of groundwater containing excess naturally occurring fluoride leads to
31 skeletal fluorosis, a debilitating health condition that disproportionately affects² children by
32 damaging their developing bones and joints¹ through the deposition and accumulation of
33 fluoride. Skeletal fluorosis is endemic in 25 countries worldwide, but it is predominantly
34 reported in resource-constrained rural regions of India, China, and the East African Rift Valley³,
35 where populations must rely heavily on contaminated groundwater as their primary drinking
36 water source^{2,4}. Despite almost a century of reported causative understanding for endemic
37 fluorosis⁵⁻⁸, an appropriate technology to address this global health crisis has not yet been
38 implemented at scale in such isolated regions. Numerous materials (e.g. bio-sorbents, bone char,
39 synthetic hydroxyapatite, activated alumina, etc.) have been tested and proposed as adsorbents
40 for fluoride removal⁹⁻¹⁶. However, neither natural nor lab-derived technologies have successfully
41 scaled up in rural, resource-constrained regions due to various barriers including sourcing and
42 cost of materials, processing methods, complexity of operation and maintenance, labor intensity,
43 and social acceptability.

44 Bauxite, a globally abundant ore of aluminum, is a viable, effective, and low-cost
45 fluoride adsorbent alternative. Earlier researchers have reported the fluoride-affinity of bauxite
46 ores from specific sources¹⁷⁻³¹ and red mud (alumina refineries' residue)^{32,33}, but most of them

47 did not explore the specific dose needed to remediate contaminated groundwater to the World
48 Health Organization's Maximum Contaminant Limit (WHO-MCL= 1.5 ppm F⁻). In a recent
49 study, our team established that bauxite ores from different parts of the world differ significantly
50 in their fluoride adsorption efficiency³⁴. We determined that in comparison to bauxite from sites
51 in Ghana, Guinea, and U.S., an Indian-sourced bauxite had the poorest fluoride removal
52 performance because it contained the trace mineral calcium carbonate (CaCO₃), which upon
53 dissolution increased solution pH well above the optimal pH (of 5.0- 6.0) for fluoride removal.

54 India represents one-third of the global fluorosis burden (66 million people)^{2,35}. Excess
55 fluoride contamination of groundwater occurs in approximately 70% of India's states³⁶.
56 However, India is also the fifth major global producer of bauxite³⁷, so there exists a promising
57 opportunity to better utilize the abundant bauxite available throughout India for affordable
58 defluoridation. Indian bauxite, if successfully modified through a low-energy, low-cost
59 processing method, could be a practical, locally available, and inexpensive route to alleviate a
60 significant source of chronic human suffering for millions of people. To further advance relevant
61 knowledge and overcome the challenges with using Indian bauxite presented in our previous
62 study³⁴, here we report novel findings to enhance the fluoride removal performance of Indian
63 bauxite through mild thermal treatment at 300°C. We also investigate the feasibility and impact
64 of acidifying fluoride-contaminated groundwater using mineral acids (e.g., HCl) or carbon
65 dioxide gas (CO₂).

66 The primary objectives of this paper are to 1) report the impact of heating and chemical
67 transformation of bauxite on fluoride removal at molecular scale and explain its practical
68 significance, 2) discuss the effects of groundwater acidification on fluoride removal, and 3)
69 evaluate cost tradeoffs of the various combinatorial treatment scenarios to determine the

70 feasibility of using Indian bauxite as an effective groundwater defluoridation method in low-
71 income regions.

72 **2. MATERIALS AND METHODS**

73 **2.1. Preparation of Bauxite Samples.** The bauxite used in this study was collected from a
74 mine in Visakhapatnam, Andhra Pradesh, India. For brevity, we hereafter refer to this bauxite in
75 this paper as “Indian Bauxite” while recognizing that diverse bauxite ores (with differing
76 physical and chemical compositions) could exist within India. This bauxite was dried overnight
77 ($T=100^{\circ}\text{C}$) to remove moisture prior to milling 15 g for 15 minutes in an agate milling jar of a
78 shaker ball mill (SPEX8000) to generate micron-sized powders, as confirmed by dynamic light
79 scattering (Malvern Zetasizer Nano ZSP). The powdered Indian bauxite was then heated in a
80 muffle furnace (Fisher Scientific, Isotemp) for 4h at the desired temperatures (100°C , 200°C ,
81 300°C , and 400°C) for heat activation studies, based on previously documented methods^{27,29,38}.
82 Scanning electron microscopy (SEM) images of some thermally activated bauxite samples are
83 shown in the Supporting Information (Section 1, Fig. S1).

84 **2.2. Materials Characterization.** Percent mass loss and chemical composition of effluent gases
85 from heating the bauxite samples were measured using Thermogravimetric Analysis and Mass
86 Spectrometry (TA Instruments Q5000IR TGA, with attached Pfeiffer Vacuum Thermostar MS).
87 Procedures to determine bulk crystalline mineral composition from X-ray diffraction (XRD)
88 patterns and specific surface area (SSA) using multipoint Brunauer-Emmett-Teller (BET)
89 measurements have been described in our previous publication³⁴ and are detailed in Section 2 of
90 the SI. Our previous publication also reports additional material characterization details for the
91 raw Indian bauxite ore used here, including point of zero charge, elemental composition, and
92 adsorption isotherms and envelopes.

93 **2.3. Batch Adsorption Studies.** Standard batch adsorption experiments were designed to
 94 determine the respective effects of reaction time, bauxite activation temperature, groundwater
 95 acidification method, and bauxite dose (g/L) on fluoride removal in a synthetic Sri Lankan
 96 groundwater matrix. Table 1 shows the groundwater recipe, which was selected to overlap with
 97 our previous work³⁴ and was prepared using stock solutions of 100 mM CaCl₂, 100 mM MgCl₂,
 98 200 mM NaHCO₃, 100 mM Na₂SO₄, 10 mM SiO₂ (Na₂SiO₃•5H₂O), and 10 mM NaNO₃. Initial
 99 fluoride concentrations of all lab-synthesized groundwater were set to 10 ± 0.5 mg F⁻/L using a
 100 stock solution of 100 mg/L NaF and sample fluoride concentrations were measured as outlined in
 101 our previous work³⁴.

Table 1. Chemical composition of the synthetic Sri Lankan groundwater matrix used in this study, borrowed from the British Geologic Survey¹². Aside from alkalinity (which is reported in mM as HCO₃⁻), all component values are reported as gravimetric target concentrations in ppm (mg/L)

Component	Sri Lankan Groundwater (mg/L)
F	10.0
Ca	173.0
Mg	179.0
HCO₃⁻	516.0
SO₄²⁻	15.5
Si	45.0
NO₃⁻ as N	9.0
Alkalinity (mM as HCO₃⁻)	8.5

102 To determine the effect of reaction time on fluoride removal, kinetics experiments were
 103 conducted for 2 h and samples were taken at 5,10, 20, 40, 60, 90, and 120 min. All subsequent

104 batch adsorption studies were conducted for a shorter reaction time (20 min) because subsequent
105 fluoride removal was marginal and shorter reaction times reduce field operational costs, making
106 the overall process more attractive for real-world application.

