

Adsorption of Fluoride from Water Using Aluminum Coated Sand: Kinetics, Equilibrium, Effect of pH, and Coexisting Ions

Kiana Modaresahmadi, Amid P. Khodadoust*, James Wescott

Department of Civil, Materials, and Environmental Engineering, University of Illinois Chicago, Chicago, IL, USA
Email: *akhodado@uic.edu

How to cite this paper: Modaresahmadi, K., Khodadoust, A. P., & Wescott, J. (2022). Adsorption of Fluoride from Water Using Aluminum Coated Sand: Kinetics, Equilibrium, Effect of pH, and Coexisting Ions. *Journal of Geoscience and Environment Protection*, 10, 224-241.
<https://doi.org/10.4236/gep.2022.1012013>

Received: October 26, 2022

Accepted: December 26, 2022

Published: December 29, 2022

Copyright © 2022 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).
<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

An aluminum coated sand (AICS) was evaluated as a metal oxide adsorbent for adsorption and removal of fluoride from water using a low-cost adsorbent with potential application in continuous flow adsorber systems. Surface characterization of the AICS sorbent was performed using TEM, SEM/EDX, XRD and BET. The AICS sorbent contained mostly amorphous aluminum oxides based on adsorbent characterization results. Favorable adsorption of fluoride onto the AICS sorbent occurred according to the Langmuir and Freundlich adsorption equations, while physical adsorption of fluoride onto the AICS sorbent was observed based on results from the Dubinin-Radushkevich equation. Fluoride adsorption onto the AICS sorbent followed pseudo-second order kinetics, while surface charge analysis indicated a pH_{PZC} of 7.1 for the AICS sorbent. Effective fluoride removal occurred over a broad pH range from 3 to 11 with a maximum fluoride removal observed at pH 4 to 5. The effect of co-existing ions in water resulted in a decrease in fluoride uptake in the presence of bicarbonate, while resulting in an increase in fluoride uptake in the presence of calcium. The AICS sorbent was a low-cost and sustainable adsorbent for effective adsorption and rapid removal of fluoride from water within an hour.

Keywords

Fluoride, Removal, Adsorption, Coated Sand, Aluminum

1. Introduction

Fluoride levels in groundwater and surface water are elevated due to geological causes such as slow dissolution of fluoride minerals and industrial discharge like semiconductor production (between 10 mg/L and 1000 mg/L release) (Bhatna-

gar et al., 2011; Narsimh & Sudarshan, 2017). Fluoride is quickly absorbed and distributed in the human body via oral ingestion, inhalation, and skin contact (Fordyce, 2011; Liu et al., 2019). It can easily attach to calcium ions across the cell membrane and condense in highly compacted calcium sites like bone and teeth, lowering calcium levels in the body and causing fluorosis (Yang et al., 2019). Although a fluoride (F^-) content of less than 0.5 mg/L in drinking water is beneficial to oral health, particularly in children, any amount above 1.5 mg/L can cause serious health problems such as fluorosis, brain damage, thyroid disease, and cancer (Jha et al., 2013). Fluoride contamination and health issues such as fluorosis are estimated to affect over 200 million people worldwide, primarily in India, China, Africa, and Latin America (Rasool et al., 2017). Fluoride levels in groundwater have been found to be high in several states in the United States, including up to 3.58 mg/L in Ohio, 13 mg/L in Arizona, and 7.60 mg/L in Wisconsin (Ali et al., 2016). The US Public Health Service (PHS) recommends a fluoride concentration of 0.7 mg/L in drinking water (U.S. Department of Health and Human Services, 2015), while the US Environmental Protection Agency (EPA) mandates a maximum contamination level (MCL) of 4.0 mg/L in public water systems (National Research Council, 2006), and the World Health Organization (WHO) recommends a fluoride concentration of 1.5 mg/L in drinking water (Tiemann, 2013).

Several technologies have been applied to remove fluoride (F^-) from water, including chemical precipitation, membrane filtration, ion exchange, electrocoagulation, and adsorption. All of these techniques have advantages and disadvantages that make them less desirable or more appealing to use, particularly for large-scale treatment. Chemical precipitation is one of the successful removal methods discussed, but it generates a lot of hazardous sludge and has a low removal efficiency (Eskandarpour et al., 2008). Membrane technology has a high operating and capital cost, as well as concerns about fouling and clogging, making it a difficult solution to implement, especially for large-scale treatment (He et al., 2020). Electrocoagulation has shown to be effective for removal of fluoride from water using different electrode materials such as aluminum and aluminum alloys (Vasudevan et al., 2009a, 2011). Although the ion-exchange technique is a promising technology to apply, several disadvantages have been considered, including the high resin cost, pH sensitivity, ion interference, and the high level of toxic liquid production due to the regeneration of resins used in the process (Liu et al., 2002; Velazquez-Jimenez et al., 2015).

The removal of fluoride by adsorption is a convenient and cost-effective method, among others, where the development of effective and sustainable adsorbents is desirable (Habuda-Stanić et al., 2014; Tamrakar et al., 2019). Low-cost and environmentally acceptable adsorbents are needed for effective removal of fluoride (Habuda-Stanić et al., 2014). Metal oxides, agricultural and biosorbents, geomaterials, carbonaceous and carbon-based adsorbents, building and industrial wastes and by-products adsorbents, and nanoparticles are among the different adsorbent categories that have been studied so far for fluoride removal

(Teng et al., 2009; Bhatnagar et al., 2011; Habuda-Stanić et al., 2014; Velazquez-Jimenez et al., 2015; Yadav et al., 2018).

Metal oxide adsorbents have shown to be capable of removing fluoride ions from water. In addition, they are excellent choices for use in larger-scale work due to their high selectivity and removal efficiency, and as a result, more attention is being drawn to this group of adsorbents (Velazquez-Jimenez et al., 2015). Various metal oxides adsorbents have been studied including activated alumina, ferric oxide/hydroxide, calcium-modified adsorbents, magnesium-modified adsorbents, and titanium-derived adsorbents. Among the adsorbents previously mentioned, aluminum-based adsorbents have the advantage of being locally available, environmentally friendly, and low-cost adsorbents (Fan et al., 2003; Jagtap et al., 2012), as well as potential application in flow-through water filtration systems (Alhassan et al., 2021); the positive surface charge of aluminum and the negative surface charge of fluoride provides a strong attraction, resulting in the removal of fluoride from water (Chai et al., 2013; Vázquez-Guerrero et al., 2016).

In this study, an aluminum coated sand (AICS) sorbent was prepared at bench-scale as a low-cost and sustainable adsorbent to evaluate the adsorption and removal of fluoride from water. The base material used in this study, silica sand, is the second most abundant mineral (28.2%) (Zheng et al., 2021), with the United States being the world's leading producer and exporter of this product (United States Bureau of Mines, 1980). It is an ideal filtration medium because of its high level of durability, nontoxicity, and ability to capture bacteria and remove the majority of the suspended solid material. Aluminum, the metal used as a coating in this design, is also the most abundant metal (8.2%) (Siddiqui & Chaudhry, 2017) and the eighth cheapest element (1.79 \$/kg) (U.S. Geological Survey, 2013). This study investigated the removal of fluoride from water using the AICS sorbent as a function of time, solution pH, adsorbent dosage, and co-existing ions.

2. Materials and Methods

2.1. Chemicals

Silica sand (white quartz, 50 - 70 mesh particle size) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Aluminum chloride hexahydrate (99% purity, ACS grade), sodium hydroxide (ACS reagent pellets), hydrochloric acid (ACS plus grade), sodium fluoride (ACS grade), sodium bicarbonate (ACS grade), calcium chloride (ACS grade), and sodium sulfate (ACS grade) were obtained from Fisher Scientific (NJ, USA).

