Journal of Environmental Protection, 2025, 16(6), 574-592
https://www.scirp.org/journal/jep
ISSN Online: 2152-2219
ISSN Print: 2152-2197

# Evaluation of pH Adjustment Chemical for Arsenic-Fluoride Removal Using Activated Alumina

**Shubhashini Oza[1], Kayla Bauhs[2], Giridhar Upadhyaya[3], Joey Romo[4], Sandy A. Smith[5], Brian Hamrick[6], Katherine Y. Bell[7]**

[1]Research and Innovation, Brown and Caldwell, Charlotte, NC, USA
[2]Treatability Laboratory, Brown and Caldwell, Nashville, TN, USA
[3]Brown and Caldwell, Irvine, CA, USA
[4]City of Buckeye, Buckeye, AZ, USA
[5]Burnett Inc., Campobello, SC, USA
[6]Brown and Caldwell, Phoenix, AZ, USA
[7]Research and Innovation, Brown and Caldwell, Nashville, TN, USA
Email: soza@brwncald.com

**How to cite this paper:** Oza, S., Bauhs, K., Upadhyaya, G., Romo, J., Smith, S.A., Hamrick, B. and Bell, K.Y. (2025) Evaluation of pH Adjustment Chemical for Arsenic-Fluoride Removal Using Activated Alumina. *Journal of Environmental Protection*, **16**, 574-592.
https://doi.org/10.4236/jep.2025.166030

**Received:** May 24, 2025
**Accepted:** June 24, 2025
**Published:** June 27, 2025



## Abstract

Arsenic and fluoride are co-existing contaminants commonly found in groundwater used for drinking water supply and often exceeding drinking water maximum contaminant levels of 10 µg/L and 4 mg/L, respectively. Adsorption and coagulation followed by filtration are technologies used for treatment. The USA-EPA has identified alumina adsorption as the best available technology. While arsenic removal with activated alumina was not pH-dependent in this study, fluoride removal was pH dependent, with an optimal range between 5.0 - 6.0. A bench study was conducted comparing sulfuric acid, hydrochloric acid, and carbon dioxide as alternatives for pH adjustment. While arsenic and fluoride removal were independent of chemicals used for pH adjustment, the costs of pH adjustment with carbon dioxide and sulfuric acid were similar for the site considered, indicating that carbon dioxide can be a safer and better alternative for pH adjustment if a carbon dioxide generating facility is closer to treatment site.

## Keywords

Arsenic, Fluoride, Activated Alumina, pH Adjustment, Carbon Dioxide, Adsorption

## 1. Introduction

The co-existence of arsenic and fluoride in groundwater used as a drinking water supply is well-documented worldwide [1]-[3]. Global health concerns associated with these constituents have been recognized and tracked for more than six decades [4]. The World Health Organization (WHO) published international standards for drinking water as early as 1958 and identified arsenic as one of five toxic substances and provided a maximum allowable concentration in drinking water of 0.2 milligrams per liter (mg/L) [5]. WHO has also listed specific chemical substances which may affect health if present at concentrations greater than definite limits, which also includes fluoride with a limit of 1.0 to 1.5 mg/L. Higher concentrations of fluoride in drinking water are associated with dental fluorosis in children [5]. In the United States (USA), the Environmental Protection Agency (EPA) regulates fluoride at a maximum contaminant level (MCL) of 4 mg/L with a secondary MCL of 2 mg/L [6]). More recently, a federal judge ordered the EPA to further regulate fluoride in drinking water after a lawsuit arguing that fluoride poses an unreasonable risk for neurological development in children [7].

Fluorine is plentifully present in the earth crust and forms minerals in soils and sediments. There are various pathways for fluoride accumulation in surface and groundwater sources [8]. Podgorski and Berg conducted a global analysis and prediction on fluoride in groundwater and created a hazard map, which indicated hotspots for fluoride in central Australia, western North America, eastern Brazil and several areas in Africa and Asia [9].

Like fluoride contamination, researchers have created tools, such as maps and prediction models for estimating the arsenic concentration in groundwater globally, noting hotspots in countries like Argentina [10], China [11], India [12], Mexico [13], and the USA [14] [15]. Further, studies have indicated that more than 100 countries are affected by fluoride contamination in groundwater [16] and 50 countries by arsenic [17].

Co-existence of arsenic and fluoride in groundwaters is well documented [18]-[22]. Currell *et al*. studied the Yuncheng Basin in China and observed higher concentrations of arsenic and fluoride in agriculturally impacted shallow groundwater, but the deeper groundwater did not have significant impacts from anthropogenic sources [23]. Bondu *et al*. assessed source and distribution of arsenic and fluoride in groundwater from southern Quebec, Canada and concluded that fluoride concentrations are closely tied to calcium concentrations, and higher arsenic concentrations are not directly related to sulfide oxidation, rather from reductive dissolution of iron and manganese oxyhydroxides [24]. The USA Geological Survey has conducted a detailed investigation in the Newark Basin, Southeastern Pennsylvania to understand the elevated arsenic and fluoride concentration in the groundwater [25]. Alcaine *et al*. reviewed the hydrogeochemical controls on the mobility of arsenic and fluoride in shallow aquifers of the northeastern La Pampa Province in Argentina and concluded that higher arsenic concentrations were associated with geochemical reactions, hydrogeological characteristics of the local

aquifer, and climatic factors [26].

The health hazards associated with fluoride are predominantly dental and skeletal fluorosis [27] although more recent studies are pointing to risks to neurological development in children [28] [29]. Arsenic, on the other hand, is a carcinogen and has various health effects based on the duration of exposure. Noting that the coexistence of arsenic and fluoride in groundwater is well documented, the hazards associated with co-contaminated drinking water is a concern [13] [30]-[32] because they may function independently or synergistically or antagonistically to one another [33]. In animal studies, co-exposure of arsenic and fluoride, even at low concentrations resulted in decreased comet tail and detrimental effects on livers and kidneys [34]-[36]. Thus, co-existence of fluoride and arsenic in groundwater and drinking water necessitates an evaluation of treatment methods for their simultaneous removal.

The most common treatment processes for fluoride removal are membranes, coagulation/precipitation, ion-exchange, electrochemical treatment, and adsorption [37]. Similarly, arsenic removal can be achieved by pre-oxidation, pH adjustment, ion-exchange, adsorption with activated alumina, reverse osmosis, and enhanced lime softening [38] [39]. Because there is much overlap in the treatment processes for the removal of individual elements, the same treatment processes have also been evaluated for simultaneous removal of these two constituents from groundwater [30]-[32] [40]-[43]. Among the various treatment options, activated alumina adsorption has received significant interest among researchers for arsenic and fluoride co-removal. Researchers have documented that adsorption is a cost-benefit technique for simultaneous removal of arsenic and fluoride from water [44].

Concurrent removal of arsenic and fluoride with activated alumina is dependent on the operational pH, regardless of the concentrations of these constituents in the water [32] [42] [45]. Fluoride is effectively removed at lower pH (4.5 to 6.5) [46], while arsenic (V) is most effectively removed at pH ranges 6 to 8 [47] with arsenic (III) removal being independent of pH [48]. Lakshmanan *et al*., have evaluated arsenic removal (both V and III) with aluminum, iron, titanium and zirconium coagulants and reported that iron coagulant is the most cost effective in removal or arsenic in pH ranges 6.5 to 8.5 [48]. Design of activated alumina adsorption treatment processes typically include pH reduction of source water with sulfuric acid, prior to adsorption [49]. The primary reason for selection of this mineral acid is the more moles of hydrogen ion per mole of sulfuric acid compared to monovalent mineral acids, such as hydrochloric acid. Carbon dioxide gas can be a simple, safe, and affordable alternative to mineral acids for pH adjustment, especially when total dissolved solids (TDS) are of concern. Further, adding a mineral acid in the pre-treatment step increases the concentration of TDS. For example, chloride and sulfate concentration will increase when using hydrochloric acid and sulfuric acid, respectively. These ions can compete for adsorption sites on activated alumina making the adsorption process less efficient.