107 In each acidification experiment, 20 mL of Sri Lankan groundwater matrix was acidified
108 using either 1.1M Hydrochloric acid (HCl) or pressurized CO₂. The desired solution pH for these
109 experiments was selected based on previous studies^{25,34,29}, which experimentally verified pH 6.0
110 \pm 0.1 as an optimal pH for fluoride adsorption with bauxite ore. To determine differences in
111 fluoride removal based on groundwater acidification timing, we examined the following two
112 cases where (1) the acidification source was gradually added in small quantities over the study
113 duration to maintain solution pH at 6.0 \pm 0.1, and (2) the total measured volumes of HCl and
114 CO₂ required in case (1) were added initially at once in bulk, so that the desired pH was reached
115 by the experiment end. In total, per liter of water, addition of approximately 211 - 401 mg HCl or
116 bubbling of 22.5 - 34.7 g CO₂ maintained the solution pH 6.0. Theoretical calculations in Section
117 6 of the SI indicate that much lower quantities of CO₂ (about 35-53x less) actually need to be
118 dissolved in the water to reach a solution pH of 6.0. Fluoride measurements taken at regular
119 time intervals for 1 hour of settling after these 20-minute batch adsorption experiments
120 demonstrated no fluoride desorption. Even in cases where groundwater was acidified with CO₂
121 and the solution pH rose slightly during the settling period due to CO₂ evolution, adsorbed
122 fluoride did not return to the groundwater matrix. To determine the influence of drastic solution
123 pH changes in case (2) on the potential leaching of harmful trace contaminants from the
124 dispersive bauxite adsorbent, we used an Inductively Coupled Plasma Mass Spectrometer (ICP-
125 MS, Agilent Technologies 7000 series) to measure drinking water contaminants regulated by the
126 US Environmental Protection Agency's enforceable Maximum Contaminant Limits (EPA-MCL)

127 for primary contaminants (e.g., Ag, As, Cd, Cr, Pb, Se) and by non-mandatory Secondary
128 Maximum Contaminant Limits (SMCL) for secondary contaminants (e.g., Al, Cu, Fe, Mn, Zn) in
129 the product water³⁹.

130 Six combinatorial treatment scenarios using bauxite heated at 100°C and 300°C, with and
131 without groundwater acidification using HCl or CO₂, were compared in terms of fluoride
132 removal performance by calculating the optimal solid: liquid ratio (referred to henceforth as
133 “minimum required dose”) to remediate 10 mg F⁻/L down to the WHO-MCL (1.5 mg F⁻/L) using
134 a method described in our previous publication³⁴ (SI Section 3, Fig. S2).

135 **2.4. Estimation of Combinatorial Treatment Costs.** For each treatment scenario described
136 above, we estimated annual per-capita costs of remediating fluoride-contaminated groundwater
137 using conservative assumptions about material and electricity costs, supply chain logistics, and
138 bauxite processing and water treatment plant design.

139 As schematically shown in the SI Figure S3, our model assumes that raw bauxite is first
140 transported from a mine to a central processing plant (CPP) located 500 km away, the average
141 estimated distance between bauxite-producing mines and Indian districts with endemic skeletal
142 fluorosis⁴⁰ (Section 4). The CPP in our analysis was designed to have appropriate infrastructure
143 to process (e.g., crush, mill, and heat-treat) enough raw bauxite for 500 villages of 1,000 people
144 each. We assumed each village would have a separate community-scale water treatment plant
145 (WTP) and that the villages were located approximately 25 km from the CPP. The average
146 village population was chosen based on a previous publication⁴¹ and the population density for
147 the circular area covered by the CPP was calculated (~300 people/km²) using Indian Census
148 data⁴² for the three most heavily affected states with endemic fluorosis (i.e., Gujarat, Rajasthan,
149 and Madhya Pradesh).

150 Fig. 1a shows a map of Indian districts with reported endemic fluorosis, excess
151 groundwater fluoride contamination, and bauxite mine locations. The example in Fig. 1b
152 demonstrates the feasibility of the assumptions used in our general cost model by showing that
153 the bauxite used in this study (from Visakhapatnam) could realistically be transported to a CPP in
154 Nalgonda District (a fluorosis affected region located approximately 500km away). Additional
155 details on generation of Fig.1 and population density calculations are in the SI (Section 4).

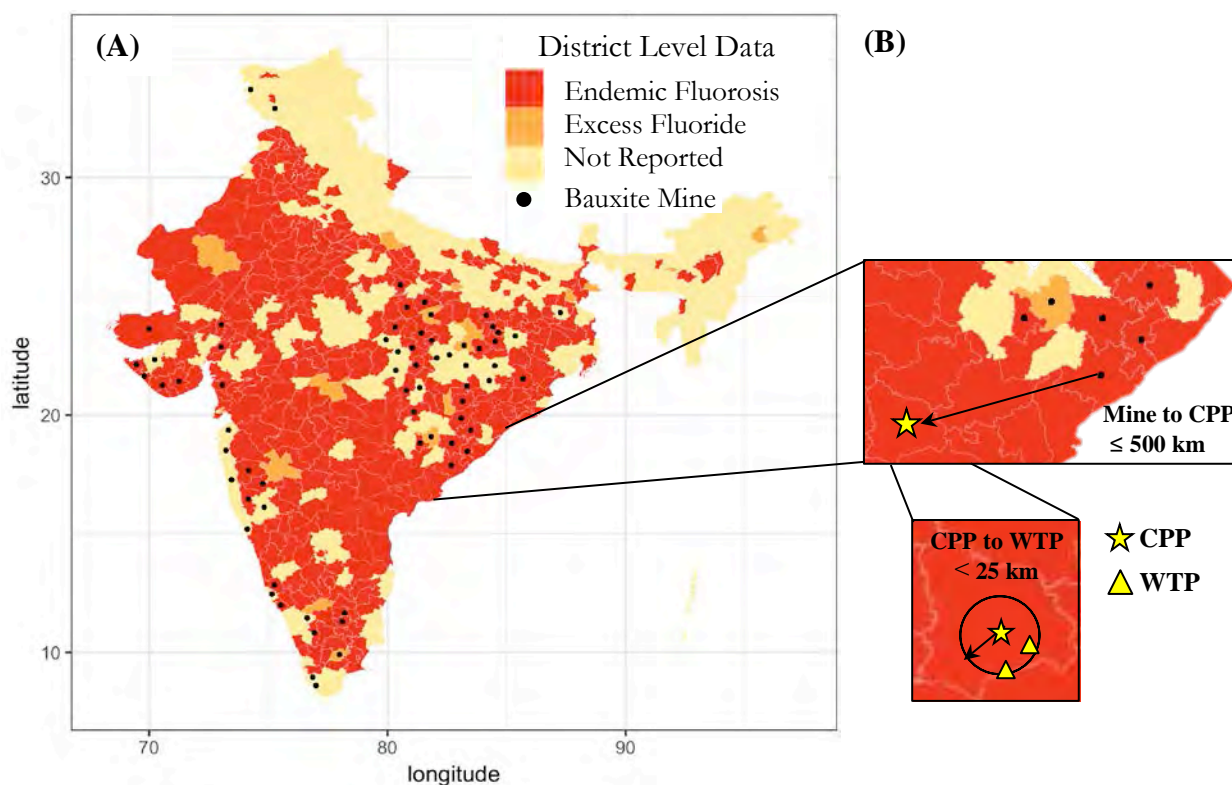


Fig. 1. Map of **A)** districts in India with endemic fluorosis (red), excess groundwater fluoride (orange), and bauxite mines locations (black dots), and **B)** A realistic example of the relative locations of a bauxite mine in Visakhapatnam, a central processing plant (CPP, shown as a yellow star) in Nalgonda District, and water treatment plants (WTP, shown as yellow triangles) to demonstrate the feasibility of the assumptions used in our cost model. This figure was generated from data presented in Section 4 of the SI using R visualization packages.