2.2. Sorbent Preparation

To prepare the AICS sorbent, 40 g of sand were mixed with 100 mL of 1 M solution of aluminum chloride for 24 hours. The residual coating solution was removed after 24 hours of mixing, and the wet coated sand was air-dried in a drying hood for 12 hours followed by heating in a drying oven at 110°C for four

hours. The dried coated sand was then calcined inside a furnace at 330°C for 24 hours. The final sorbent was removed from the furnace, allowed to cool down to room temperature, and was then stored in a plastic bottle.

2.3. Sorbent Characterization

The microstructural characterization of the AlCS sorbent was performed by Transmission Electron Microscopy (TEM) coupled with Energy Dispersive X-ray analysis using a JEOL JEM-3010 300 KV TEM. Surface characterization of the AlCS sorbent was obtained by Scanning Electron Microscopy (SEM) with a TOPCON ABT-150S SEM; Electron Dispersive X-ray Spectroscopy (EDX) was carried out at 10 kV in variable pressure mode at 10 Pa. The X-ray diffraction (XRD) pattern for the AlCS sorbent was obtained with Cu K α radiation at 40KV and 30 mA using an XRD-Bruker D8 Discover System. The BET specific surface area of the AlCS sorbent was measured with an Accelerated Surface Area and Porosimetry system, ASAP 2010 (Micromeritics Instrument Corporation).

2.4. Batch Adsorption Experiments

Batch adsorption experiments were performed for the following experiments: adsorption dosage, adsorption kinetics, adsorption isotherm, effect of pH on adsorption, and effect of co-existing ions on adsorption, and zeta-potential measurements. All batch adsorption experiments were carried out in triplicate. The fluoride removal and the adsorption capacity of AlCS sorbent for fluoride uptake were determined as follows:

$$\text{Removal}(\%) = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) / m \times V \quad (2)$$

where C_0 (mg/L) is the initial fluoride concentration, C_e (mg/L) is the final or equilibrium fluoride concentration, m (kg) is the mass of AlCS sorbent applied (kg), V (L) is the volume of fluoride solution, and q_e (mg/kg) is the uptake of fluoride by the AlCS sorbent. In batch adsorption experiments, different masses of the AlCS sorbent and 50 mL of solution with an initial fluoride concentration of 5 mg/L were placed inside HPDE bottles. The bottles containing mixtures of the AlCS sorbent and fluoride solutions were shaken using a rotating tumbler at 20 rpm. After shaking the bottles for 24 hours, the fluoride solution was separated from the AlCS sorbent using centrifugation at 8000 rpm. The samples were analyzed for fluoride using an ion selective fluoride electrode according to Standard Method 4500 F⁻ (Standard Methods for the Examination of Water and Wastewater, 2018). Batch adsorption experiments were performed for the following experiments: adsorption dosage, adsorption kinetics, adsorption isotherm, effect of pH on adsorption, effect of co-existing ions on adsorption, and zeta-potential measurements.

2.5. Effect of pH on Fluoride Removal Experiments

The effect of pH on fluoride removal using the AlCS sorbent was evaluated using

batch adsorption experiments with 1 g of the AlCS sorbent and 50 mL fluoride solution with an initial pH value ranging from pH 3 to pH 11; the initial pH was adjusted using 0.1 M NaOH and 0.1 M HCl. All pH experiments were performed in triplicate.

2.6. Effect of Co-Existing Ions on Fluoride Removal

The effect of co-existing ions on fluoride removal was evaluated using batch adsorption experiments with 1 g of the AlCS sorbent and 50 mL fluoride solution with different concentrations of co-existing ions. Initial fluoride solutions were prepared separately for each co-existing ion; fluoride solutions were prepared containing different concentrations of calcium (Ca^{2+}), bicarbonate (HCO_3^-), and sulfate (SO_4^{2-}). All co-existing ion experiments were performed in triplicate.

2.7. Zeta Potential Experiments

One gram of AlCS sorbent was mixed with 1 liter of 1 mM solution of NaCl to prepare suspensions of the AlCS sorbent for zeta potential measurements. The zeta potential of each suspension was measured using the Zeta-meter system 3.0 (Zeta meter Inc., VA). The zeta potential of suspension samples was measured as function of initial solution pH from pH 3 to pH 11. The initial pH of samples was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

3. Results and Discussion

3.1. Sorbent Characterization

The XRD analysis of the AlCS sorbent shown in **Figure 1** indicates the presence

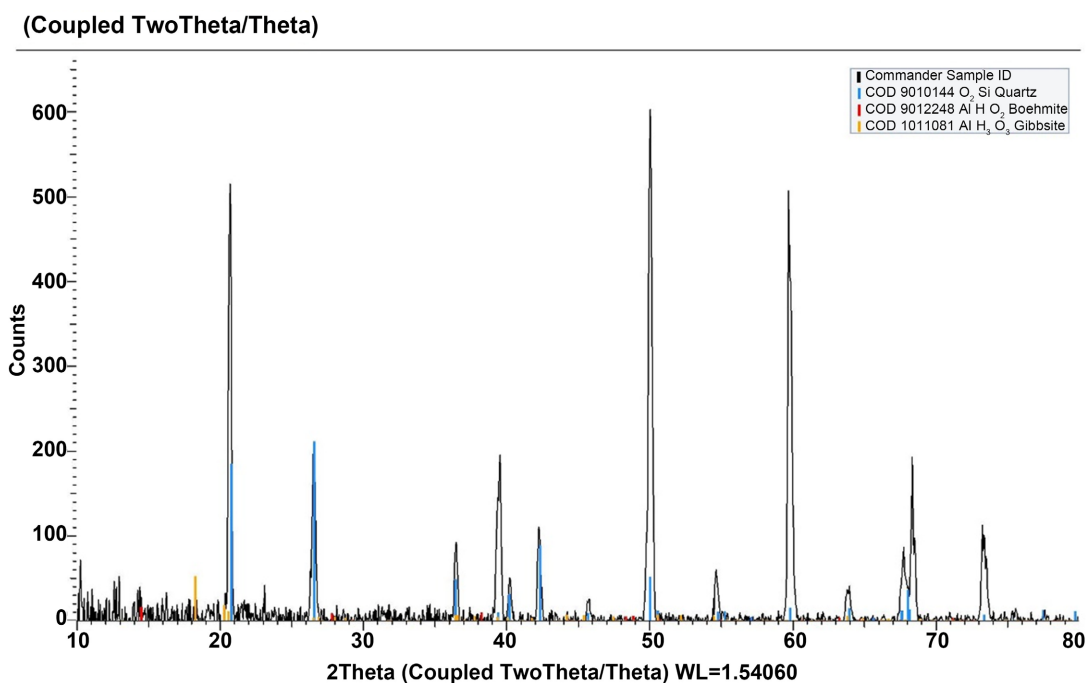


Figure 1. XRD pattern for the AlCS sorbent.

of crystalline silica and low levels of crystalline aluminum oxides. The TEM and SEM micrographs are shown in **Figure 2**. The TEM analysis of the AlCS sorbent showed the presence of aluminum oxides (AlO_x) on the surface of the AlCS sorbent, while indicating that the aluminum oxides contained in the aluminum coating were mostly amorphous. The SEM and TEM images of the AlCS sorbent show that the aluminum coating contained clusters of aluminum oxide ranging from 1 to 10 μm in size. The SEM/EDX analysis of the AlCS sorbent presented in **Figure 3** show that the AlCS sorbent contained aluminum, oxygen, and silicon, indicating the presence of aluminum oxides on the surface of silica sand. The BET surface area of the AlCS sorbent was determined to be $1.648 \text{ m}^2/\text{g}$.

