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Fluoride removal by Al, Ti, and Fe hydroxides and coexisting ion effect

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ABSTRACT

Batch experiments were conducted to evaluate fluoride removal by Al, Fe, and Ti-based coagulants and adsorbents, as well as the effects of coexisting ions and formation of aluminum–fluoride complexes on fluoride removal by co-precipitation with alum ($Al_2(SO_4)_3{\cdot}18H_2O$). Aluminum sulfate was more efficient than the other coagulants for fluoride removal in the pH range between 6 and 8. Nano-crystalline TiO_2 was more effective for fluoride removal than Al and Fe hydroxides in a pH range of 3–5. Coexisting anions in water decreased the removal of fluoride in the order: phosphate (2.5 mg/L) > arsenate (0.1 mg/L) > bicarbonate (200 mg/L) > sulfate (100 mg/L) = nitrate (100 mg/L) > silicate (10 mg/L) at a pH of 6.0. The effect of silicate became more significant at pH > 7.0. Calcium and magnesium improved the removal of fluoride. Zeta-potential measurements determined that the adsorption of fluoride shifted the PZC of $Al(OH)_3$ precipitates from 8.9 to 8.4, indicating the chemical adsorption of fluoride at the surface. The presence of fluoride in solution significantly increased the soluble aluminum concentration at pH < 6.5. A Visual MINTEQ modeling study indicated that the increased aluminum solubility was caused by the formation of AlF^{2+}, AlF_2^+, and AlF_3 complexes. The AlF_x complexes decreased the removal of fluoride during co-precipitation with aluminum sulfate.

Introduction

Naturally occurring fluoride in groundwater is typically below 0.5 mg/L. However, in many parts of the world, the fluoride concentration is elevated to 8.0 mg/L and even exceeds 20.0 mg/L. Weathering and erosion of geologic formations cause fluoride to be released from minerals and create unsafe drinking water conditions. Groundwater with elevated fluoride is, to a large degree, found in locations where volcanic igneous rocks are; such areas include India, China and the desert southwest of the United States, among others (Brindha and Elango, 2011).

Fluoride in drinking water has a narrow optimum concentration range in relation to human health. It can prevent dental caries in the range of 0.7–1.2 mg/L, but is responsible for dental and skeletal fluorosis if it is higher than 1.5 mg/L. The World Health Organization (WHO) Guidelines for Drinking Water Quality put forth a recommendation that fluoride be present in the range of 0.5–1.0 mg/L (WHO (World Health Organization), 2011). In the United States, the US Environmental Protection Agency (US EPA) has mandated a maximum contaminant level (MCL) of 4.0 mg/L, while states like California have adopted a strict 2.0 mg/L limit for fluoride in drinking water.

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Many methods can be used to remove fluoride from water, including adsorption by activated alumina (AA) (Ghorai and Pant, 2005; Sovinelli and Black, 1958), reverse osmosis (Cohen and Conrad, 1998), electrodialysis and electro-sorption (Amor et al., 2001; Lounici et al., 1997), adsorption by limestone (Reardon and Wang, 2000), goethite (Hiemstra and Van Riemsdijk, 2000) and kaolinite (Weerasooriya et al., 1998), acid-treated spent bleaching earth (Mahramanlioglu et al., 2002), red mud (Çengeloğlu et al., 2002), polyaluminum chloride (Malhbtra et al., 1997), and various other low-cost materials, including bentonite, char fines, lignite and nirmali seeds (Srimurali et al., 1998) and some novel hybrid adsorbents (Bhatnagar et al., 2011). Although WHO and US EPA classify activated alumina adsorption as one of the best demonstrated available technologies (BDAT) for fluoride removal, it is relatively expensive and its adsorption capacity is affected by pH and the presence of coexisting ions in water such as silicate, sulfate, bicarbonate and phosphate (Tang et al., 2009; Tressaud, 2006).

Aluminum sulfate hydrolyzes and forms $Al(OH)_3$ precipitates, which are highly effective at removing fluoride from groundwater. Common concerns when using alum as a treatment option are aluminum residuals in the effluent stream and a reduction in water pH, since alum is an acidic salt. The aims of this study were to compare the effectiveness of Al, Fe, and Ti-based coagulants for fluoride removal, to evaluate the effect of anions and cations on fluoride removal, and to determine the influence of aluminum fluoride complexation on the removal of fluoride and on the solubility of aluminum.

1. Materials and methods

Alum ($Al_2(SO_4)_3{\cdot}18H_2O$) was purchased from Eaglebrook Inc. located in Quebec, Canada. All other chemicals used in the experiments were analytical grade and purchased from Aldrich or Fisher Scientific and used as received.