To our knowledge, there is limited information on the use of carbon dioxide at drinking water facilities for simultaneous removal of arsenic and fluoride. This study evaluated the impact of the type of acid used for pH adjustment on arsenic and fluoride removal from a groundwater source using activated alumina. The effectiveness of each acid type on arsenic and fluoride removal was assessed by considering the acid addition rate, alkalinity changes, impact of competing anions, and optimal pH. Further, a cost-benefit analysis of acid selection for pH adjustment was conducted.

## 2. Materials and Methods

### 2.1. Groundwater

Ground water samples were collected from the entry point into the distribution system (prior to disinfection) of a groundwater treatment facility in Arizona. Samples were stored at 4 degrees Celsius (˚C) and brought to room temperature (20-25˚C) prior to testing.

### 2.2. Activated Alumina

ActiGuard® Fluorograde Activated Alumina, with a mesh size of 14 × 28, was purchased from Delta Adsorbents. The activated alumina was rinsed with 18-ohm water (generated from Millipore Sigma IQ 7005 water purification system) fifteen times to remove small particles (fines). The cleaned media was dried at 105˚C overnight before the testing.

### 2.3. Analytical Methods

The groundwater and activated alumina treated water samples were filtered through 0.45-micron filter paper using vacuum filtration prior to analysis. Filtered samples were analyzed for fluoride, chloride, nitrate, and sulfate using ion chromatography (IC) [AG18-Fast-4 micron RFIC 4 * 30 mm and Separation column Dionex IonPac AS18-fast-4 micron RFIC 4 * 150 mm] on a Thermo Fisher Dionex Integrion HPICTM System. Duplicate samples were analyzed with quality control samples with each batch of ten samples. Quality control samples included a laboratory blank, laboratory control standard, and laboratory spike sample. Thermo Scientific's Dionex Six Anion-II standard (P/N 057590) was used to prepare laboratory control standards and to develop a five-point calibration curve. Analysis of total organic carbon (TOC) and dissolved organic carbon (DOC) was conducted using a Sievers M9 Laboratory TOC Analyzer. Unfiltered samples were analyzed for TOC and samples filtered through 0.45-micron syringe filters were analyzed for DOC. Hach TNTplus 843 test kits (range 0.05 - 1.50 mg P/L) were used for orthophosphate analysis with Method 10209/10210 (equivalent to USEPA Method 365.3). Hach Silica Powder Pillows (range 1 - 100 mg/L as $SiO_2$) were used for silica measurement using Method 8185. TDS was measured according to Standard Methods 2540 C.

Arsenic was analyzed using inductively coupled plasma-mass spectrometry fol-

lowing USEPA Method 6020, to capture the low level (μg/L) concentrations in samples. The samples were filtered through 0.45-micron filter paper using a vacuum filtration apparatus and acid-preserved prior to the analysis.

Alkalinity was analyzed using Hach TNTplus 870 test kits, with a range of 25 - 400 mg/L as calcium carbonate ($CaCO_3$), using Method 10239. Bicarbonate concentration was calculated from total alkalinity using the equation provided in the Standard Method 4500-$CO_2$.

## 2.4. Batch Adsorption Experiment

Each batch adsorption experiment was conducted using 500 mL of pH-adjusted source water placed in high density polyethylene (HDPE) bottles at room temperature (20 - 25˚C). The optimum amount of activated alumina required, and the mixing time were evaluated by preliminary testing.

After measuring initial pH, temperature, and alkalinity of the groundwater, samples were aliquoted into HDPE bottles and pH was adjusted to 5.5 to 7.5 (**Table 1**), except the control sample. A 1 normal (N) hydrochloric acid solution, 1 N sulfuric acid solution, and carbonated water were used for adjusting sample pH. All experiments were conducted in duplicate. Both mineral acids, hydrochloric and sulfuric, were obtained from Fischer Chemicals, and carbonated water was supplied by Burnett-Inc, which contained approximately 2,000 mg/L we carbon dioxide. Alkalinity was also measured in the pH adjusted samples.

Bottles were leak-tested and placed on an Eberbach E6145 orbital shaker at 150 rotations per minute (rpm) for 180 minutes (50, 51). After mixing the treated water was filtered through 0.45-micron filters and analyzed for parameters described in Section 2.3. After treatment with activated alumina adsorption, the pH of the water was adjusted with 0.1 N sodium hydroxide to match the initial pH of the groundwater. The alkalinity was measured once more, after sodium hydroxide addition.

## 2.5. Preliminary Evaluation

To determine the optimum activated alumina dose required, a preliminary evaluation was conducted at a constant mixing time of 180 minutes, constant mixing speed of 150 rpm, and an adjusted initial pH of 6 (with hydrochloric acid). Activated alumina concentrations evaluated were 0.1, 0.5, 1, 2, 3, 5, 7.5 and 10 g/L and experiments were conducted in duplicate. Results showed a diminishing efficiency of treatment after 5 g/L activated alumina, where fluoride removal plateaued above 7 g/L (**Figure 1**). Therefore, 5 g/L of activated alumina was chosen for further testing (considered optimum) for simultaneous removal of fluoride and arsenic.

Following optimization of the activated alumina dose, pH optimization was conducted with initial pH values of 5.5, 6.0, 6.5, 7.0 and 7.5 with 5 g/L of activated alumina, using a mixing time of 180 minutes, and mixing speed of 150 rpm. Experiments were conducted in duplicate. Results confirmed the pH dependance of

fluoride removal, however, arsenic removal was independent of pH within the range evaluated; notably, in this case study, the observed initial concentration of arsenic in the groundwater was comparatively lower than other studies (Figure 2). With the maximum fluoride removal observed at pH 5.5, its removal efficiency declined with increasing pH and plateaued after pH 7.0.

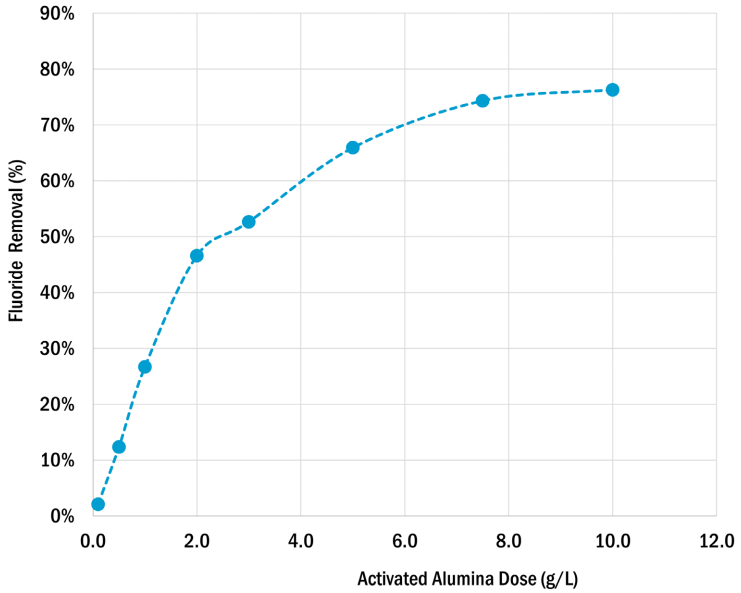


Figure 1. Fluoride removal percentage with respect to activated alumina dosage.