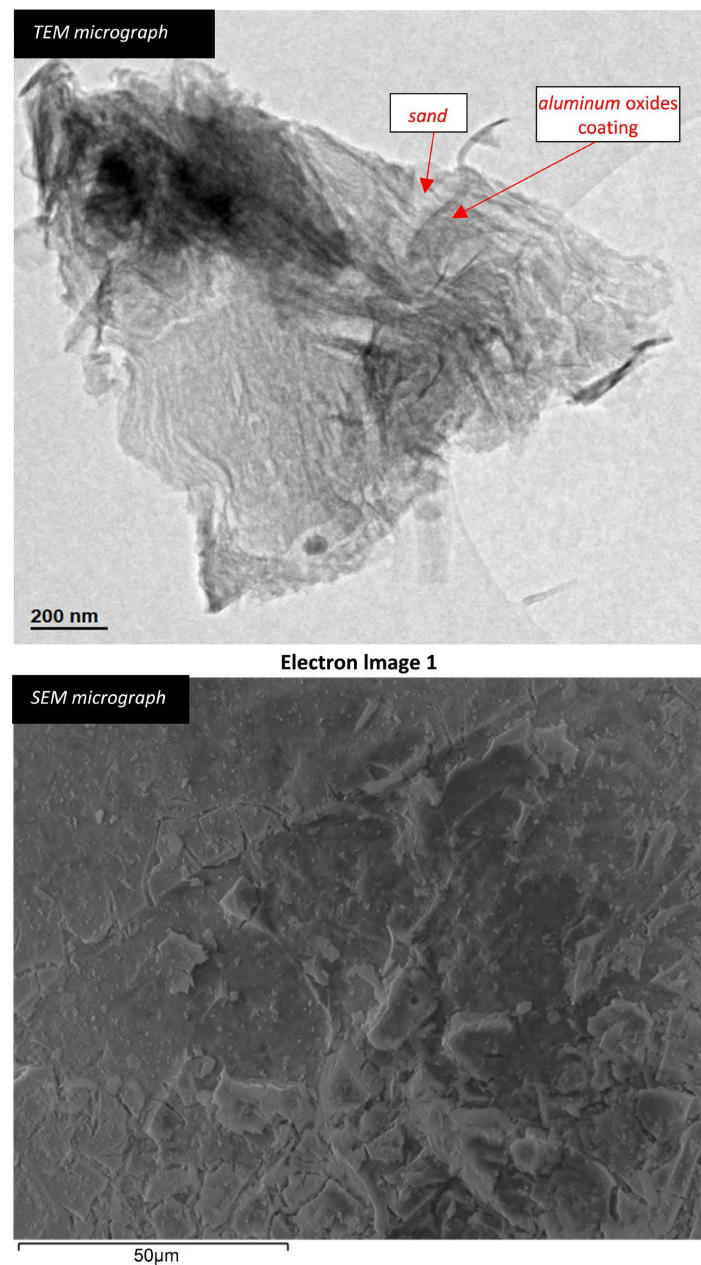


Figure 2. TEM and SEM micrographs of the AlCS sorbent.

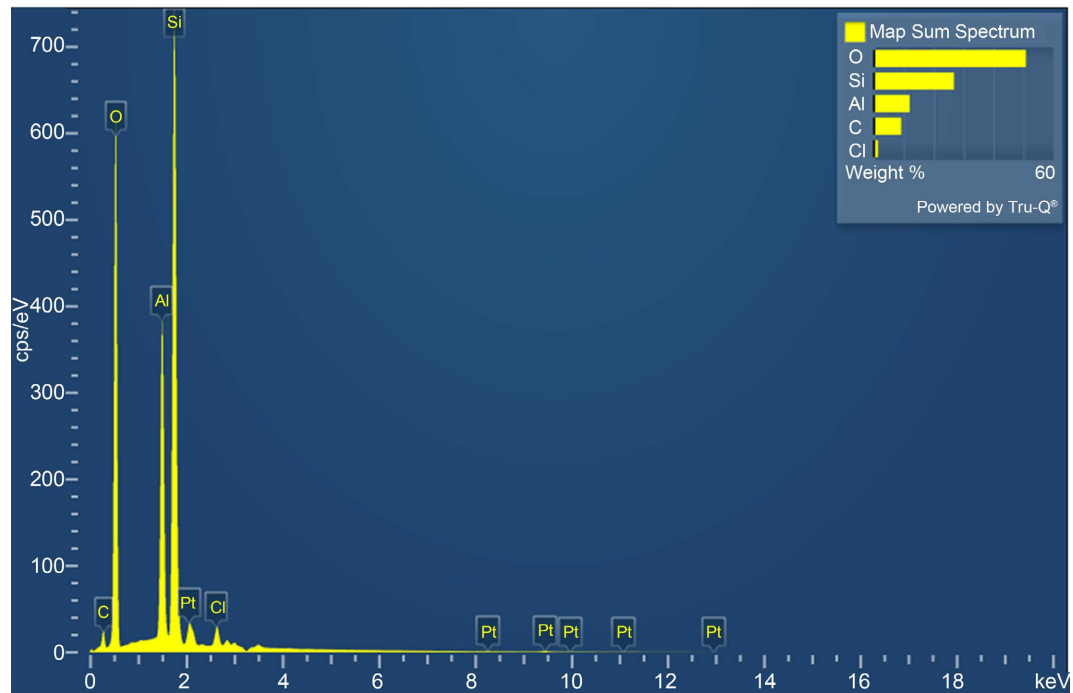


Figure 3. SEM-EDX Analysis of the AICS sorbent.

3.2. Adsorption Kinetics

The adsorption of fluoride onto the AICS sorbent was evaluated as function of time by determining the adsorption kinetics of fluoride using an initial fluoride concentration of 5 mg/L and an adsorbent dosage of 20 g/L. All adsorption kinetics experiments were performed in triplicate. The concentration of fluoride remaining in solution as function of time is shown in **Figure 4**. The results from **Figure 4** indicate that most of the fluoride was adsorbed and removed within 60 minutes while adsorption equilibrium was reached within 12 hours. About 73 percent of total fluoride removal was obtained within the first 60 minutes of contact time, which was followed by an additional 27 percent removal of fluoride up to 12 hours of contact time. The adsorption kinetics of fluoride was investigated using the pseudo-first order and pseudo-second order adsorption kinetic models. The Lagergren pseudo-first order model is described using the following differential and integral forms (Lagergren, 1898):

$$dq_t/dt = k_1(q_e - q_t) \quad (3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

The adsorption (uptake) of fluoride is q_e (mg/kg) at equilibrium and q_t (mg/kg) at time t , with a first-order adsorption rate constant of k_1 (min^{-1}). The pseudo-second order adsorption kinetics model is described in differential and integral forms as follows with a second-order adsorption constant of k_2 ($\text{kg}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$):

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (5)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

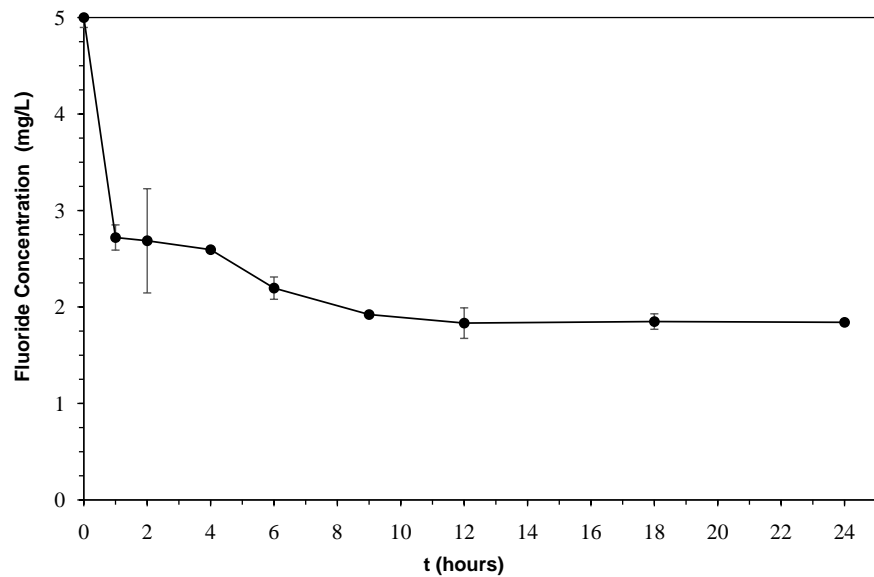


Figure 4. Adsorption of fluoride onto the AICS sorbent as function of time.