156 The WTP shown in Fig. 2 was designed to operate at a minimum capacity of 5000 L
157 water/day to meet the daily need for the village, assuming a per capita use of 5 L/person. We
158 selected this value as a field-relevant compromise between the anecdotal reports of daily per

159 capita water purchase value in rural regions (2 L/person) from small commercial water providers
160 in India (e.g., WaterLife, and WaterHealth (India)) and the WHO's recommendation for daily
161 per capita drinking and cooking water needs (7.5 L/person)⁴³. We assumed that a realistic field
162 pilot WTP relying on bauxite-based defluoridation would require a mixing tank (for addition and
163 mixing of treated bauxite and acid/CO₂ to fluoride-contaminated groundwater), a
164 presedimentation basin (for initial clarification), alum addition prior to running water through a
165 tube settler and micron filter (to reduce water turbidity to < 1 NTU), and a holding tank (for
166 storing treated water) (Fig. 2).

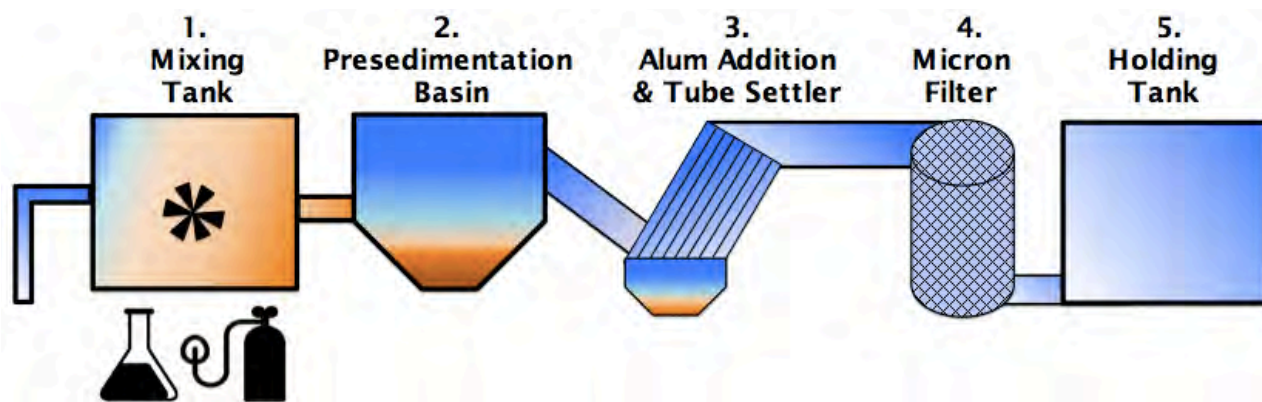


Fig. 2. Schematic representation of treatment processes at a village-scale community water treatment plant. Bauxite is injected and mixed into pumped groundwater for 20 minutes after which it enters a presedimentation basin. The supernatant water is then dosed with 30 mg/L alum and run through a tube 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. The acid flask and CO₂ cylinder icons were sourced from The Noun Project and respectively created by Gabor Fulop and Arosh Khan.

167 Machinery was assumed to have a lifetime of 10 years, a conservative estimate that also
168 accounts for the possibility of premature obsolescence due to up-scaling and growth. For each
169 piece of equipment, cost estimates were solicited for products currently available in (or for
170 delivery to) India (Section 5, SI). Additionally, we made the conservative assumption that
171 physical assets had no resale value at the end of their lifetimes. The costs of specific portions of
172 the WTP, namely the pumps, tube settlers, and power supply, were obtained from actual

173 fabrication cost estimates of a 10,000 L/day field implementation of an electrochemical arsenic
174 remediation technology in operation since April 2016 in West Bengal, India⁴⁴. This large pilot
175 demonstration plant is a scaled up implementation of a 600L prototype, whose cost estimates are
176 reported by our group in an earlier publication⁴⁵. Since that field trial involved daily processing
177 twice the amount of water as ours (10,000L versus 5,000L), we are comfortable with these
178 estimates being especially conservative.

179 For cost estimation, we chose current market prices of tanks (3), pumps (5), and
180 consumables (e.g. bauxite, alum, acid, and CO₂), and reasonable values for shipping costs, which
181 are outlined in a spreadsheet found in Section 5 of the SI. We estimated electricity costs based on
182 machinery power rating; the number of hours of use based on laboratory tests; and an assumed
183 electricity tariff of \$0.07/kWh. The WTP was assumed to be able to operate up to 16 hours per
184 day. Additional cost estimation details related to the mining, transportation, central processing
185 plant, and water treatment plant (e.g. equipment model numbers, commercial supplier
186 companies, lifetime, duration, and usage assumptions, etc.) are provided in the SI (Section 5).

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

195

196

197 **3. RESULTS AND DISCUSSION**

198 **3.1. Characterization of thermally activated bauxite.** Fig. 3a shows the percent mass loss
199 from the Indian bauxite ore during heating, as determined by TGA-MS. The majority of the mass
200 loss (~15% due to dehydroxylation) occurred at temperatures between 250°C and 300°C, and the
201 compound given off was confirmed via mass spectrometry to be water. Fig. 3b shows the XRD
202 patterns of Indian bauxite heated at four temperatures (100°C, 200°C, 300°C, and 400°C). The
203 main crystalline Al phase was gibbsite, and additional crystalline Fe oxide phases (goethite and
204 hematite) and Ti oxide phase (anatase) were detected. The diffraction patterns for crystalline
205 gibbsite in bauxite samples heated at 100°C and 200°C were indistinguishable (100°C peaks
206 have been truncated in Fig. 3b for convenient display) and these same major peaks were absent
207 when the bauxite was heated at 300°C or 400°C. The iron and titanium oxide phases present in
208 bauxite did not show the same structural deformations or changes in crystallinity at 300°C or
209 400°C. Fig. 3c presents surface area and particle size measurements of the heated Indian bauxite.
210 The particle size remained constant across samples heated between 100°C and 400°C but the
211 surface area increased dramatically (> 15X) from approximately 11 m²/g at 100°C to 170 m²/g at
212 300°C.

213 Taken together, the results in Fig. 3 show that the major impacts of heating Indian bauxite
214 occur between 200°C and 300°C, indicated by the decrease in crystallinity and increase in
215 surface area due to loss of structural waters of hydration. Other studies have observed a similar
216 structural deformation of crystalline gibbsite minerals present in bauxite when heated between
217 200°C and 300°C, as it transforms to the more amorphous boehmite phase through partial
218 dehydroxylation (e.g., loss of two waters of hydration)^{24,29,46,47}.