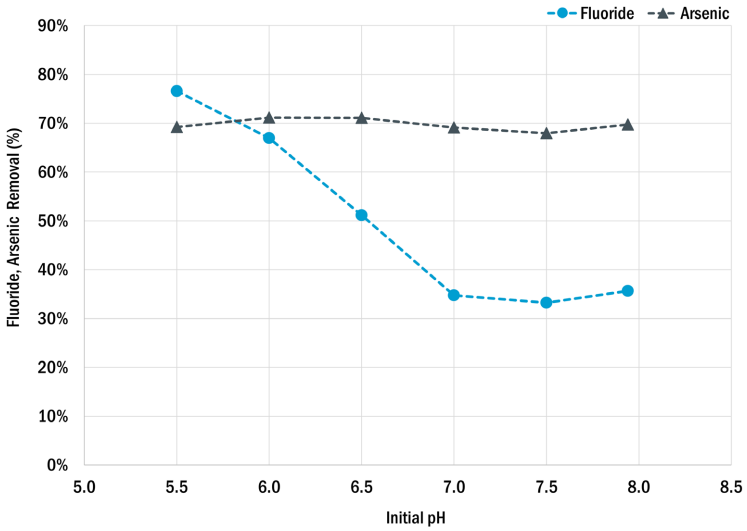


Figure 2. Fluoride and arsenic removal with respect to pH.

Mixing time ranges were evaluated after the activated alumina dose (5 g/L) and initial pH of 6.0 were optimized. The mixing/contact times evaluated were 7.5, 15, 30, 60, 90, 120, 180 and 240 minutes. Both arsenic and fluoride removal increased with the mixing time (Figure 3). Table 1 summarizes all the preliminary testing tests carried out.

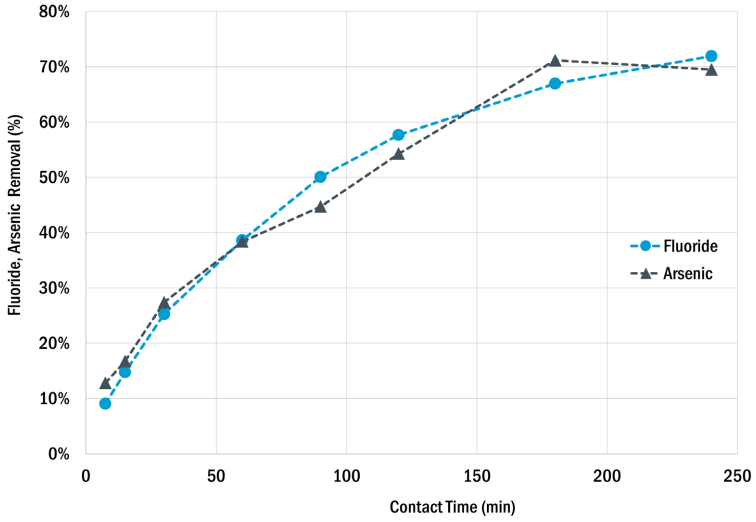


**Figure 3.** Fluoride and arsenic removal with respect varying contact time.

Based on these preliminary evaluations, further experiments were conducted with 5 g/L of activated alumina, at a mixing time of 180 minutes and mixing speed of 150 rpm.

**Table 1.** Preliminary testing.

| Step 1: Test to determine optimum amount of activated alumina | | | | |
|---|---|---|---|---|
| Test number | Activated alumina dose (g/L) | Mixing time (minutes) | Adjusted pH (s.u.) | Mixing speed (rotations per minute) |
| 1 | 0.1 | 180 | 6.0 | 150 |
| 2 | 0.5 | 180 | 6.0 | 150 |
| 3 | 1.0 | 180 | 6.0 | 150 |
| 4 | 2.0 | 180 | 6.0 | 150 |
| 5 | 3.0 | 180 | 6.0 | 150 |
| 6 | 5.0 | 180 | 6.0 | 150 |
| 7 | 7.5 | 180 | 6.0 | 150 |
| | 10.0 | 180 | 6.0 | 150 |
| Step 2: Test to determine optimum pH | | | | |
| Test number | Activated alumina dose (g/L) | Mixing time (minutes) | Adjusted pH (s.u.) | Mixing speed (rotations/minute) |
| 8 | 5 | 180 | 5.5 | 150 |
| 9 | 5 | 180 | 6.0 | 150 |
| 10 | 5 | 180 | 6.5 | 150 |
| 11 | 5 | 180 | 7.0 | 150 |
| 12 | 5 | 180 | 7.5 | 150 |
| 13 | 5 | 180 | 7.98/as such | 150 |
| Step 3: Test to determine optimum mixing time | | | | |
| Test number | Activated alumina dose (g/L) | Mixing time (minutes) | Adjusted pH (s.u.) | Mixing speed (rotations/minute) |
| 14 | 5 | 7.5 | 6.0 | 150 |
| 15 | 5 | 15 | 6.0 | 150 |
| 16 | 5 | 30 | 6.0 | 150 |
| 17 | 5 | 60 | 6.0 | 150 |

Continued

| | | | | |
|---|---|---|---|---|
| 18 | **5** | **90** | **6.0** | **150** |
| 19 | 5 | 120 | 6.0 | 150 |
| 20 | 5 | 180 | 6.0 | 150 |
| 21 | 5 | 240 | 6.0 | 150 |

## 3. Results and Discussion

### 3.1. Groundwater Characteristics

The initial groundwater quality characterization is summarized in Table 2.

Table 2. Groundwater characteristics.

| Parameter | Units | Range |
|---|---|---|
| pH | Standard units | 8.0 - 8.2 |
| Temperature | ˚C | 24 - 25 |
| Alkalinity | mg/L as $CaCO_3$ | 62 - 70 |
| Dissolved organic carbon | mg/L as C | 1.0 - 1.6 |
| Calcium | mg/L | 16 |
| Magnesium | mg/L | 1.10 |
| Sodium | mg/L | 85.0 |
| Potassium | mg/L | 2.20 |
| Arsenic | µg/L | 9.9 - 10.0 |
| Chloride | mg/L | 61 - 63 |
| Fluoride | mg/L | 4.0 - 4.1 |
| Sulfate | mg/L | 39 - 43 |
| Nitrate | mg/L | 5.7 - 6.2 |
| Phosphate | mg/L | 0.61 |
| Bicarbonate | mg/L as $CaCO_3$ | 61 - 70 |

### 3.2. Type of Acid Used for pH Adjustment and Its Impact on Arsenic and Fluoride Adsorption

Fluoride removal rate was marginally lower when sulfuric acid was used for pH adjustment versus hydrochloric acid and carbon dioxide, in the pH range of 5.5 and 6.5 (Figure 4). As pH approaches a neutral range, fluoride removal is similar among the three acids tested for pH adjustment. This is specifically attributed to the fluoride removal chemistry, which is predominantly higher at lower pH ranges (Figure 4), and not the type of acid used. Rathore *et al*. observed similar trends reporting that below pH of 3.5, the predominant species present is hydrogen fluoride, which is non-ionic; and, as pH increases the concentration of fluoride ion (F-)—the ionic species—increases and becomes predominant above pH of 5 [42]. While arsenic removal was marginally lower with both carbon dioxide and sulfuric acid in comparison to hydrochloric acid, arsenic removal with activated alumina is generally not pH dependent at the concentrations observed in the water evaluated in this study (Figure 5).