Table 1 shows the results obtained for pseudo-first order kinetics and pseudo-second order kinetics. According to **Table 1**, the adsorption and uptake of fluoride by the AICS sorbent followed second order kinetics with $R^2 = 0.9988$, a k_2 value of 0.0001296 kg/mg/min (0.1296 g/mg/min) and a calculated q_e of 188.7 mg/kg which is close to the experimental q_e of 183 mg/kg. The adsorption kinetics results obtained for the AICS sorbent were similar to other aluminum based adsorbents which also followed second-order kinetics (Maliyekkal et al., 2006; Maliyekkal et al., 2008; Salifu et al., 2013). Second-order adsorption kinetics was similarly observed by other researchers (Vasudevan et al., 2010; Vasudevan & Lakshmi, 2012; Kamaraj et al., 2016).

3.3. Adsorption Equilibrium

The effect of adsorbent dosage on fluoride removal is presented in **Figure 5** for an initial fluoride concentration of 5 mg/L. All adsorption dosage experiments were performed in triplicate. The results from **Figure 5** show that near maximum removal of fluoride was obtained with a dosage of 40 g/L of the AICS sorbent.

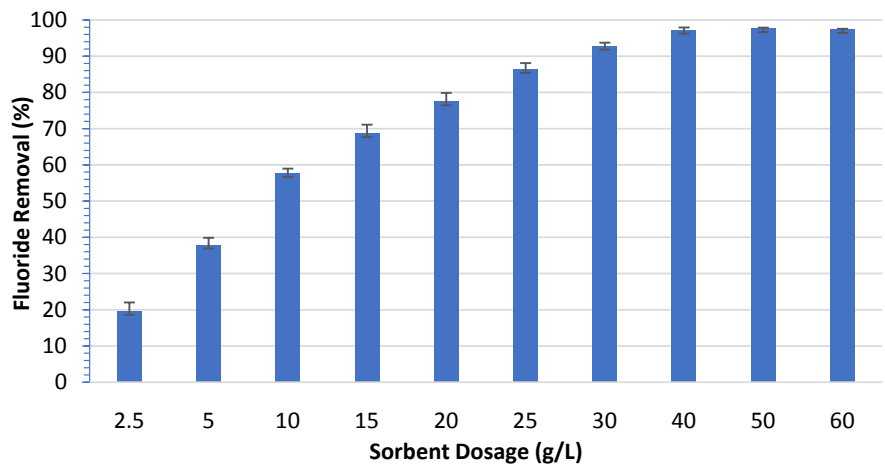
The equilibrium adsorption parameters for adsorption of fluoride onto the AICS sorbent were determined using the following adsorption isotherm equations: Langmuir, Freundlich and Dubinin-Radushkevich (D-R). The Langmuir adsorption equation is described as follows (Langmuir, 1916):

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (7)$$

The q_e (mg/kg) is the equilibrium adsorption of fluoride per mass of sorbent (uptake), q_m (mg/kg) is the maximum fluoride adsorbed (adsorption capacity of sorbent), and the Langmuir constant K_L (L/mg) is indicative of adsorption free energy. A linearization of the Langmuir equation is as follows.

Table 1. Adsorption kinetics parameters for fluoride adsorption onto AlCS sorbent.

pseudo-first order	pseudo-second order
$k_1 = 0.0053 \text{ (min}^{-1}\text{)}$	$k_2 = 0.1296 \text{ g/mg/min}$
$q_e = 96.2 \text{ mg/kg}$	$q_e = 188.7 \text{ mg/kg}$
$R^2 = 0.9714$	$R^2 = 0.9988$
experimental $q_e = 183 \text{ mg/kg}$	experimental $q_e = 183 \text{ mg/kg}$

**Figure 5.** Effect of adsorbent dosage on removal of fluoride using the AlCS sorbent.

$$C_e/q_e = C_e/q_m + 1/K_L q_m \quad (8)$$

Adsorption is considered favorable for a separation factor (R_L) value between 0 and 1 where R_L is calculated as follows:

$$R_L = 1/(1 + K_L C_0) \quad (9)$$

The Freundlich adsorption equation is described as follows (Freundlich, 1907):

$$q_e = K_F C_e^{1/n} \quad (10)$$

The $1/n$ adsorption parameter is indicative of adsorption intensity or adsorption strength, with values of $1/n$ less than 1 indicative of favorable adsorption, while K_F is indicative of adsorption capacity. A linearization of the Freundlich equation is

$$\log q_e = \log K_F + 1/n \log C_e \quad (11)$$

The Dubinin-Radushkevich (D-R) adsorption equation may be used to determine the occurrence of either physical adsorption or chemisorption (Dubinin & Radushkevich, 1947). The D-R adsorption equation is written as follows:

$$q_e = q_m \exp(-K_{DR} \varepsilon^2) \quad (12)$$

The D-R constant is K_{DR} and the Polanyi potential (ε) is equal to $RT \ln(1 + 1/C_e)$, T is absolute temperature (K) and R is the universal gas constant (8.314 J/mol-K). The linearization of the D-R equation is as follows:

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \quad (13)$$

The mean free energy of adsorption (E) is determined as follows:

$$E = 1/\sqrt{2K_{DR}} \quad (14)$$

E values less than 8 kJ/mol are indicative of physical adsorption and E values from 8 to 16 kJ/mol are indicative of chemisorption.

The adsorption equilibrium isotherm data for adsorption of fluoride onto the AlCS sorbent are shown in **Figure 6**. The adsorption results presented in **Figure 6** were used to determine the adsorption parameters from the linearized plots of the three adsorption equations. The adsorption parameters for adsorption of fluoride onto the AlCS sorbent are presented in **Table 2**. The adsorption capacity q_m (maximum uptake) determined from the Langmuir equation is 454.5 mg/kg and the Langmuir adsorption constant K_L is 1.22 L/mg for the AlCS sorbent. The separation factor (R_L) value is determined to be 0.141 for AlCS indicating that adsorption of fluoride was very favorable. The Freundlich adsorption constants K_F and $1/n$ determined from the Freundlich equation are 220.2 and 0.3865, respectively. The Freundlich $1/n$ value of 0.3865 is indicative of favorable adsorption of fluoride by the AlCS sorbent. The mean free energy of adsorption (E) obtained from the D-R adsorption equation is 3.34 kJ/mol, which indicates that physical adsorption was predominant in the adsorption of fluoride onto the AlCS sorbent. Similar values of Langmuir constant K_L and Freundlich constant ($1/n$) were obtained by other researchers (Vasudevan et al., 2012; Ganesan et al., 2013). The free energy of adsorption (ΔG°) related to the K_L value was negative,

Table 2. Adsorption equilibrium parameters for fluoride adsorption onto AlCS.