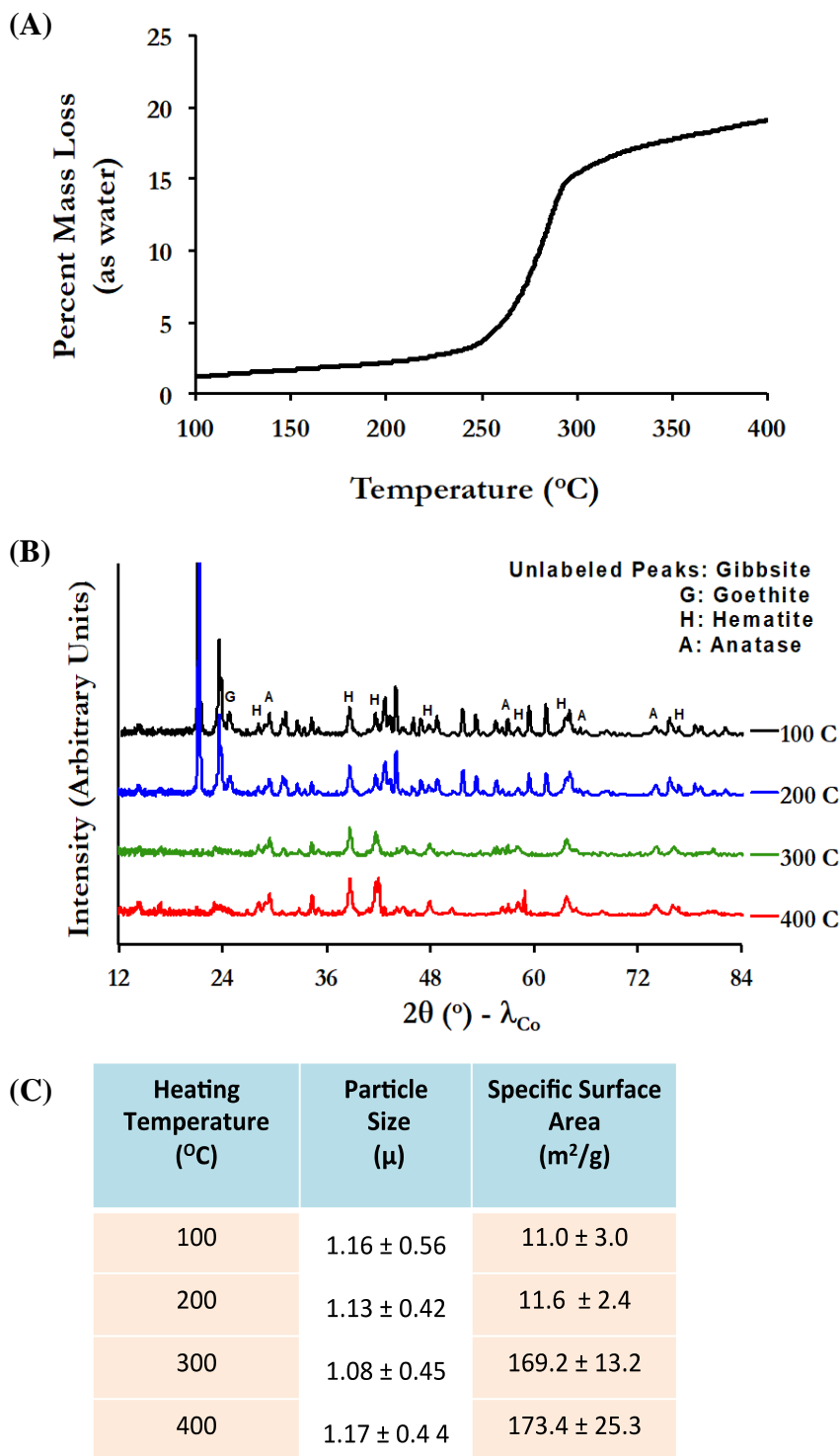


Fig. 3. Characterization of thermally-activated Indian bauxite in terms of **A)** Mass loss measured using Thermogravimetric Analysis and Mass Spectrometry (TGA-MS), **B)** Mineralogy as determined by X-ray diffraction patterns, and **C)** Particle size and specific surface area measurements. In panel **C)**, we present averages from duplicate experiments and errors are the largest of the range from duplicate tests and measurement errors associated with the analytical equipment used (e.g., DLS, Tristar II 3020).

220 **3.2. Effect of thermal activation of bauxite on fluoride removal.** Bauxite samples heated
221 at temperatures greater than 200°C showed substantial improvement in fluoride removal
222 performance in batch adsorption studies using finely powdered bauxite as single-use dispersive
223 media (Fig. 4). Consistent with the similar XRD peaks and surface area measurements presented
224 in Fig. 3b & 3c, fluoride removal performance of bauxite samples heated at $T \leq 200^\circ\text{C}$ or $T \geq$
225 300°C were comparable. Fig. 4 also demonstrates that fluoride adsorption using bauxite was
226 rapid; within 20 minutes the system was close to equilibration (fluoride concentrations did not
227 vary greatly between 20 min. and 2 hr.), a finding confirmed in our prior study³⁴. This initial
228 rapid uptake is likely due to surface adsorption and the flattening of the curve after 20 minutes
229 represents diffusion of fluoride into interior pores of micron-sized bauxite particles. Researchers
230 studying other aluminum-based adsorbents used for fluoride removal have reported similar
231 kinetic trends^{48–50}.

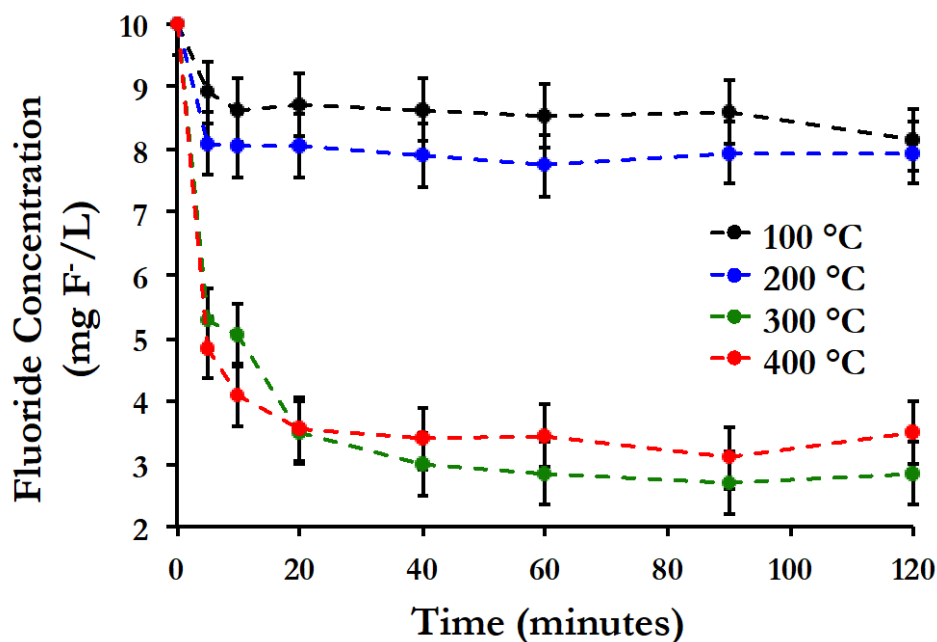
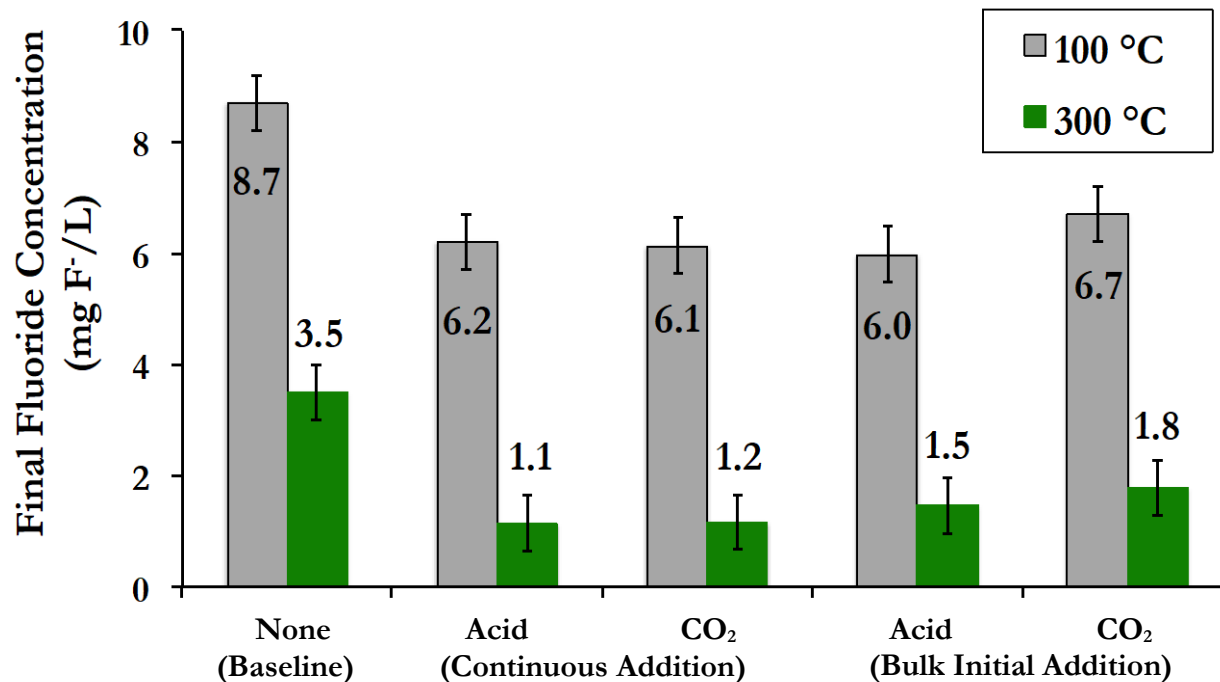