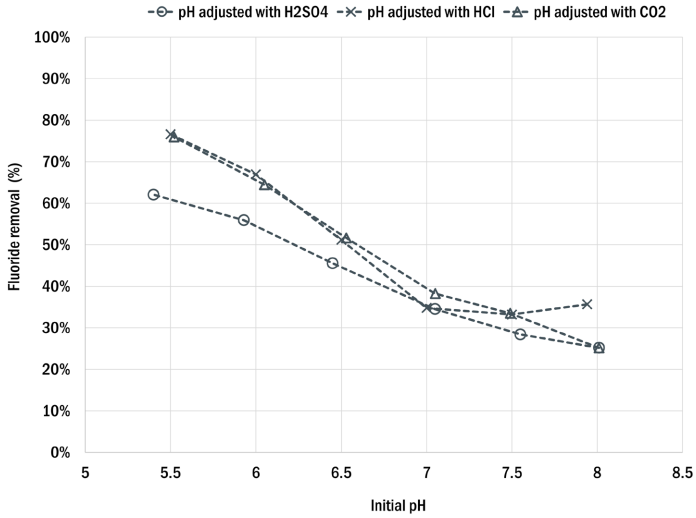


**Figure 4.** Fluoride removal rates with different acids used for initial pH adjustment.

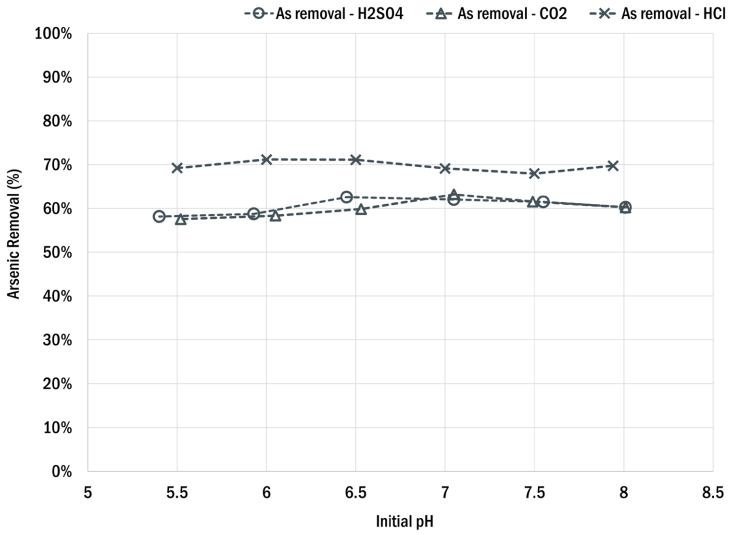


**Figure 5.** Arsenic removal rates with different acids used for initial pH adjustment.

### 3.3. Impact of Alkalinity on the Type of Acid Used for pH Adjustment

Alkalinity was measured after pH adjustment before batch testing and after batch testing. Alkalinity decreased significantly post-pH adjustment with both mineral acids (**Figure 6**). Further alkalinity measured after activated alumina treatment was lower for mineral acid pH adjusted tests. When initial pH was adjusted to 6, the alkalinity prior to activated alumina testing with sulfuric acid was 22 mg/L as $CaCO_3$, with hydrochloric acid was 27 mg/L as $CaCO_3$, and with carbon dioxide was 65 mg/L as $CaCO_3$ (**Figure 6**). The observed percent difference in alkalinity between carbon dioxide and sulfuric acid treated samples was 195% and between carbon dioxide and hydrochloric acid was 141%. Alkalinity marginally decreased with carbon dioxide addition, and the observed alkalinity, post-treatment with activated alumina, was higher than the initial alkalinity of 70 - 75 mg/L as $CaCO_3$.

This indicates that pH adjustment with carbon dioxide can enhance buffering capacity through changes in the carbonate buffer system (bicarbonate and carbonate ions) in the water. The changes in the buffering capacity depends on the raw water characteristics, such as pH, alkalinity and hardness.

Although alkalinity is not a primary or secondary parameter as part of the National Drinking Water Regulations, the recommended alkalinity level in drinking water ranges between 75 mg/L to 150 mg/L as $CaCO_3$. Alkalinity, pH, dissolved inorganic carbon (DIC) and corrosion inhibitors are the critical water quality parameters that impact lead and copper release in the distribution system. Further, alkalinity, pH, and DIC also impact the corrosion of pipes in the distribution system [50]. To prevent pipe corrosion, water treatment plants typically maintain alkalinity greater than 20 mg/L as $CaCO_3$ and pH ~ 8 [51]. Given that carbon dioxide may help maintain higher alkalinity, pre-treatment with carbon dioxide could help address corrosion control in the distribution network.

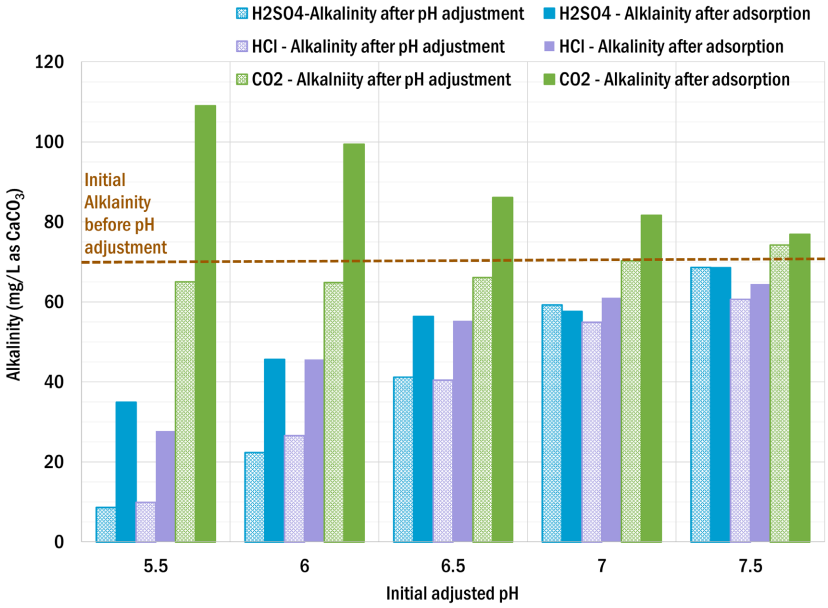


**Figure 6.** Alkalinity post pH adjustment with different acids used for initial pH adjustment.

## 3.4. pH Adjustment Post Activated Alumina Treatment

Post activated alumina treatment, prior to disinfection, chemicals are added to the water to maintain reasonable pH and alkalinity in the distribution system. This is achieved by addition of various chemicals (such as caustic, lime, calcium chloride) and EPA provides guidance documents on the choice of chemical selection based on the water quality [49]. Mimicking full-scale application, pH adjustment after activated alumina treatment was evaluated using a 0.1 N sodium hydroxide solution; the adjustment was performed for samples pretreated with sulfuric acid and carbon dioxide. Water pre-treated with hydrochloric acid was not chosen because it had a high percentage difference in alkalinity, between the pre and post activated alumina treatment.

Based on the initial pH, varying amounts of sodium hydroxide were required for post-stabilization, as expected (Figure 7). When the initial pH is reduced to 5.5, 2 ml/L of 0.1 sodium hydroxide were required for sulfuric acid pre-treated samples while 9.6 ml/L of 0.1 sodium hydroxide was required for carbon dioxide pre-treated samples. But when the initial pH was 6, 1.6 ml/L of 0.1 sodium hydroxide was required for sulfuric acid pretreated samples, while 3.6 ml/L of 0.1 sodium hydroxide was required for carbon dioxide pretreated samples. Because carbon dioxide enhances buffering capacity, the amount of sodium hydroxide required for pH adjustment post-treatment was higher than waters pre-treated with sulfuric acid.