Langmuir	Freundlich	D-R
q_m (mg/kg) = 454.4	$K_F = 220.2$	
K_L (L/mg) = 1.22	$1/n = 0.3865$	E (kJ/mol) = 3.34
$R^2 = 0.947$	$R^2 = 0.916$	$R^2 = 0.798$

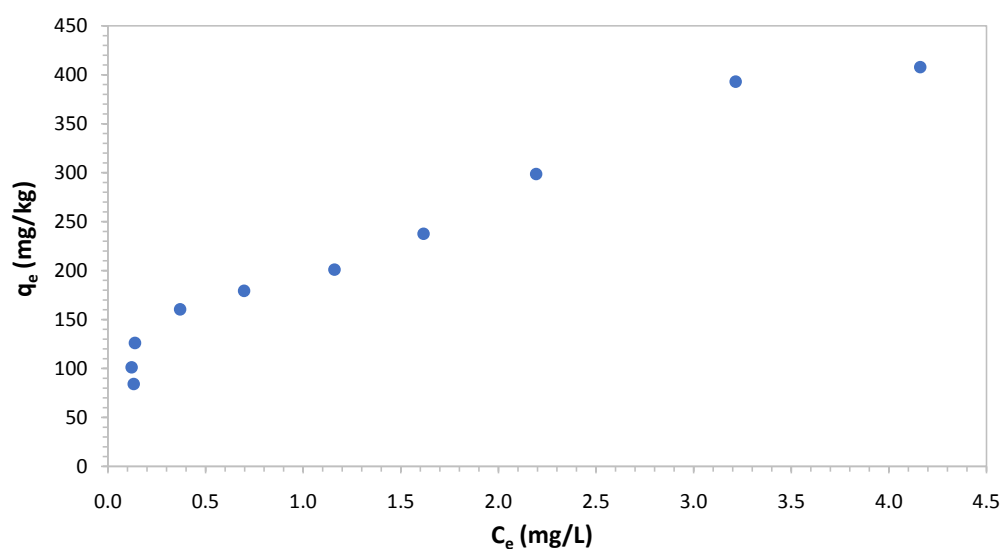


Figure 6. Adsorption isotherm data for adsorption of fluoride onto AlCS sorbent.

indicating that the adsorption of fluoride onto the AlCS sorbent was spontaneous; the free energy of adsorption was negative, similar to findings by other researchers (Vasudevan et al., 2009b).

The adsorption capacity may be reported based on the adsorbent surface area instead of adsorbent mass; the surface normalized adsorption capacity of the AlCS sorbent based on the BET surface area of the AlCS sorbent ($1.648 \text{ m}^2/\text{g}$) is $275.7 \text{ }\mu\text{g}/\text{m}^2$. For comparison, the adsorption capacity of an established adsorbent such as activated alumina has been reported for several activated alumina adsorbents as follows: $1450 \text{ mg}/\text{kg}$ with surface area of $250 \text{ m}^2/\text{g}$ (Ghorai & Pant, 2004), $4040 \text{ mg}/\text{kg}$ with surface area of $242.1 \text{ m}^2/\text{g}$ (Maliyekkal et al., 2006), and $1077 \text{ mg}/\text{kg}$ with surface area of $204.1 \text{ m}^2/\text{g}$ (Maliyekkal et al., 2008); the surface normalized adsorption capacities of these three activated alumina adsorbents are $5.8 \text{ }\mu\text{g}/\text{m}^2$, $16.7 \text{ }\mu\text{g}/\text{m}^2$, and $5.28 \text{ }\mu\text{g}/\text{m}^2$, respectively. The surface normalized adsorption capacities of the three activated alumina adsorbents are lesser than the corresponding value obtained for the AlCS sorbent ($275.7 \text{ }\mu\text{g}/\text{m}^2$). The Langmuir adsorption constant K_L obtained for the AlCS sorbent is $1.22 \text{ L}/\text{mg}$, while the Langmuir adsorption constant K_L reported for the three aforementioned activated alumina adsorbents are $0.31 \text{ L}/\text{mg}$ (Ghorai & Pant, 2004), $0.675 \text{ L}/\text{mg}$ (Maliyekkal et al., 2006), and $0.177 \text{ L}/\text{mg}$ (Maliyekkal et al., 2008); the K_L value for the AlCS sorbent is greater than the K_L values reported for the three activated alumina adsorbents, indicating that the binding and adsorption of fluoride onto the AlCS is stronger than the three activated alumina adsorbents.

3.4. Effect of pH on Fluoride Adsorption

The results for the adsorption and removal of fluoride by $20 \text{ g}/\text{L}$ of the AlCS sorbent from a $5 \text{ mg}/\text{L}$ fluoride solution are presented in Figure 7 as function of initial solution pH. Figure 7 shows that the AlCS sorbent removed fluoride over

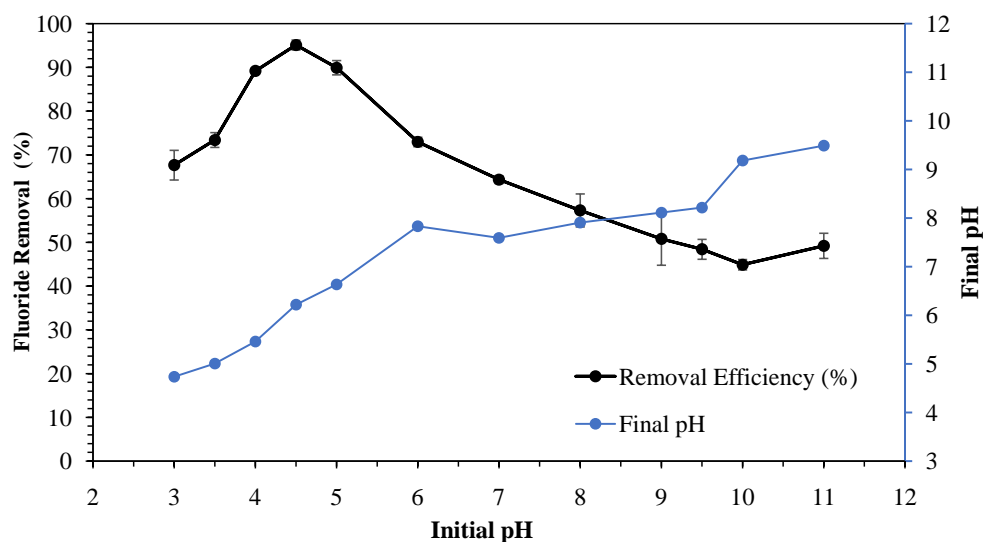
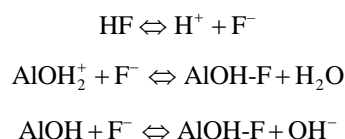


Figure 7. Effect of pH on adsorption and removal of fluoride by the AlCS sorbent.

a broad pH range of 3 - 11, while removal of fluoride was most effective in the pH range of 3 to 7. The equilibrium pH increased under acidic conditions and decreased at initial solution pH values above 7 suggesting that adsorption mechanism may differ by pH range. The increase in equilibrium pH is likely due to ligand exchange between the fluoride and the hydroxyl anion (OH^-), while the decrease in equilibrium pH is associated with competitive adsorption of hydroxyl anion.

The speciation of fluoride is pH dependent due to the dissociation of hydrofluoric acid (HF) over a pH range of 1 - 11. The acid dissociation constant of HF is 3.17, which results in the following distribution of fluoride species: HF at pH below 1.17, mixture of HF and F^- at pH from 1.17 to 5.17, F^- at pH greater than 5.17. The interaction of F^- with the aluminum oxides groups present on the surface is likely to occur as follows, where AlOH_2^+ and AlOH are the surface aluminum groups present at lower pH and higher pH, respectively:



The data from **Figure 7** show that maximum removal of fluoride occurred at pH 4 - 5 where F^- was adsorbed onto the positively charged surface of the AlCS sorbent. Less fluoride was adsorbed at pH greater than 5 where the surface of the AlCS became less positively charged. Lesser adsorption of fluoride occurred at pH greater than 7 was due to the presence of less positive surface of the AlCS sorbent in addition to competition between F^- and OH^- anions for adsorption sites. Similar results were obtained for the effect of pH on adsorption of fluoride by aluminum hydroxides (Vasudevan et al., 2009a).

3.5. Effect of Adsorbent Surface Charge on Fluoride Adsorption

Figure 8 shows the zeta potential of the AlCS sorbent as function of solution pH with and without fluoride in solution.