Fig. 4. Fluoride concentration as a function of contact time for thermally activated Indian Bauxite (raw dose 10 g/L) in alkaline synthetic Sri Lankan groundwater (initial pH 8.7). We present averages and error bars as the largest of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

232 **3.3. Effect of groundwater acidification on defluoridation and leaching of metals.** Fig. 5
233 shows the improvement in fluoride removal performance as a result of lowering the alkaline
234 initial pH of Sri Lankan groundwater (pH ~ 8.7) down to 6.0 ± 0.1 through addition of HCl or
235 bubbling of CO₂ gas. In all the experiments summarized in Fig 5, a dose of 10 g/L (= 0.169 g/20
236 mL) of raw bauxite (with or without heating) was added to synthetic Sri Lankan groundwater
237 containing an initial fluoride concentration of 10 mg F⁻/L. Regardless of the source of
238 acidification, the improvement in fluoride removal due to groundwater acidification appears to
239 be consistent. Furthermore, regardless of whether the acid source was added continually over the
240 experimental duration or whether it was added in bulk initially did not make a difference in the
241 overall percent fluoride removal. At a dose of 10 g/L, bauxite heated to 300°C and added to
242 acidified water is nearing the WHO-MCL for fluoride, but a much larger dose of 100°C bauxite is
243 required to remediate an initial concentration of 10 mg F⁻/L. Our ICP-MS data indicate the
244 product water for all the treatment scenarios in Fig. 5 is compliant with EPA guidelines for
245 drinking water for a majority of the primary and secondary contaminants. In all scenarios, the
246 aqueous concentrations of Ag, As, Cd, Cu, Fe, Ni, Pb, Se, and Zn were below 25% of the EPA-
247 MCL.



Groundwater Acidification Method

Fig. 5. 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 CO₂ (rate 0.25 L/min). We present averages and error bars as the larger of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

248 Table 2 highlights three elements of concern (e.g., Cr, Mn, and Al) that approached or
 249 exceeded the EPA limit in the product water for some of the scenarios outlined in Fig. 5. Our
 250 data indicate that Cr dissolution was more prominent in treatment scenarios using 300°C bauxite,
 251 perhaps due to a temperature-dependent increase in oxidation rate of insoluble Cr (III) to its
 252 more soluble Cr (VI) form. Although the Cr concentrations in our product water were below
 253 75% of the current national EPA-MCL (100 ppb total Cr), the primary drinking water standard
 254 for Cr (VI) is being revisited by the US-EPA and has recently been lowered in particular states
 255 (e.g., CA, where the EPA-MCL for total Cr is 50 ppb).

256 In scenarios where 300°C bauxite was added to acidified groundwater, Mn concentrations
 257 tended to be higher. The Mn concentration exceeded the SMCL (50 ppb Mn) for one particular
 258 scenario where 300°C bauxite was used in groundwater acidified through bulk acid addition. It
 259 was also observed that for all treatment scenarios where 100°C bauxite was added to acidified
 260 groundwater, the concentration of Al in the product water exceeded the SMCL (200 ppb Al).
 261 One explanation for why Al dissolution is less prominent in 300°C bauxite is that bauxite
 262 dehydroxylates to boehmite in that temperature range and boehmite is generally less soluble than
 263 gibbsite, as reported by other theoretical studies^{51,52}.

Table 2. Concentrations (in ppb) of metals of concern in product water of batch experiments outlined in Fig. 5 measured using ICP-MS. We present averages and error bars as the range from duplicate batch adsorption tests.

EPA Standards (MCL in ppb)	100° C					300° C				
	No pH Adjustment	Continuous Addition Acid		Bulk Addition CO ₂		No pH Adjustment	Continuous Addition Acid		Bulk Addition CO ₂	
Cr 100	0.7 ± 0.2	0.9 ± 0.2	0.8 ± 0.0	1.3 ± 0.2	1.0 ± 0.3	64.4 ± 3.4	53.8 ± 0.5	64.2 ± 1.5	48.7 ± 0.4	60.1 ± 1.4
Mn 50	1.6 ± 0.5	21.1 ± 1.5	25.3 ± 1.4	36.5 ± 8.7	23.3 ± 3.9	2.4 ± 0.8	45.9 ± 1.2	41.3 ± 1.7	56.6 ± 2.4	44.9 ± 3.3
Al 200	49.1 ± 4.2	252.8 ± 6.5	261.3 ± 38.6	619.4 ± 37.0	373.1 ± 18.6	65.4 ± 3.0	45.8 ± 2.1	100.6 ± 1.3	58.5 ± 11.2	102.9 ± 10.6

Ratio of Measured Concentration to MCL			
< 25%	25-74%	75-99%	≥ 100%

264 **3.4. Comparing combinatorial treatment scenarios.** Fig. 6 presents the minimum
 265 bauxite doses required to remediate 10 mg F/L down to the WHO-MCL in synthetic Sri Lankan
 266 groundwater. For the baseline (no acidification) scenario, the minimum required dose for 100°C
 267 bauxite (~287 g/L) is impractically large, approximately 13.5 times larger than for 300°C bauxite
 268 (~21 g/L). Groundwater acidification by acid or CO₂ reduces the required doses, but not in the
 269 same proportion: the resulting average minimum required dose for 100°C bauxite (~77 g/L) is
 270 approximately 6.4x larger than for 300°C bauxite (~12 g/L). As a result, based on doses alone,

271 the most practically feasible options for defluoridation with manageable material handling and
 272 disposal requirements appear to be any of the scenarios using bauxite heat-activated ($T = 300^\circ\text{C}$).