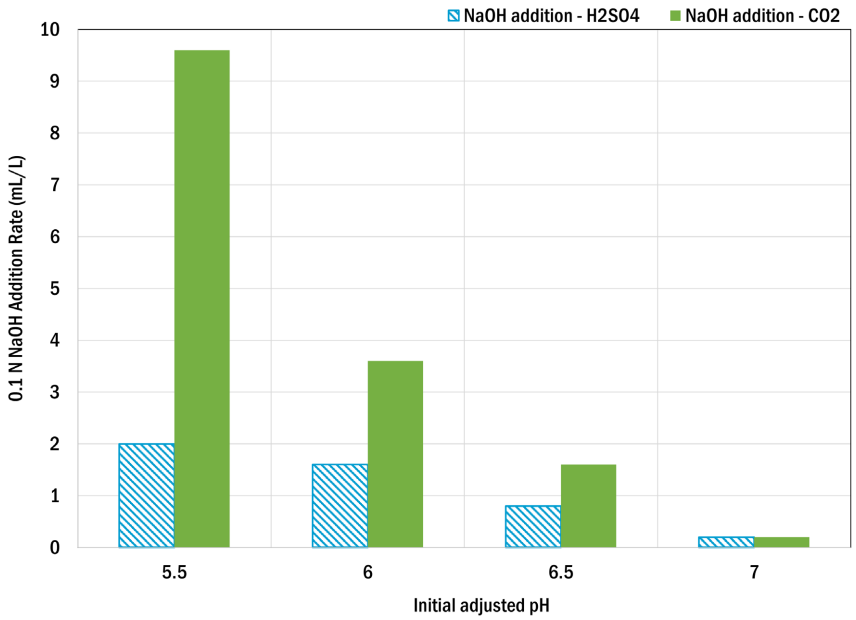


Figure 7. NaOH requirement post activated alumina treatment for experiments using $H_2SO_4$ and $CO_2$ for initial pH adjustment.

## 3.5. Behaviors of Competing Ions

Activated alumina can remove other competing anions such as, nitrate, chloride, sulfate, etc. To elucidate the effects of competing anions, the removal efficiency of other anions, such as chloride, sulfate, nitrate, bicarbonate, and silica were also evaluated for the three different pretreatments, used for initial pH adjustment. For chloride, no significant removal was observed when initial pH was adjusted with sulfuric acid and hydrochloric acid, but with carbon dioxide, ~ 10% chloride removal was observed at a pH of 5.5. Chloride removal decreased with increasing pH (Figure 8). The sulfate trend was like chloride where, when pH was adjusted with carbon dioxide, higher sulfate removal (45%) was observed at the lower initial adjusted pH of 5.5, its removal rate decreased with increasing pH. Twenty percent sulfate removal was observed at the lower initial pH of 5.5 with both hydrochloric acid and sulfuric acid, and sulfate removal decreased with increasing pH (Figure 9).

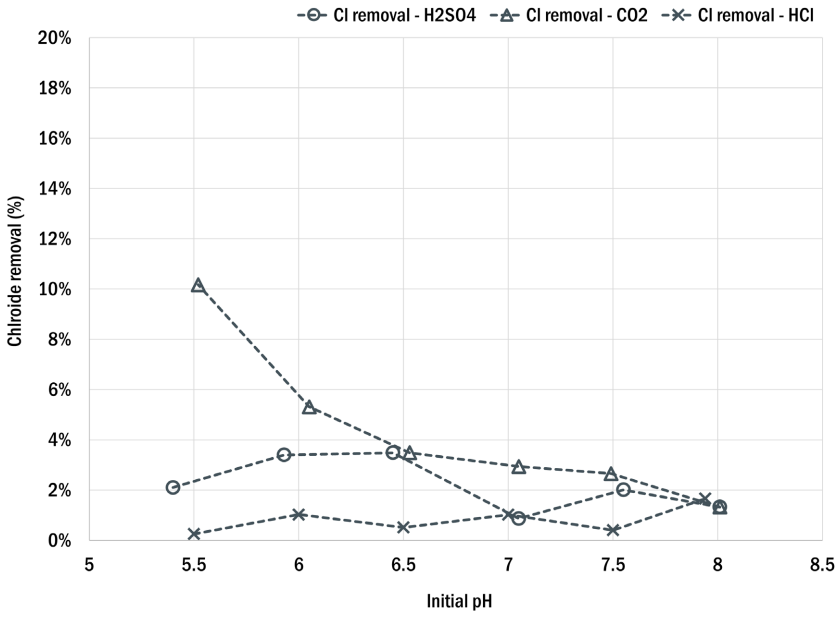


**Figure 8.** Chloride removal rate comparison at various initial pH and with different acids.

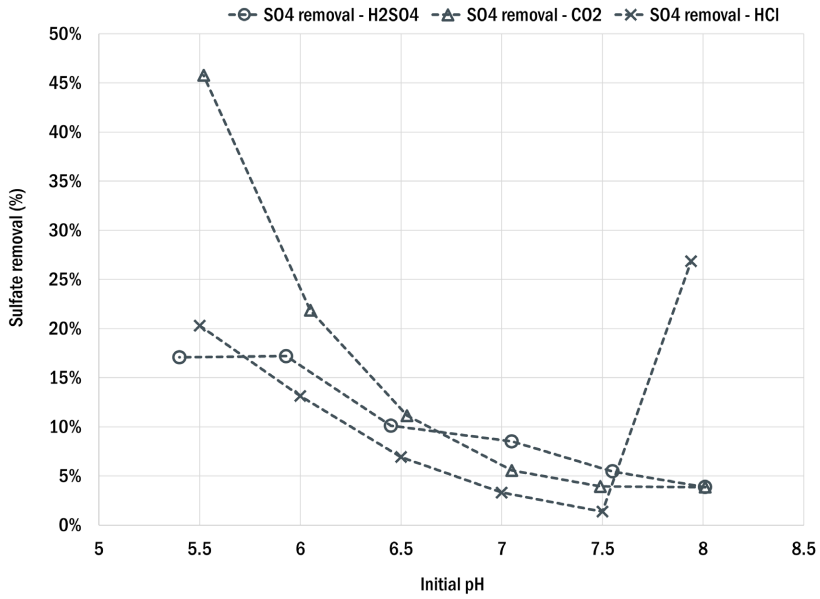


**Figure 9.** Sulfate removal rate comparison at various initial pH and with different acids.

In the case of nitrate, no removal was observed when pH was adjusted with hydrochloric acid or carbon dioxide, but a 10% removal was observed when the initial pH was adjusted to 5.5 with sulfuric acid. The nitrate removal rate decreased with increased initial adjusted pH, like that of chloride and sulfate (**Figure 10**). The bicarbonate trend was not evaluated when pH was adjusted with carbon dioxide because increases in pH would increase the bicarbonate concentration. Both sulfuric acid and hydrochloric acid adjusted samples showed 50% - 55% bicarbonate removal at the lower initial adjusted pH of 5.5 and like other anions, the removal rate decreased with an increase in initial adjusted pH (**Figure 11**).