The results from **Figure 8** show that the point of zero charge (PZC) of the AlCS sorbent occurred at pH 7.1, indicating that the surface of the AlCS sorbent was positively charged at pH less than 7.1, while the surface became more negatively charged at pH greater than 7.1, leading to the observed decrease in fluoride adsorption and removal at pH greater than 7 as shown in **Figure 7**. The pH_{PZC} of the AlCS sorbent was 3.5 in the presence of fluoride in solution, showing a strong shift in pH_{PZC} from 7.1 in the absence of fluoride to 3.5 in the presence of fluoride; the major shift of PZC to the left was indicative of inner sphere complexation or specific adsorption of fluoride onto the surface of the AlCS sorbent which made the surface of the AlCS sorbent more negatively charged after adsorption of the anionic fluoride species. Based on the results from **Figure 7** and **Figure 8**, the adsorption of fluoride onto the AlCS sorbent is mainly due to electrostatic adsorption at lower pH and due to ion exchange at higher pH.

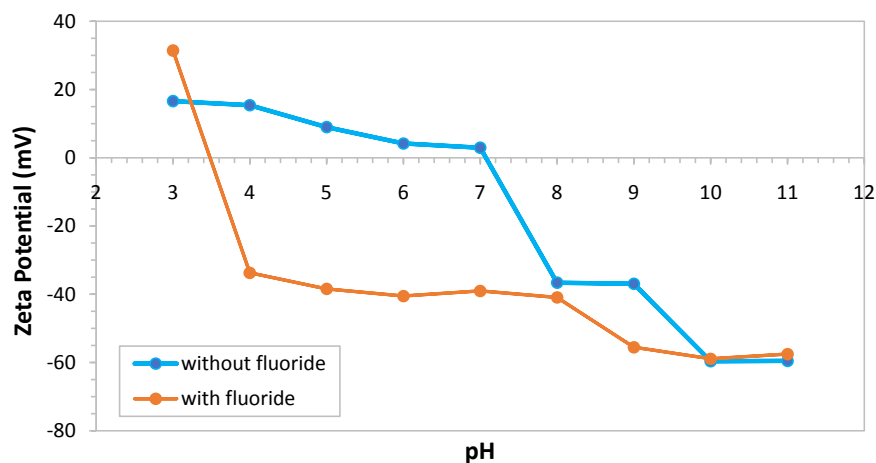


Figure 8. Zeta potential results for the AlCS sorbent.

3.6. Effect of Coexisting Ions on Fluoride Adsorption

Natural water contains different anions and cations. Natural water such as fresh water lakes and rivers, and groundwater may become contaminated with fluoride naturally or from industrial effluents. The effect of the common co-existing ions found in natural water was investigated by preparing fluoride solutions with the following concentrations of coexisting ions: 0.5 mM to 2 mM (20 to 80 mg/L) for calcium (Ca^{2+}), 0.5 mM to 2 mM (48 to 192 mg/L) for sulfate (SO_4^{2-}), and 1 mM to 5 mM (61 to 305 mg/L) for bicarbonate (HCO_3^-). The adsorption and removal of fluoride by the AlCS sorbent in the presence of co-existing ions is shown in **Figure 9**.

The results from **Figure 9** show that the adsorption and removal of fluoride improved in the presence of calcium while the adsorption and removal of fluoride decreased in the presence of bicarbonate, whereas the removal of fluoride remained relatively constant in the presence of sulfate. The AlCS sorbent surface positive charge was enhanced by the adsorption of the calcium cation, thereby increasing the adsorption and uptake of the anionic fluoride species by the AlCS sorbent. The results show that the adsorption and uptake of fluoride by the AlCS sorbent was not significantly influenced by sulfate. The bicarbonate (HCO_3^-) decreased the uptake of fluoride by the AlCS sorbent primarily due to competition for adsorption sites on the surface of the AlCS sorbent between the anionic bicarbonate species and the fluoride anion. These results can be attributed to both the competing effects and the unfavorably higher solution pH due to increasing concentration of bicarbonate; similar results were observed for other metal oxide adsorbents (Sundaram et al., 2009; Zhang et al., 2012). Possible binding of bicarbonate onto the AlCS sorbent surface may have occurred, which is consistent with spectroscopic evidence indicating inner-sphere monodentate complexation on $\gamma\text{-Al}_2\text{O}_3$, amorphous aluminum oxide, and AlOOH (Wijnja & Schulthess 1999). Similar results were obtained for the effect of carbonate/bicarbonate on adsorption of fluoride by aluminum hydroxides (Vasudevan et al., 2009a, 2011).

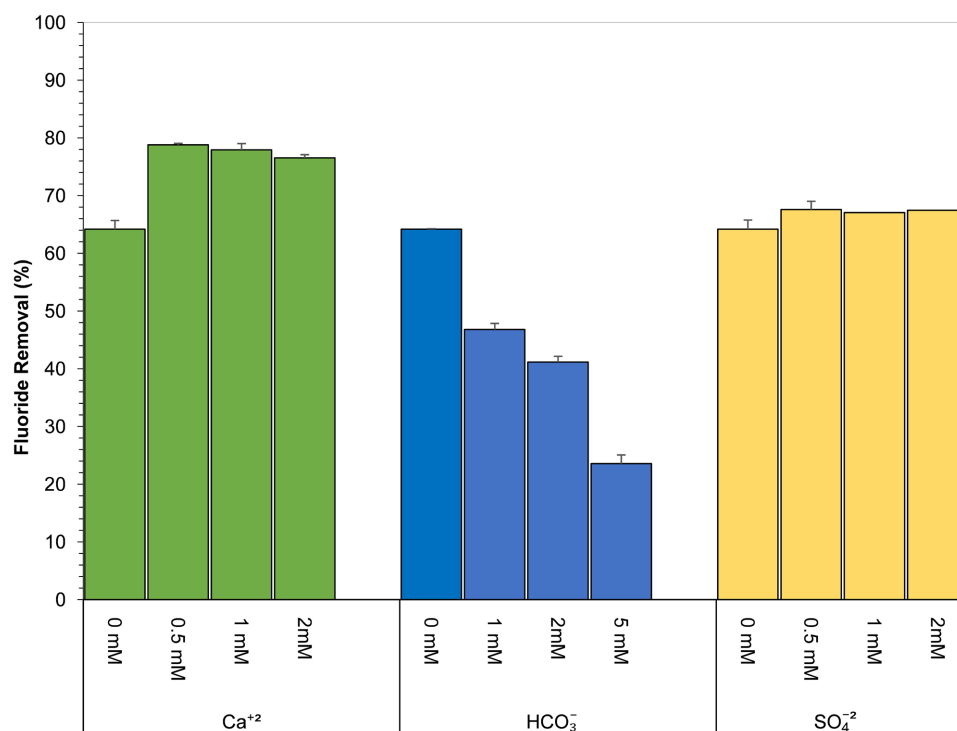


Figure 9. Effect of co-existing ions on removal of fluoride by the AlCS sorbent.

3.7. Adsorbent Recycling

To evaluate the recyclability and reuse of the AlCS sorbent, the AlCS sorbent was applied in several adsorption cycles in series. One gram of the AlCS sorbent was repeatedly mixed in three consecutive adsorption cycles with 50 mL of 5 mg/L solution of fluoride. For the regeneration of spent AlCS sorbent after three consecutive adsorption cycles, the spent AlCS sorbent from the third adsorption cycle was regenerated using the following aqueous solutions of sodium hydroxide: 0.001M NaOH, 0.01M NaOH, and 0.1M NaOH. The regenerated AlCS sorbent was then applied for continued removal of fluoride. The AlCS sorbent removed 72, 32, and 22.7 percent of fluoride in adsorption cycles 1, 2, and 3, respectively. Overall, 1 g of the AlCS sorbent removed 56.8 percent, 25.3 percent, and 17.9 percent of the total removable fluoride for the adsorption cycles 1, 2, and 3, respectively, where about 43.2 percent of the total removable fluoride was removed during the second and third adsorption cycles. The regeneration of the spent AlCS sorbent was highest using 0.001 M NaOH solution; after regeneration, the AlCS sorbent removed 34.3 percent of fluoride.