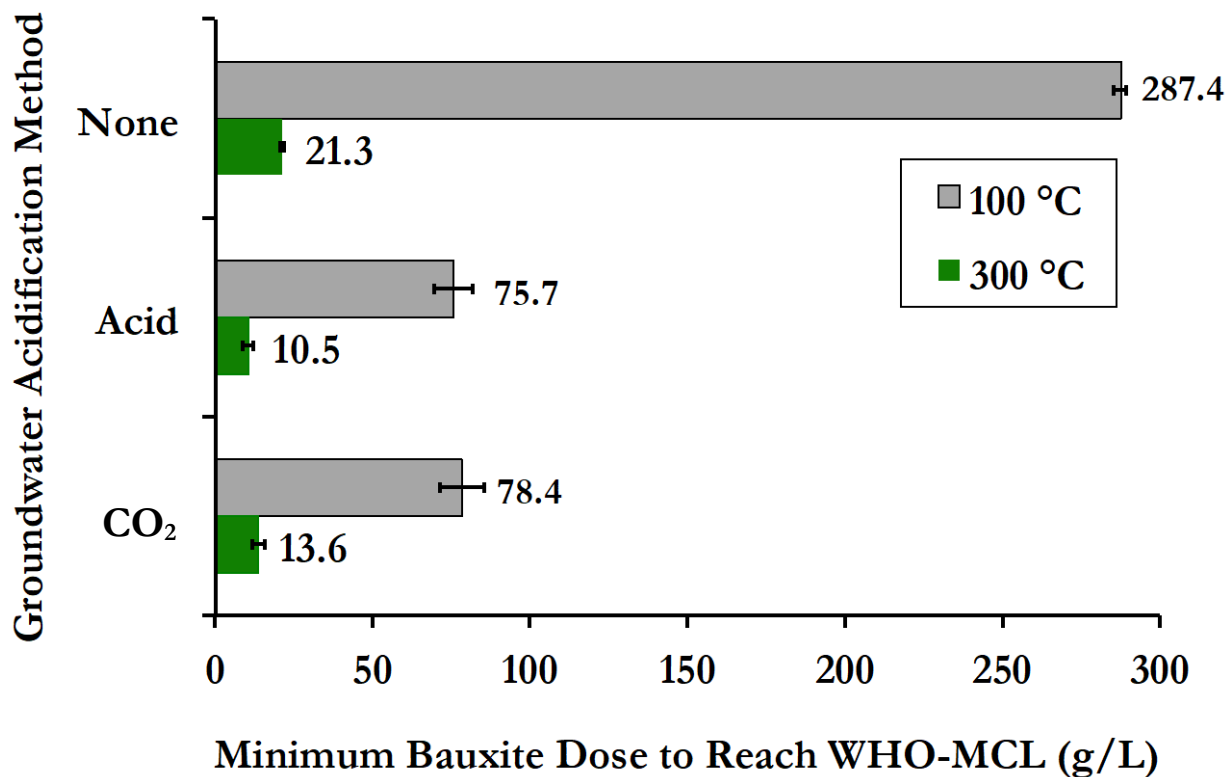


Fig. 6. Comparison of minimum required doses for various combinatorial treatment scenarios. Batch experiments run for 20 minutes in Sri Lanka groundwater. In certain scenarios, groundwater pH was maintained at 6.0 ± 0.5 through addition of acid (1.1 M HCl) or CO₂ (rate 0.25 L/min). We present averages and error bars as the larger of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

273 In addition, Table 3 presents the total cost for treating water for each of the possible
 274 processing methods. This analysis takes into account the capital and operational costs of the
 275 entire bauxite processing and water treatment process. Numbers are reported in USD per person
 276 per year and where multiple cost estimates were obtained, the median value is reported
 277 plus/minus the low-end range. The results indicate that the total cost of the unheated bauxite is
 278 up to an order of magnitude higher than for the heated bauxite. This implies that the additional
 279 cost of purchasing and operating an oven is offset by the substantially higher material and

280 transportation costs associated with using the much larger required doses of raw unheated
 281 bauxite. The general trends were as expected; the raw material and transportation costs were
 282 significantly higher for the processes requiring additional bauxite. On the other hand, the cost of
 283 the CPP step was lower for the unheated bauxite since no oven would be required. The costs at
 284 the WTP were highly dependent on the costs of hydrochloric acid and CO₂ for the cases where
 285 they are used.

Table 3. Treatment costs (in \$ per person per year) of combinatorial treatment scenarios including heating Indian bauxite and acidifying groundwater using acid or CO₂. Costs for the baseline treatment scenario (no heating or groundwater acidification) are not reported because the minimum required dose (Fig. 6) is unrealistically high for field operation. The values and errors presented in this table reflect the median cost estimate \pm 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. Additional details can be found in Section 5 of the SI.

Groundwater Acidification Method	Heating Temperature (°C)	Mining & Transport Costs	CPP Costs	WTP Costs	Total Costs
None	100	-	-	-	-
	300	7.22	0.059 \pm 1.6E-04	1.60 \pm 1.02E-02	8.88 \pm 1.04E-02
Acid	100	25.8	0.018 \pm 3.6E-04	4.72 \pm 5.04E-01	30.6 \pm 5.04E-01
	300	3.56	0.059 \pm 1.6E-04	3.24 \pm 2.69E-01	6.86 \pm 2.70E-01
CO ₂	100	26.7	0.022 \pm 3.6E-04	31.4 \pm 17.7E+00	58.1 \pm 17.7E+00
	300	4.61	0.059 \pm 1.6E-04	21.9 \pm 10.5E+00	26.5 \pm 10.5E+00

286 We found that using 300°C heat-treated bauxite in groundwater acidified with
 287 hydrochloric acid (“300-acid”) was the cheapest option at \$6.86 per person per year. This option
 288 benefits from significantly reduced raw material and transportation costs relative to the other
 289 options, though it makes the WTP process more expensive due to the cost of the acid. The
 290 second cheapest option was using heated bauxite without the additional groundwater
 291 acidification step (“300-only”); the total cost of this process was \$8.88 per person per year. The
 292 other three options (300-CO₂, 100-acid, and 100-CO₂) were significantly more expensive than

293 the cheapest option. However, the empirically calculated mass of CO₂ used in this cost estimate
294 is likely much higher than the actual amount of CO₂ that would be needed, in practice, to adjust
295 the groundwater pH to 6.0. Additional discussions on the differences in empirical and theoretical
296 estimations of CO₂ requirements are in Section 6 of the SI (Fig. S4).

297 Within the range considered here, our estimates suggest that the most field-relevant and
298 favorable processing option is likely to be to use 300°C heat-treated bauxite without groundwater
299 acidification because this treatment scenario balances the benefits of lower bauxite doses (Fig. 6)
300 with increased logistical simplicity. Moreover, pH reduction using mineral acids and the
301 Cr/Mn/Al data reported in Table 2 requires additional safety constraints, the costs of which are
302 not included in this cost analysis but would certainly increase labor and operational costs.
303 Therefore, heating without any acidification appears for now to be the most optimal and practical
304 treatment scenario to follow in field operation. It is worth noting that low-end ranges reported in
305 Table 3 are lower than median total cost estimates, and the overall conclusion of the analysis
306 remains unchanged. We therefore believe that uncertainty in the costs that were included is not a
307 major source of error.

308 In future work, it will be desirable to measure the total dissolved solids (TDS) in product
309 water for certain groundwater acidification scenarios where addition of HCl could increase the
310 TDS and adversely affect treated water taste. Additional research is needed to compare the
311 fluoride removal efficiency and energy requirements of the current batch reactor configuration to
312 regenerative filter columns using coarsely milled bauxite particles. To assess feasibility for large-
313 scale field application of the proposed defluoridation process, it would also be valuable to study
314 solids removal and handling and disposal of spent bauxite sludge. Potential applications include
315 incorporation of bauxite waste into construction materials (e.g., cement, bricks) or resource

316 recovery of Al for use in the metal manufacturing industry. Otherwise, proper disposal costs of
317 used bauxite should also be taken into account in future cost models.

318 **ASSOCIATED CONTENT**

319 **Supporting Information.** Details of methodology including electrolyte and sample preparation
320 and characterization, calculations for minimum required dose, and information on map
321 generation and cost estimation process are all provided in the SI, in addition to supporting tables
322 and figures referenced in the text. The SI is available free of charge on the ACS Publications
323 website.

324

325 **AUTHOR INFORMATION**

326 **Corresponding Author.** * Katya Cherukumilli, E-mail: katyacherukumilli@gmail.com; Phone:
327 407-529-9943; Address: 410 O'Brien Hall, Berkeley, CA 94720.

328 **Notes.** The authors declare no competing financial interest.