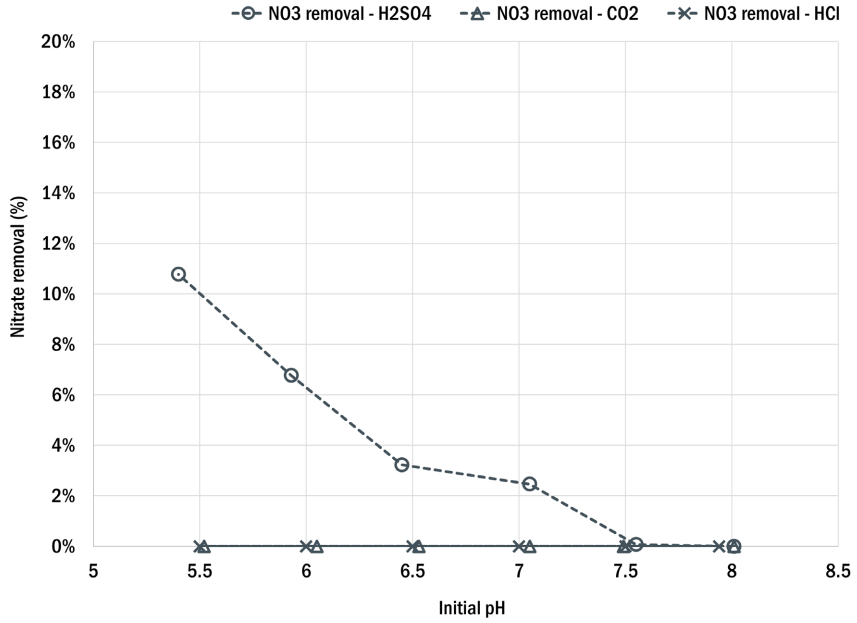


**Figure 10.** Nitrate removal rate comparison at various initial pH and with different acids.

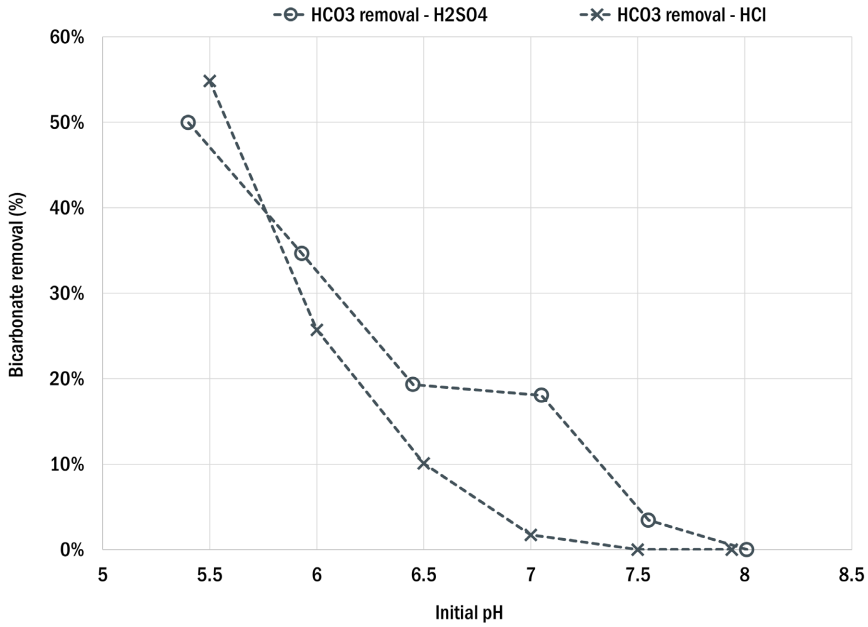


**Figure 11.** Bicarbonate removal rate comparison at various initial pH and with different acids.

Silica had a different trend compared to the other anions evaluated, which is expected because silica solubilizes at higher pH. The removal rate increased with an increase in initial adjusted pH from approximately 40% - 60%. Although all three acids indicated similar trends in anion removal, the overall removal rates were marginally higher with hydrochloric acid (**Figure 12**).

Based on these results, it may be concluded that the influence of competing ions for active sites on activated alumina can be ranked as bicarbonate > silica > sul-

fate > nitrate > chloride with sulfuric acid [52]. For hydrochloric acid, bicarbonate and silica adsorption was similar and in case of carbon dioxide, silica showed higher adsorption in comparison to chloride and sulfate. The added advantage observed in these experiments is that along with arsenic and fluoride, 40 to 60% silica as $SiO_2$ can be removed from the water with activated alumina adsorption. Furthermore, it is important to understand the water quality before activated alumina treatment since the concentration levels of other competing ions can hinder removal rates for arsenic and fluoride.

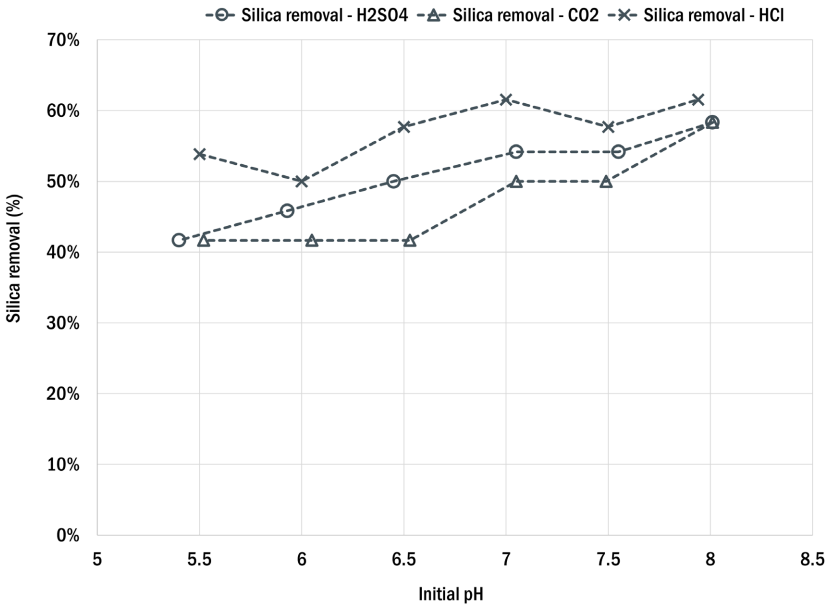


**Figure 12.** Silica removal rate comparison at various initial pH and with different acids.

Post treatment with blended phosphates and pH adjustment with NaOH will deliver a required finished water pH. However, to address the ever evolving lead corrosion chemical stability of treated water is estimated by alkalinity (in the range 40 to 80 mg/L as $CaCO_3$), tendency of the water to precipitate calcium carbonate (measured as Langelier Saturation Index, LSI; expected to be greater than "zero"), and concentration of soluble calcium ions in the water to be in the range of 50 to 120 mg/L as $CaCO_3$ [53]. These three targets can be achieved by post stabilization with lime versus NaOH.

### 3.6. Cost Comparison

To evaluate the cost implications associated with the choice of chemical employed for pH adjustment, four chemical supply vendors were contacted to provide proposal costs per pound for hydrochloric acid, sulfuric acid, and carbon dioxide. The cost of the chemicals varied marginally around the US and depended on the delivery distance from the production site to where the chemical was used. The average cost per pound (lb.) of chemical was $0.29 lb. for 37% hydrochloric acid: $ 0.24 lb for 93% sulfuric acid and $0.165/lb for liquid carbon dioxide. These costs

were used to evaluate the chemical required for a 1 million gallons per day (MGD) water treatment plant with the same groundwater quality and the final adjusted pH of 6.0 prior to activated alumina treatment. Based on this evaluation, the cost of carbon dioxide is comparable to sulfuric acid, which is most used at water treatment plants (Table 3). However, the cost of capital equipment required to deliver these chemicals into the treatment process has not been accounted in this evaluation.

Table 3. Cost of chemicals per year for 1 MGD water treatment plant.

| Chemical | Daily requirement | Yearly cost |
|---|---|---|
| **Hydrochloric acid** | 741 lb/day of 37% | $78,000 |
| **Sulfuric acid** | 392 lb/day of 93% | $34,000 |
| **Carbon dioxide** | 434 lb/day of | $33,000 |

## 4. Conclusion

Three chemicals—carbon dioxide, hydrochloric acid, and sulfuric acid—were evaluated for pH adjustment prior to activated alumina adsorption of arsenic and fluoride from groundwater. The adsorption of arsenic and fluoride was not influenced by the type of chemical used for pH adjustment. Experiments with carbon dioxide indicated enhanced buffering capacity compared to the mineral acids, hydrochloric acid, and sulfuric acid. Chemical cost evaluation suggested that carbon dioxide costs were comparable to sulfuric acid for this specific site and carbon dioxide may be an ideal candidate for pH adjustment with no significant chemical cost implications and is a safer alternative in comparison to mineral acids such as hydrochloric acid and sulfuric acid.