Fluoride stock solution ($F^- = 1000$ mg/L) was prepared by dissolving 2.21 g of sodium fluoride (NaF) (Fisher Scientific, Pittsburgh, PA, USA) in 1 L of deionized water and was prepared monthly. A 0.4 mol/L sodium chloride (NaCl) (Fisher) stock solution was made by dissolving 23.2 g of NaCl in 1 L of DI water for background ionic strength adjustment. Phosphate (as P), silicate (as Si), bicarbonate (as HCO_3), calcium, magnesium, sulfate (as SO_4) and nitrate (as NO_3) stock solutions (1000 mg/L) were prepared by dissolving 4.39 g of KH_2PO_4, 7.6 g of Na_2SiO_3 $5H_2O$, 1.4 g of $NaHCO_3$, 2.8 g of $CaCl_2$, 3.91 g of $MgCl_2$, 1.48 g of $Na(SO_4)_2$ and 1.37 g of $NaNO_3$ (Fisher) in 1 L of DI water respectively. The bicarbonate stock solution was made weekly, while anionic stock solutions were made monthly. Fluoride concentration was measured using ion selective electrodes (Corning and Thermo Orion ISE) and a pH meter (Thermo Orion 925/525). A buffer solution was used for accurate analysis of soluble F according to Method 4500-F-C in Standard Methods for Examination of Water and Wastewater. The buffer solution contained CDTA (1,1,2, N′N′N′diamino–tetraacetic acid), which preferentially complexes aluminum and iron, allowing accurate determination of soluble fluoride (Farrah et al., 1987).

Fluoride solutions were prepared by diluting the fluoride stock solution to 8.0 mg/L of F^- with DI water; the ionic strength of solution was controlled at 0.04 mmol/L using NaCl as a background electrolyte. After desired amounts of alum or other coagulants were added into the solutions, the suspensions formed were separated into 10,125-mL polypropylene bottles for each coagulant. The pH of the suspensions was adjusted to pH values ranging between about 2 and 12 using NaOH and HCl solutions. After 60 min of mixing, the final pH was measured and a portion of the suspensions were centrifuged at 10,000 r/min for 10 min to separate the liquid from the solids for the analysis of residual soluble fluoride and other target compounds.

Simulated groundwater was prepared by diluting $MgCl_2$, $CaCl_2$, $NaHCO_3$, Na_2SiO_3, NaH_2PO_4, and $Na(SO_4)_2$ stock solutions in DI water to determine anion or cation effects on fluoride removal. The highest concentrations of the solutes found in groundwater were used in most of the tests to determine the maximum competitive effect. In some cases lower concentrations were used to determine factors that might be encountered in real world settings. All adsorption experiments were repeated to confirm the adsorption results. However, only a set of representative data were presented for each experiment in the figures and no experimental errors were calculated because the final or equilibrium pH values in the duplicate experiments were not the same.

Aluminum, silicon, and other metals were analyzed using an atomic absorption spectrometer (FAAS, Varian Zeeman 400 Spectra-AA) and an inductively coupled plasma optical emission spectrometer (ICP–OES, Varian Vista MPX). Phosphorus was determined using a HACH 2000 spectrophotometer following the ascorbic acid Method 4500-P-E in Standard Methods for Examination of Water and Wastewater. Zeta-potential measurements were completed using a Nano ZetaSizer ZEN3600 (Malvern Instrument, UK). Turbidity readings were completed using a HACH 2100P turbidity NTU meter.

2. Results and discussion

2.1. Fluoride removal

The batch experimental results in Fig. 1 show the fluoride removal efficiency by $FeCl_3$, $Al_2(SO_4)_3$, $TiSO_4$ and nano-crystalline TiO_2 as a function of final solution pH. The pH had significant effects on the removal of fluoride. The optimum pH for fluoride removal was about 6.5 for aluminum sulfate and about 3.5 for Ti and Fe coagulants and adsorbents. Among the materials, aluminum sulfate performed most effectively under circumneutral pH conditions, which was consistent with the reported optimum pH values between 5.5–7.5 for various aluminum-based coagulants (Bhatnagar et al., 2011; Sovinelli and Black, 1958; Sujana et al., 1998). It should be noted that the nano-crystalline TiO_2 had much higher fluoride removal than the other precipitates in a pH range 3–5. Other batch experimental results indicate that the removal of fluoride reached equilibrium rapidly in about 5 min (data not reported).

2.2. Anion and cation effects on fluoride removal

Batch experimental results in Table 1 show that an Al dose of 10 mg/L was not sufficient to treat all samples collected from