329 **ACKNOWLEDGEMENTS**

330 This work was supported by the Andrew and Virginia Rudd Foundation Endowed Chair in Safe
331 Water and Sanitation to A. Gadgil administered by the UCB Blum Center and NSF Graduate
332 Research Fellowships to K. Cherukumilli and T. Maurer. The Office of Basic Energy Sciences of
333 the U.S. DOE under Contract No. DE-AC02-05CH11231 supported material characterization
334 work at the Molecular Foundry. We are grateful to Durga and Gandhi Cherukumilli for
335 collecting bauxite samples from India and for valuable assistance given by Laura Lammers,
336 Tracy Mattox, Caroline Delaire, Alyssa Brand, Sanjay Srivatsan, James Barazesh, Daniel
337 Wilson, Katherine Boden, Dana Hernandez, Siva Bandaru, Chinmayee Subban, Shreya Agarwal,
338 and Arpad Horvath.

339 **REFERENCES**

- 340 (1) National Resource Council. *Fluoride in Drinking Water : A Review*; The National
341 Academies Press: Washington D.C., 2006.
- 342 (2) Fluorosis Research and Rural Development Foundation. *State of Art Report on Extent of*
343 *Fluoride In Drinking Water and the Resulting Endemicity in India*; New Delhi, India,
344 1999.
- 345 (3) Ozsvath, D. L. Fluoride and environmental health: A review. *Rev. Environ. Sci.*
346 *Biotechnol.* **2009**, *8* (1), 59–79 DOI: 10.1007/s11157-008-9136-9.
- 347 (4) Fewtrell, L.; Smith, S.; Kay, D.; Bartram, J. An attempt to estimate the global burden of
348 disease due to fluoride in drinking water. *J. Water Health* **2006**, *4* (4), 533–542 DOI:
349 10.2166/wh.2006.045.
- 350 (5) Churchill, H. V. Occurrence of fluorides in some waters of the United States. *Ind. Eng.*
351 *Chem. Res* **1931**, *23*, 996–998.
- 352 (6) Smith, M. C. and; Lantz, E. The Cause Of Mottled Enamel, A Defect Of Human Teeth.
353 *Tech. Bull. Univ. Arizona* **1931**, *32*, 253–282.
- 354 (7) Dean, H. T. Classification of mottled enamel diagnosis. *J. Am. Dent. Assoc.* **1934**, *21*,
355 1421–1426.
- 356 (8) Shortt, H. E.; McRobert, G. R.; Barnard, T. .; Nayar, A. S. Endemic Fluorosis in the
357 Madras Presidency. *Indian J. Med. Res.* **1937**, *25* (2), 533–564.
- 358 (9) Bhatnagar, A.; Kumar, E.; Sillanpää, M. Fluoride removal from water by adsorption-A
359 review. *Chem. Eng. J.* **2011**, *171* (3), 811–840 DOI: 10.1016/j.cej.2011.05.028.
- 360 (10) Jagtap, S.; Yenkie, M. K.; Labhsetwar, N.; Rayalu, S. Fluoride in Drinking Water and
361 Defluoridation of Water. *Chem. Rev.* **2012**, *112* (4), 2454–2466 DOI: 10.1021/cr2002855.

- 362 (11) Khairnar, M. R.; Dodamani, A. S.; Jadhav, H. C.; Naik, R. G.; Deshmukh, M. A.
363 Mitigation of Fluorosis - A Review. *J. Clin. DIAGNOSTIC Res.* **2015**, *9* (6), 5–9 DOI:
364 10.7860/JCDR/2015/13261.6085.
- 365 (12) Edmunds, W. M.; Smedley, P. L. Chapter 12: Fluoride in Natural Waters. In *Essentials of*
366 *Medical Geology*; Selinus, O., Ed.; Springer Netherlands: Dordrecht, 2013; pp 311–336.
- 367 (13) Osterwalder, L.; Johnson, C. A.; Yang, H.; Johnston, R. B. Multi-criteria assessment of
368 community-based fluoride-removal technologies for rural Ethiopia. *Sci. Total Environ.*
369 **2014**, *488–489* (1), 532–538 DOI: 10.1016/j.scitotenv.2013.10.072.
- 370 (14) Meenakshi; Maheshwari, R. C. Fluoride in drinking water and its removal. *J. Hazard.*
371 *Mater.* **2006**, *137* (1), 456–463 DOI: 10.1016/j.jhazmat.2006.02.024.
- 372 (15) Madhukar, M.; Murthy, B. M. S.; Udayashankara, T. H. A Review on Conventional and
373 Alternative Methods for Defluoridation of Water. *J. Water Pollut. Purif. Res.* **2014**, *1* (2),
374 1–12.
- 375 (16) Johnson, C. A.; Bretzler, A. *EAWAG WRQ Geogenic Contamination Handbook*; 2015.
- 376 (17) Buamah, R.; Mensah, R. A.; Salifu, A. Adsorption of fluoride from aqueous solution using
377 low cost adsorbent. *Water Sci. Technol. Water Supply* **2013**, *13* (2), 238 DOI:
378 10.2166/ws.2013.016.
- 379 (18) Craig, L.; Stillings, L. L.; Decker, D. L.; Thomas, J. M. Comparing activated alumina with
380 indigenous laterite and bauxite as potential sorbents for removing fluoride from drinking
381 water in Ghana. *Appl. Geochemistry* **2015**, *56*, 50–66 DOI:
382 10.1016/j.apgeochem.2015.02.004.
- 383 (19) Kalista, P. H. Defluoridation of High Fluoride Waters from Natural Water Sources by
384 Using Soils Rich in Bauxite and Kaolinite. *J. Eng. Appl. Sci.* **2009**, *4* (4), 240–246.

- 385 (20) Kayira, C.; Sajidu, S.; Masamba, W.; Mwatseteza, J. Defluoridation of Groundwater
386 Using Raw Bauxite: Kinetics and Thermodynamics. *CLEAN - Soil, Air, Water* **2014**, *42*
387 (5), 546–551 DOI: 10.1002/clen.201200488.
- 388 (21) Lavecchia, R.; Medici, F.; Piga, L.; Rinaldi, G.; Zuorro, A. Fluoride removal from water
389 by adsorption on a high alumina content bauxite. *Chem. Eng. Trans.* **2012**, *26*, 225–230
390 DOI: 10.3303/CET1226038.
- 391 (22) Mohapatra, D.; Mishra, D.; Mishra, S. P.; Chaudhury, G. R.; Das, R. P. Use of oxide
392 minerals to abate fluoride from water. *J. Colloid Interface Sci.* **2004**, *275* (2), 355–359
393 DOI: 10.1016/j.jcis.2004.02.051.
- 394 (23) Sajidu, S.; Kayira, C.; Masamba, W.; Mwatseteza, J. Defluoridation of Groundwater
395 Using Raw Bauxite: Rural Domestic Defluoridation Technology. *Environ. Nat. Resour.*
396 *Res.* **2012**, *2* (3), 1–9 DOI: 10.5539/enrr.v2n3p1.
- 397 (24) Sajidu, S. M., I.; Masamba, W. R., L.; Thole, B.; Mwatseteza, F. Groundwater fluoride
398 levels in villages of Southern Malawi and removal studies using bauxite. *Int. J. Phys. Sci.*
399 **2008**, *3* (1), 1–11.
- 400 (25) Sujana, M. G.; Anand, S. Fluoride removal studies from contaminated ground water by
401 using bauxite. *Desalination* **2011**, *267* (2–3), 222–227 DOI: 10.1016/j.desal.2010.09.030.
- 402 (26) Thole, B.; Mtalo, F.; Masamba, W. Groundwater Defluoridation with Raw Bauxite,
403 Gypsum, Magnesite, and Their Composites. *CLEAN - Soil, Air, Water* **2012**, *40* (11),
404 1222–1228 DOI: 10.1002/clen.201100111.
- 405 (27) Atasoy, A. D.; Yesilnacar, M. I.; Sahin, M. O. Removal of fluoride from contaminated
406 ground water using raw and modified bauxite. *Bull. Environ. Contam. Toxicol.* **2013**, *91*
407 (5), 595–599 DOI: 10.1007/s00128-013-1099-z.