## Acknowledgements

The authors would like to acknowledge: (i) the City of Buckeye for their financial support, (ii) Brown and Caldwell Treatability Laboratory, Nashville, TN, USA, for their support in conducting these evaluations, and (iii) Burnett-Inc to aid in the evaluation of carbon-di-oxide pH adjustment experiments.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

## References

[1] Jha, P.K. and Tripathi, P. (2021) Arsenic and Fluoride Contamination in Groundwater: A Review of Global Scenarios with Special Reference to India. *Groundwater for Sustainable Development*, **13**, Article 100576. https://doi.org/10.1016/j.gsd.2021.100576

[2] Kumar, M., Goswami, R., Patel, A.K., Srivastava, M. and Das, N. (2020) Scenario, Perspectives and Mechanism of Arsenic and Fluoride Co-Occurrence in the Groundwater: A Review. *Chemosphere*, **249**, Article 126126. https://doi.org/10.1016/j.chemosphere.2020.126126

[3] Brindha, K. and Elango, L. (2011) Fluoride in Groundwater: Causes, Implications and Mitigation Measures. https://www.researchgate.net/publication/220000345_Fluoride_in_Groundwater_Causes_Implications_and_Mitigation_Measure

[4] Fawell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L. and Magara, Y. (2006) Fluoride in Drinking-Water. https://iris.who.int/bitstream/handle/10665/43514/9241563192_eng.pdf?sequence=1

[5] WHO (1958) International Standards for Drinking Water. https://iris.who.int/bitstream/handle/10665/43845/a91160.pdf?sequence=1

[6] USEPA (2024) Secondary Drinking Water Standards: Guidance for Nuisance Chemicals. https://www.epa.gov/sdwa/secondary-drinking-water-standards-guidance-nuisance-chemicals

[7] CBS (2024) Federal Court Rules against EPA in Lawsuit over Fluoride in Water. https://www.cbsnews.com/news/epa-fluoride-drinking-water-federal-court-ruling/

[8] Schlesinger, W.H., Klein, E.M. and Vengosh, A. (2020) Global Biogeochemical Cycle of Fluorine. *Global Biogeochemical Cycles*, **34**, e2020GB006722. https://doi.org/10.1029/2020gb006722

[9] Podgorski, J. and Berg, M. (2022) Global Analysis and Prediction of Fluoride in Groundwater. *Nature Communications*, **13**, Article No. 4323. https://doi.org/10.1038/s41467-022-31940-x

[10] Nicolli, H.B., Suriano, J.M., Gomez Peral, M.A., Ferpozzi, L.H. and Baleani, O.A. (1989) Groundwater Contamination with Arsenic and Other Trace Elements in an Area of the Pampa, Province of Córdoba, Argentina. *Environmental Geology and Water Sciences*, **14**, 3-16. https://doi.org/10.1007/bf01740581

[11] Rodríguez-Lado, L., Sun, G., Berg, M., Zhang, Q., Xue, H., Zheng, Q., *et al*. (2013) Groundwater Arsenic Contamination Throughout China. *Science*, **341**, 866-868. https://doi.org/10.1126/science.1237484

[12] Nath, B., Stüben, D., Mallik, S.B., Chatterjee, D. and Charlet, L. (2008) Mobility of Arsenic in West Bengal Aquifers Conducting Low and High Groundwater Arsenic. Part I: Comparative Hydrochemical and Hydrogeological Characteristics. *Applied Geochemistry*, **23**, 977-995. https://doi.org/10.1016/j.apgeochem.2007.11.016

[13] Alarcón-Herrera, M.T., Bundschuh, J., Nath, B., Nicolli, H.B., Gutierrez, M., Reyes-Gomez, V.M., *et al*. (2013) Co-Occurrence of Arsenic and Fluoride in Groundwater of Semi-Arid Regions in Latin America: Genesis, Mobility and Remediation. *Journal of Hazardous Materials*, **262**, 960-969. https://doi.org/10.1016/j.jhazmat.2012.08.005

[14] Ayotte, J.D., Medalie, L., Qi, S.L., Backer, L.C. and Nolan, B.T. (2017) Estimating the High-Arsenic Domestic-Well Population in the Conterminous United States. *Environmental Science & Technology*, **51**, 12443-12454. https://doi.org/10.1021/acs.est.7b02881

[15] Wickramasinghe, S., Han, B., Zimbron, J., Shen, Z. and Karim, M. (2004) Arsenic Removal by Coagulation and Filtration: Comparison of Groundwaters from the United States and Bangladesh. *Desalination*, **169**, 231-244. https://doi.org/10.1016/s0011-9164(04)00530-2

[16] Shaji, E., Sarath, K.V., Santosh, M., Krishnaprasad, P.K., Arya, B.K. and Babu, M.S. (2024) Fluoride Contamination in Groundwater: A Global Review of the Status, Processes, Challenges, and Remedial Measures. *Geoscience Frontiers*, **15**, Article 101734.

https://doi.org/10.1016/j.gsf.2023.101734

[17] WHO (2022) Arsenic. https://www.who.int/news-room/fact-sheets/detail/arsenic

[18] Saeed, M., Rehman, M.Y.A., Farooqi, A. and Malik, R.N. (2022) Arsenic and Fluoride Co-Exposure through Drinking Water and Their Impacts on Intelligence and Oxidative Stress among Rural School-Aged Children of Lahore and Kasur Districts, Pakistan. *Environmental Geochemistry and Health*, **44**, 3929-3951. https://doi.org/10.1007/s10653-021-01141-4

[19] Das, A., Das, S.S., Chowdhury, N.R., Joardar, M., Ghosh, B. and Roychowdhury, T. (2020) Quality and Health Risk Evaluation for Groundwater in Nadia District, West Bengal: An Approach on Its Suitability for Drinking and Domestic Purpose. *Groundwater for Sustainable Development*, **10**, Article 100351. https://doi.org/10.1016/j.gsd.2020.100351

[20] Martínez-Prado, M.A., Pérez-López, M.E., Rosa, M.G.V.l. and González-Nevarez, C.C. (2013) Concentration of Fluoride and Arsenic in Bottled Drinking Water in Durango City, Mexico. *Journal of Environmental Protection*, **4**, 8-13. https://doi.org/10.4236/jep.2013.412a2002

[21] Niu, B., Loáiciga, H.A., Wang, Z., Zhan, F.B. and Hong, S. (2014) Twenty Years of Global Groundwater Research: A Science Citation Index Expanded-Based Bibliometric Survey (1993-2012). *Journal of Hydrology*, **519**, 966-975. https://doi.org/10.1016/j.jhydrol.2014.07.064

[22] Parrone, D., Ghergo, S., Frollini, E., Rossi, D. and Preziosi, E. (2020) Arsenic-Fluoride Co-Contamination in Groundwater: Background and Anomalies in a Volcanic-Sedimentary Aquifer in Central Italy. *Journal of Geochemical Exploration*, **217**, Article 106590. https://doi.org/10.1016/j.gexplo.2020.106590

[23] Currell, M., Cartwright, I., Raveggi, M. and Han, D. (2011) Controls on Elevated Fluoride and Arsenic Concentrations in Groundwater from the Yuncheng Basin, China. *Applied Geochemistry*, **26**, 540-552. https://doi.org/10.1016/j.apgeochem.2011.01.012

[24] Bondu, R., Cloutier, V., Rosa, E. and Roy, M. (2020) An Exploratory Data Analysis Approach for Assessing the Sources and Distribution of Naturally Occurring Contaminants (F, Ba, Mn, As) in Groundwater from Southern Quebec (Canada). *Applied Geochemistry*, **114**, Article 104500. https://doi.org/10.1016/j.apgeochem.2019.104500

[25] Senior, L.A. and Sloto, R.A. (2006) Arsenic, Boron, and Fluoride Concentrations in Ground Water in and Near Diabase Intrusions, Newark Basin, Southeastern Pennsylvania. USGS Scientific Investigations Report 2006-5261. Cooperation with the U.S. Environmental Protection Agency. https://doi.org/10.3133/sir20065261

[26] Aullón Alcaine, A., Schulz, C., Bundschuh, J., Jacks, G., Thunvik, R., Gustafsson, J., *et al*. (2020) Hydrogeochemical Controls on the Mobility of Arsenic, Fluoride and Other Geogenic Co-Contaminants in the Shallow Aquifers of Northeastern La Pampa Province in Argentina. *Science of The Total Environment*, **715**, Article 136671. https://doi.org/10.1016/j.scitotenv.2020.136671