4. Conclusion

The adsorption and removal of fluoride from water were investigated using an aluminum-coated sand (AlCS) sorbent. Based on TEM and XRD analysis, the AlCS sorbent contained a mostly amorphous coating of aluminum oxides. The adsorption equilibrium parameters for the AlCS sorbent were determined from adsorption isotherm experiments using an initial fluoride concentration of 5

mg/L. The adsorption of fluoride was favorable based on the adsorption parameters determined from the Langmuir and the Freundlich adsorption equations. The adsorption capacity of 454 mg/kg was obtained for the AlCS sorbent based on the Langmuir adsorption equation. Physical adsorption of fluoride onto the AlCS sorbent occurred according to the D-R adsorption equation with an E value of 3.34 kJ/mol. The adsorption kinetics for adsorption of fluoride onto the AlCS sorbent followed second-order kinetics. The AlCS sorbent removed fluoride from water at pH from 3 to 11, with maximum removal of fluoride occurring at pH 4 - 5. The surface charge analysis of the AlCS sorbent determined a pH_{PZC} of 7.1, while the adsorption of fluoride made the surface of the AlCS sorbent more negative with a significant shift in the PZC to the left. The AlCS sorbent removed less fluoride in the presence of bicarbonate in water while removing more fluoride in the presence of calcium in water with no significant change in removal in the presence of sulfate. The AlCS sorbent was recycled and reused in three adsorption cycles.

Acknowledgements

The authors thank the University of Illinois Chicago for supporting this research.

Conflicts of Interest

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

References

- Alhassan, S. I., Huang, L., He, Y., Yan, L., Wu, B., & Wang, H. (2021). Fluoride Removal from Water Using Alumina and Aluminum-Based Composites: A Comprehensive Review of Progress. *Critical Reviews in Environmental Science and Technology*, 51, 2051-2085. <https://doi.org/10.1080/10643389.2020.1769441>
- Ali, S., Thakur, S. K., Sarkar, A., & Shekhar, S. (2016). Worldwide Contamination of Water by Fluoride. *Environmental Chemistry Letters*, 14, 291-315. <https://doi.org/10.1007/s10311-016-0563-5>
- Bhatnagar, A., Kumar, E., & Sillanpää, M. (2011). Fluoride Removal from Water by Adsorption—A Review. *Chemical Engineering Journal*, 171, 811-840. <https://doi.org/10.1016/j.cej.2011.05.028>
- Chai, L., Wang, Y., Zhao, N., Yang, W., & You, X. (2013). Sulfate-Doped Fe_3O_4/Al_2O_3 Nanoparticles as a Novel Adsorbent for Fluoride Removal from Drinking Water. *Water Research*, 47, 4040-4049. <https://doi.org/10.1016/j.watres.2013.02.057>
- Dubinin, M. M., & Radushkevich, L. V. (1947). Equation of the Characteristic Curve of Activated Charcoal. *Chemische Zentral*, 1, 875.
- Eskandarpour, A., Onyango, M. S., Ochieng, A., & Asai, S. (2008). Removal of Fluoride Ions from Aqueous Solution at Low pH Using Schwertmannite. *Journal of Hazardous Materials*, 152, 571-579. <https://doi.org/10.1016/j.jhazmat.2007.07.020>
- Fan, X., Parker, D. J., & Smith, M. D. (2003). Adsorption Kinetics of Fluoride on Low Cost Materials. *Water Research*, 37, 4929-4937. <https://doi.org/10.1016/j.watres.2003.08.014>

- Fordyce, F. M. (2011). Fluorine: Human Health Risks. In J. O. Nriagu (Ed.), *Encyclopedia of Environmental Health* (Vol. 2, pp. 776-785). Elsevier.
<http://nora.nerc.ac.uk/id/eprint/13816>
<https://doi.org/10.1016/B978-0-444-52272-6.00697-8>
- Freundlich, H. (1907). Über die Adsorption in Lösungen. *Zeitschrift für Physikalische Chemie*, 57, 385-470. <https://doi.org/10.1515/zpch-1907-5723>
- Ganesan, P., Lakshmi, J., Sozhan, G., & Vasudevan, S. (2013). Removal of Manganese from Water by Electrocoagulation: Adsorption, Kinetics and Thermodynamic Studies. *The Canadian Journal of Chemical Engineering*, 91, 448-458.
<https://doi.org/10.1002/cjce.21709>
- Ghorai, S., & Pant, K. K. (2004). Investigations on the Column Performance of Fluoride Adsorption by Activated Alumina in a Fixed-Bed. *Chemical Engineering Journal*, 98, 165-173. <https://doi.org/10.1016/j.cej.2003.07.003>
- Habuda-Stanić, M., Ravančić, M., & Flanagan, A. (2014). A Review on Adsorption of Fluoride from Aqueous Solution. *Materials*, 7, 6317-6366.
<https://doi.org/10.3390/ma7096317>
- He, J., Yang, Y., Wu, Z., Xie, C., Zhang, K., Kong, L., & Liu, J. (2020). Review of Fluoride Removal from Water Environment by Adsorption. *Journal of Environmental Chemical Engineering*, 8, Article ID: 104516. <https://doi.org/10.1016/j.jece.2020.104516>
- Jagtap, S., Yenkie, M. K., Labhsetwar, N., & Rayalu, S. (2012). Fluoride in Drinking Water and Defluoridation of Water. *Chemical Reviews*, 112, 2454-2466.
<https://doi.org/10.1021/cr2002855>
- Jha, S. K., Singh, R. K., Damodaran, T., Mishra, V. K., Sharma, D. K., & Rai, D. (2013). Fluoride in Groundwater: Toxicological Exposure and Remedies. *Journal of Toxicology and Environmental Health—Part B: Critical Reviews*, 16, 52-66.
<https://doi.org/10.1080/10937404.2013.769420>
- Kamaraj, R., Pandiarajan, A., Jayakiruba, S., Naushad, M., & Vasudevan, S. (2016). Kinetics, Thermodynamics and Isotherm Modeling for Removal of Nitrate from Liquids by Facile One-Pot Electrosynthesized Nano Zinc Hydroxide. *Journal of Molecular Liquids*, 215, 204-211. <https://doi.org/10.1016/j.molliq.2015.12.032>
- Lagergren, S. (1898). Zur Theorie der Sogenannten Adsorption Gelöster Stoffe. *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24, 1-39.
- Langmuir, I. (1916). The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids. *Journal of American Chemical Society*, 38, 2221-2295.
<https://doi.org/10.1021/ja02268a002>
- Liu, H., Cui, Y., & Zhang, B. (2019). Effects of Iodine and Fluorine in Drinking Water on Human Health. In *Encyclopedia of Environmental Health* (pp. 256-263). Elsevier.
<https://doi.org/10.1016/B978-0-12-409548-9.10990-X>
- Liu, R. X. et al. (2002). Adsorption of Fluoride, Phosphate, and Arsenate Ions on a New Type of Ion Exchange Fiber. *Journal of Colloid and Interface Science*, 248, 268-274.
<https://doi.org/10.1006/jcis.2002.8260>
- Maliyekkal, S. M., Sharma, A. K., & Philip, L. (2006). Manganese-Oxide-Coated Alumina: A Promising Sorbent for Defluoridation of Water. *Water Research*, 40, 3497-3506.
<https://doi.org/10.1016/j.watres.2006.08.007>
- Maliyekkal, S. M., Shukla, S., Philip, L., & Nambi, I. M. (2008). Enhanced Fluoride Removal from Drinking Water by Magnesia-Amended Activated Alumina Granules. *Chemical Engineering Journal*, 140, 183-192. <https://doi.org/10.1016/j.cej.2007.09.049>
- Narsimha, A., & Sudarshan, V. (2017). Contamination of Fluoride in Groundwater and