- 408 (28) Malakootian, M.; Javdan, M.; Iranmanesh, F. Fluoride Removal from Aqueous Solutions
409 Using Bauxite Activated Mines in Yazd Province (Case Study : Kuhbanan Water). *J.*
410 *Community Heal. Res.* **2014**, 3 (2), 103–114.
- 411 (29) Das, N.; Pattanaik, P.; Das, R. Defluoridation of drinking water using activated titanium
412 rich bauxite. *J. Colloid Interface Sci.* **2005**, 292 (1), 1–10 DOI:
413 10.1016/j.jcis.2005.06.045.
- 414 (30) Salifu, A.; Petrusevski, B.; Mwampashi, E. S.; Pazi, I. A.; Ghebremichael, K.; Buamah,
415 R.; Aubry, C.; Amy, G. L.; Kenedy, M. D. Defluoridation of groundwater using
416 aluminum-coated bauxite: Optimization of synthesis process conditions and equilibrium
417 study. *J. Environ. Manage.* **2016**, 181, 108–117 DOI: 10.1016/j.jenvman.2016.06.011.
- 418 (31) Wambu, E. W.; Ambusso, W. O.; Onindo, C.; Muthakia, G. K. Review of fluoride
419 removal from water by adsorption using soil adsorbents – an evaluation of the status. *J.*
420 *Water Reuse Desalin.* **2015**, jwr2015073 DOI: 10.2166/wrd.2015.073.
- 421 (32) Çengelöglu, Y. Removal of fluoride from aqueous solution by using red mud. *Sep. Purif.*
422 *Technol.* **2002**, 28 (1), 81–86 DOI: 10.1016/S1383-5866(02)00016-3.
- 423 (33) Tor, A.; Danaoglu, N.; Arslan, G.; Cengelöglu, Y. Removal of fluoride from water by
424 using granular red mud: Batch and column studies. *J. Hazard. Mater.* **2009**, 164 (1), 271–
425 278 DOI: 10.1016/j.jhazmat.2008.08.011.
- 426 (34) Cherukumilli, K.; Delaire, C.; Amrose, S.; Gadgil, A. J. Factors Governing the
427 Performance of Bauxite for Fluoride Remediation of Groundwater. *Environ. Sci. Technol.*
428 **2017**, 51 (4), 2321–2328 DOI: 10.1021/acs.est.6b04601.
- 429 (35) Ayoob, S.; Gupta, A. K. Fluoride in Drinking Water: A Review on the Status and Stress
430 Effects. *Crit. Rev. Environ. Sci. Technol.* **2006**, 36 (6), 433–487 DOI:

- 431 10.1080/10643380600678112.
- 432 (36) Central Groundwater Board Ministry of Water Resources Government of India. *Ground*
433 *water quality in shallow aquifers of India*; Faridabad, 2010.
- 434 (37) Geologic Survey of India. *Detailed Information of Bauxite in India*; Hyderabad, India,
435 1994; Vol. 211.
- 436 (38) Thakre, D.; Rayalu, S.; Kawade, R.; Meshram, S.; Subrt, J.; Labhsetwar, N. Magnesium
437 incorporated bentonite clay for defluoridation of drinking water. *J. Hazard. Mater.* **2010**,
438 *180* (1–3), 122–130 DOI: 10.1016/j.jhazmat.2010.04.001.
- 439 (39) US-EPA. Drinking Water Contaminants – Standards and Regulations
440 <https://www.epa.gov/dwstandardsregulations> (accessed Mar 18, 2017).
- 441 (40) Fluorosis Research & Rural Development Foundation (FR&RDF). Districts Endemic for
442 Fluorosis <http://www.fluorideandfluorosis.com/fluorosis/districts.html> (accessed Dec 4,
443 2017).
- 444 (41) Singh, A.; Chakraborty, S.; Roy, T. K. Village Size in India. *Asian Popul. Stud.* **2008**, *4*
445 (2), 111–134 DOI: 10.1080/17441730802246630.
- 446 (42) The Registrar General and Census Commissioner of India. India State Census
447 <http://www.census2011.co.in/states.php>.
- 448 (43) Gorchev, H. G.; Ozolins, G.; World Health Organization. *Guidelines for drinking-water*
449 *quality, 4th ed.*, 4th ed.; World Health Organization: Geneva, 2011; Vol. 38.
- 450 (44) Gadgil, A. J.; Roy, J. *IUSSTF project final report*; 2017.
- 451 (45) Amrose, S. E.; Bandaru, S. R. S.; Delaire, C.; van Genuchten, C. M.; Dutta, A.;
452 DebSarkar, A.; Orr, C.; Roy, J.; Das, A.; Gadgil, A. J. Electro-chemical arsenic
453 remediation: Field trials in West Bengal. *Sci. Total Environ.* **2014**, *488–489* (1), 539–546

- 454 DOI: 10.1016/j.scitotenv.2013.11.074.
- 455 (46) Baranyai, V. Z.; Kristály, F.; Szűcs, I. Influence of grain and crystallite size on the
456 gibbsite to boehmite thermal transformation. *Stud. Univ. Babeş-Bolyai. Chem.* **2015**, *60*
457 (2), 27–44.
- 458 (47) Dzombak, D. A., and Karamalidis, A. K. *Surface Complexation Modeling: Gibbsite*;
459 Wiley: New York, 2010.
- 460 (48) Ayoob, S.; Gupta, A. K.; Bhakat, P. B.; Bhat, V. T. Investigations on the kinetics and
461 mechanisms of sorptive removal of fluoride from water using alumina cement granules.
462 *Chem. Eng. J.* **2008**, *140* (1–3), 6–14 DOI: 10.1016/j.cej.2007.08.029.
- 463 (49) Teng, S. X.; Wang, S. G.; Gong, W. X.; Liu, X. W.; Gao, B. Y. Removal of fluoride by
464 hydrous manganese oxide-coated alumina: Performance and mechanism. *J. Hazard.*
465 *Mater.* **2009**, *168* (2–3), 1004–1011 DOI: 10.1016/j.jhazmat.2009.02.133.
- 466 (50) Maliyekkal, S. M.; Shukla, S.; Philip, L.; Nambi, I. M. Enhanced fluoride removal from
467 drinking water by magnesia-amended activated alumina granules. *Chem. Eng. J.* **2008**,
468 *140* (1–3), 183–192 DOI: 10.1016/j.cej.2007.09.049.
- 469 (51) Peryea, F.J., Kittrick, J. A. Relative solubilities of corundum, gibbsite, boehmite, and
470 diasporite at standard state conditions. An addendum. *Clays Clay Miner.* **1988**, *36* (5), 391–
471 396 DOI: 10.1346/CCMN.1989.0370611.
- 472 (52) Valeev, D. V.; Mansurova, E. R.; Bychinskii, V. A.; Chudnenko, K. V. Extraction of
473 Alumina from high-silica bauxite by hydrochloric acid leaching using preliminary roasting
474 method. *IOP Conf. Ser. Mater. Sci. Eng.* **2016**, *110* (1), 1–6 DOI: 10.1088/1757-
475 899X/110/1/012049.