[27] Ali, S., Thakur, S.K., Sarkar, A. and Shekhar, S. (2016) Worldwide Contamination of Water by Fluoride. *Environmental Chemistry Letters*, **14**, 291-315. https://doi.org/10.1007/s10311-016-0563-5

[28] Grandjean, P., Meddis, A., Nielsen, F., Beck, I.H., Bilenberg, N., Goodman, C.V., *et al*. (2023) Dose Dependence of Prenatal Fluoride Exposure Associations with Cognitive Performance at School Age in Three Prospective Studies. *European Journal of Public Health*, **34**, 143-149. https://doi.org/10.1093/eurpub/ckad170

[29] Rajak, P., Roy, S., Khatun, S., Mandi, M., Ganguly, A., Das, K., *et al*. (2023) Fluoride Contamination, Toxicity and Its Potential Therapeutic Agents. *Toxicology International*, **29**, 553-565. https://doi.org/10.18311/ti/2022/v29i4/30844

[30] Haldar, D., Duarah, P. and Purkait, M.K. (2020) MOFs for the Treatment of Arsenic, Fluoride and Iron Contaminated Drinking Water: A Review. *Chemosphere*, **251**, Article 126388. https://doi.org/10.1016/j.chemosphere.2020.126388

[31] Yu, Y., Zhou, Z., Ding, Z., Zuo, M., Cheng, J. and Jing, C. (2019) Simultaneous Arsenic and Fluoride Removal Using {201}$TiO_2$–$ZrO_2$: Fabrication, Characterization, and Mechanism. *Journal of Hazardous Materials*, **377**, 267-273. https://doi.org/10.1016/j.jhazmat.2019.05.060

[32] Zhou, Z., Yu, Y., Ding, Z., Zuo, M. and Jing, C. (2019) Competitive Adsorption of Arsenic and Fluoride on {201} $TiO_2$. *Applied Surface Science*, **466**, 425-432. https://doi.org/10.1016/j.apsusc.2018.10.052

[33] Chouhan, S. and Flora, S.J.S. (2010) Arsenic and Fluoride: Two Major Ground Water Pollutants. *Indian Journal of Experimental Biology*, **48**, 666-678.

[34] Mittal, M. and Flora, S.J.S. (2007) Vitamin E Supplementation Protects Oxidative Stress during Arsenic and Fluoride Antagonism in Male Mice. *Drug and Chemical Toxicology*, **30**, 263-281. https://doi.org/10.1080/01480540701380075

[35] Mittal, M. and Flora, S.J.S. (2006) Effects of Individual and Combined Exposure to Sodium Arsenite and Sodium Fluoride on Tissue Oxidative Stress, Arsenic and Fluoride Levels in Male Mice. *Chemico-Biological Interactions*, **162**, 128-139. https://doi.org/10.1016/j.cbi.2006.05.018

[36] Flora, S.J.S., Mittal, M. and Mishra, D. (2009) Co-Exposure to Arsenic and Fluoride on Oxidative Stress, Glutathione Linked Enzymes, Biogenic Amines and DNA Damage in Mouse Brain. *Journal of the Neurological Sciences*, **285**, 198-205. https://doi.org/10.1016/j.jns.2009.07.001

[37] Dar, F.A. and Kurella, S. (2023) Recent Advances in Adsorption Techniques for Fluoride Removal—An Overview. *Groundwater for Sustainable Development*, **23**, Article 101017. https://doi.org/10.1016/j.gsd.2023.101017

[38] January, O., Protection, E. and EPA, T. (2006) Treatment Technologies for Arsenic Removal. *Water*, **3**, 1-12. https://pmc.ncbi.nlm.nih.gov/articles/PMC4730453/Please%20add%20this%20website

[39] Zakhar, R., Derco, J. and Čacho, F. (2018) An Overview of Main Arsenic Removal Technologies. *Acta Chimica Slovaca*, **11**, 107-113. https://doi.org/10.2478/acs-2018-0016

[40] Zhang, L., Mao, D., Qu, Y., Chen, X., Zhang, J., Huang, M., *et al*. (2023) Facile Synthesis of Ce-MOF for the Removal of Phosphate, Fluoride, and Arsenic. *Nanomaterials*, **13**, Article 3048. https://doi.org/10.3390/nano13233048

[41] Figoli, A., Hoinkis, J. and Bundschuh, J. (2016) Membrane Technologies for Water Treatment: Removal of Toxic Trace Elements with Emphasis on Arsenic, Fluoride and Uranium. Membrane. CRC Press.

[42] Rathore, V.K., Dohare, D.K. and Mondal, P. (2016) Competitive Adsorption between Arsenic and Fluoride from Binary Mixture on Chemically Treated Laterite. *Journal of Environmental Chemical Engineering*, **4**, 2417-2430. https://doi.org/10.1016/j.jece.2016.04.017

[43] Bibi, S., Farooqi, A., Hussain, K. and Haider, N. (2015) Evaluation of Industrial Based Adsorbents for Simultaneous Removal of Arsenic and Fluoride from Drinking Water.

*Journal of Cleaner Production*, **87**, 882-896.
https://doi.org/10.1016/j.jclepro.2014.09.030

[44] Ali, I. (2012) New Generation Adsorbents for Water Treatment. *Chemical Reviews*, **112**, 5073-5091. https://doi.org/10.1021/cr300133d

[45] Rathore, V.K. and Mondal, P. (2017) Competitive Adsorption of Arsenic and Fluoride onto Economically Prepared Aluminum Oxide/hydroxide Nanoparticles: Multicomponent Isotherms and Spent Adsorbent Management. *Industrial & Engineering Chemistry Research*, **56**, 8081-8094. https://doi.org/10.1021/acs.iecr.7b01139

[46] You, K., Gao, Y., Qian, W., Fu, J., Wang, J. and Zhou, W. (2021) Simultaneous Removal of Fluoride, Manganese and Iron by Manganese Oxide Supported Activated Alumina: Characterization and Optimization via Response Surface Methodology. *Water Science and Technology*, **84**, 3799-3816. https://doi.org/10.2166/wst.2021.461

[47] Donmez, M. and Akbal, F. (2011) The Removal of As(V) from Drinking Waters by Coagulation Process Using Iron Salts. *World Academy of Science*, *Engineering and Technology*, *International Journal of Environmental and Ecological Engineering*, **5**, 340-342.

[48] Lakshmanan, D., Clifford, D. and Samanta, G. (2008) Arsenic Removal by Coagulation with Aluminum, Iron, Titanium, and Zirconium. *Journal AWWA*, **100**, 76-88. https://doi.org/10.1002/j.1551-8833.2008.tb08144.x

[49] EPA (2014) Design Manual—Removal of Fluoride from Drinking Water Supplies by Activated Alumina.
https://nepis.epa.gov/Adobe/PDF/P100KFZQ.pdf

[50] USEPA (2016) Optimal Corrosion Control Treatment Evaluation Technical Recommendations for Primary Agencies and Public Water Systems.
https://www.epa.gov/sites/default/files/2016-03/documents/occtmarch2016.pdf

[51] Pennsylvania Department of Environmental Protection (2017) Drinking Water Plant Operator Certification Training. Module 20: Corrosion Control and Sequestering.
https://files.dep.state.pa.us/Water/BSDW/OperatorCertification/TrainingModules/dw-20_corrosion_control_and_sequestering_wb.pdf

[52] Tang, Y., Guan, X., Su, T., Gao, N. and Wang, J. (2009) Fluoride Adsorption ONTO Activated Alumina: Modeling the Effects of Ph and Some Competing Ions. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **337**, 33-38.
https://doi.org/10.1016/j.colsurfa.2008.11.027

[53] Feemster, V. and Smith, J. (2015) Reverse Osmosis Post-Treatment Stabilization Utilizing Liquid Lime. *Florida Water Resources Journal*, 4-9.
https://fwrj.com/techarticles/11.15%20tech%201.pdf