- Its Effect on Human Health: A Case Study in Hard Rock Aquifers of Siddipet, Telangana State, India. *Applied Water Science*, 7, 2501-2512.
<https://doi.org/10.1007/s13201-016-0441-0>
- National Research Council (2006). *Fluoride in Drinking Water: A Scientific Review of EPA's Standards*. The National Academies Press.
- Rasool, A., Farooqi, A., Xiao, T., Ali, W., Noor, S., Abiola, O., Ali, S., & Nasim, W. (2017). A Review of Global Outlook on Fluoride Contamination in Groundwater with Prominence on the Pakistan Current Situation. *Environmental Geochemistry and Health*, 40, 1265-1281. <https://doi.org/10.1007/s10653-017-0054-z>
- Salifu, A., Petrusevski, B., Ghebremichael, K. L., Modestus, L., Buamah, R., Aubry, C., & Amy, G. L. (2013). Aluminum (Hydr)oxide Coated Pumice for Fluoride Removal from Drinking Water: Synthesis, Equilibrium, Kinetics and Mechanism. *Chemical Engineering Journal*, 228, 63-74. <https://doi.org/10.1016/j.cej.2013.04.075>
- Siddiqui, S. I., & Chaudhry, S. A. (2017). Iron Oxide and Its Modified Forms as an Adsorbent for Arsenic Removal: A Comprehensive Recent Advancement. *Process Safety and Environmental Protection*, 111, 592-626.
<https://doi.org/10.1016/j.psep.2017.08.009>
- Standard Methods for the Examination of Water and Wastewater (23rd ed.) (2018). Method 4500-F Fluoride.
- Sundaram, C. S., Viswanathan, N., & Meenakshi, S. (2009). Defluoridation of Water Using Magnesia/Chitosan Composite. *Journal of Hazardous Materials*, 163, 618-624.
<https://doi.org/10.1016/j.jhazmat.2008.07.009>
- Tamrakar, S., Verma, R., Sar, S. K., & Verma, C. (2019). Cost Effective Natural Adsorbents for the Removal of Fluoride: A Green Approach. *Rasayan Journal of Chemistry*, 12, 455-463. <https://doi.org/10.31788/RJC.2019.1225106>
- Teng, S. X., Wang, S. G., Gong, W. X., Liu, X. W., & Gao, B. Y. (2009). Removal of Fluoride by Hydrous Manganese Oxide-Coated Alumina: Performance and Mechanism. *Journal of Hazardous Materials*, 168, 1004-1011.
<https://doi.org/10.1016/j.jhazmat.2009.02.133>
- Tiemann, M. (2013). *CRS Report for Congress Prepared for Members and Committees of Congress Fluoride in Drinking Water: A Review of Fluoridation and Regulation Issues*.
<https://www.crs.gov>
- U.S. Department of Health and Human Services Federal Panel on Community Water Fluoridation (2015). U.S. Public Health Service Recommendation for Fluoride Concentration in Drinking Water for the Prevention of Dental Caries. *Public Health Reports (Washington, D.C.: 1974)*, 130, 318-331.
<https://doi.org/10.1177/003335491513000408>
- U.S. Geological Survey (2013). *Metal Prices in the United States through 2010*.
<http://www.usgs.gov/pubprod>
- United States Bureau of Mines (1980). *Mineral Facts and Problems: 1980 Edition*. Report.
<https://digital.library.unt.edu/ark:/67531/metadc38793>
- Vasudevan, S., & Lakshmi, J. (2012). Electrochemical Removal of Boron from Water: Adsorption and Thermodynamic Studies. *The Canadian Journal of Chemical Engineering*, 90, 1017-1026. <https://doi.org/10.1002/cjce.20585>
- Vasudevan, S., Lakshmi, J., & Sozhan, G. (2009a). Studies on a Mg-Al-Zn Alloy as an Anode for the Removal of Fluoride from Drinking Water in an Electrocoagulation Process. *Clean*, 37, 372-378. <https://doi.org/10.1002/clen.200900031>
- Vasudevan, S., Jayaraj, J., Lakshmi, J., & Sozhan, G. (2009b). Removal of Iron from Drink-

- ing Water by Electrocoagulation: Adsorption and Kinetics Studies. *Korean Journal of Chemical Engineering*, 26, 1058-1064.
<https://doi.org/10.1007/s11814-009-0176-9>
- Vasudevan, S., Kannan, B. S., Lakshmi, J., Mohanraj, S., & Sozhan, G. (2011). Effects of Alternating and Direct Current in Electrocoagulation Process on the Removal of Fluoride from Water. *Journal of Chemical Technology & Biotechnology*, 86, 428-436.
<https://doi.org/10.1002/jctb.2534>
- Vasudevan, S., Lakshmi, J., & Sozhan, G. (2012). Electrocoagulation Studies on the Removal of Copper from Water Using Mild Steel Electrode. *Water Environment Research*, 84, 209-219. <https://doi.org/10.2175/106143011X13225991083640>
- Vasudevan, S., Sheela, S. M., Lakshmi, J., & Sozhana, G. (2010). Optimization of the Process Parameters for the Removal of Boron from Drinking Water by Electrocoagulation—A Clean Technology. *Journal of Chemical Technology & Biotechnology*, 85, 926-933. <https://doi.org/10.1002/jctb.2382>
- Vázquez-Guerrero, A., Alfaro-Cuevas-Villanueva, R., Rutiaga-Quiñones, J. G., & Cortés-Martínez, R. (2016). Fluoride Removal by Aluminum-Modified Pine Sawdust: Effect of Competitive Ions. *Ecological Engineering*, 94, 365-379.
<https://doi.org/10.1016/j.ecoleng.2016.05.070>
- Velazquez-Jimenez, L. H., Vences-Alvarez, E., Flores-Arciniega, J. L., Flores-Zuñiga, H., & Rangel-Mendez, J. R. (2015). Water Defluoridation with Special Emphasis on Adsorbents-Containing Metal Oxides and/or Hydroxides: A Review. *Separation and Purification Technology*, 150, 292-307. <https://doi.org/10.1016/j.seppur.2015.07.006>
- Wijnja, H., & Schulthess, C. P. (1999). ATR-FTIR and DRIFT Spectroscopy of Carbonate Species at the Aged γ -Al₂O₃/Water Interface. *Spectrochimica Acta A Molecular Biomolecular Spectroscopy*, 55, 861-872.
[https://doi.org/10.1016/S1386-1425\(98\)00236-4](https://doi.org/10.1016/S1386-1425(98)00236-4)
- Yadav, K. K., Gupta, N., Kumar, V., Khan, S. A., & Kumar, A. (2018). A Review of Emerging Adsorbents and Current Demand for Defluoridation of Water: Bright Future in Water Sustainability. *Environment International*, 111, 80-108.
<https://doi.org/10.1016/j.envint.2017.11.014>
- Yang, K., Liang, X., & Quan, C. (2019). Fluoride in Drinking Water: Effect on Liver and Kidney Function. In *Encyclopedia of Environmental Health* (pp. 34-40). Elsevier.
<https://doi.org/10.1016/B978-0-12-409548-9.11083-8>
- Zhang, G., He, Z., & Xu, W. (2012). A Low-Cost and High Efficient Zirconium-Modified Na-Attapulgite Adsorbent for Fluoride Removal from Aqueous Solution. *Chemical Engineering Journal*, 183, 315-324. <https://doi.org/10.1016/j.cej.2011.12.085>
- Zheng, W., He, D., Wang, Y., Chen, J., Xue, M., & Li, H. (2021). Preparation of Cement-Based Color Facing Mortar by Copper Pyrometallurgical Slag Modification: Efficient Utilization of High-Iron-Content Slag. *Journal of Environmental Chemical Engineering*, 9, Article ID: 105888. <https://doi.org/10.1016/j.jece.2021.105888>