Effect of P^H and Temperature on Deflouridationof Drinking Water by using activated Alumina Based Adsorption

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Abstract: Fluorosis, a disease caused by exposure to elevated levels of fluoride in drinking water, impacts millions of people in both developed and developing countries. It is, therefore, important to improve existing methods of defluoridation. This review discusses the sorption of fluoride to alumina sorbants, a widely used defluoridation filter material. To discover significant factors that influence the sorption process, and to thus learn how this technique might be enhanced, a select group of peer reviewed sorption studies were compared. As a result of this analysis, it is clear that fluoride sorption to alumina sorbants is a complex process in which differences in surface morphology, pH, temperature, fluoride concentration and the presence of other major ions such as sulphates and bicarbonates interact to produce a wide range of reported specific sorption values.

Key words:deflouridation ,sorbants, morphometry, bicarbonates, sulphates

I. Introduction

Fluorine is a naturally occurring element found in various minerals. However, release intoground water from dissolving activity and draught can cause elevated levels offluoride in drinking water. Fluoride, although beneficial for the mineralization of hard tissues inthe human body, can be toxic to humans with chronic exposure to elevated concentrations .The standard level for fluoride in drinking water is 1.5 mg/L, according to the World HealthOrganization (WHO)However,fluoride levels in rural areas of chikkballapurdistrict Bagepalli(Jilipigarapalli) Gudibande(adhinarayakonda) Gowribidnur(hosur) and some near by areas of these places have been found to be as high as 5-6 mg/L and levels of up to 8 mg/L have been measured. Effects can range from mottling of teeth to severe skeletal deformations,known as skeletal fluorosis. Therefore,it is crucial that effective fluoride removal methods are developed that can be used not only indeveloped nations, but also in developing countries.

Currently, a wide range of defluoridation methods exists. These methods can be dividedinto the following categories: Adsorption, chemical precipitation, removal by ion exchange, andmembrane filtration. The most currently used method utilizes alumina adsorbants to removefluoride from drinking water. In developing countries there is also a growing movement towardsthe use of natural materials such as clays, ash, and bone char, which, when found in localcommunities, can significantly increase the cost efficiency of defluoridationmethods .However, these alternative sorbants have not displayed significant fluoride removal capacities and, thus, alumina still remains a valuable material to study and pursue. Despite decades ofapplication-based research, the underlying science and specific mechanisms behind fluoridesorption to alumina based sorbants is still unclear. Therefore, this review will primarily focus ona group of peer-reviewed studies conducted with alumina and several other aluminum basedsorbants, comparing and contrasting the research in order to gain insight into the impacts of surface morphology, pH, temperature, fluoride concentration, and the presence of major ions onthe efficiency of defluoridation, as well as to determine significant gaps in knowledge whereadditional research should be conducted. Due to the limited scope of this work, factorsinfluencing on-site defluoridation of contaminated drinking water will not be discussed.
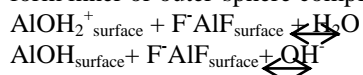
Effect of Hydration on Structure of γ-Al$_2$O$_3$

The effect of hydration on surface properties of alumina has been greatly overlooked inthe literature, but has significant implications in the sorption of fluoride. Studies have shown that hydration of alumina causes phase transitions over time, changing the surface morphology ofthe sorbant. It has been shown that γ-Al$_2$O$_3$ surfaces undergo a transformation to bayerite (α-Al(OH)$_3$), a polymorph of gibbsite (γ-Al(OH)$_3$), when hydrated for prolonged periods of time, and exposure to water vapor for one hour causes α-Al$_2$O$_3$ to produce a mixture ofbayeriteand gibbsite on its surface. Many studies do not specify whether the sorbant used was hydrated prior to sorptionexperiments. Using either dehydrated or partially hydrated sorbants may lead to morphologicalchanges during sorption, thus making it difficult to elucidate a mechanism of sorption and tocompare results between studies. Therefore, any meaningful comparison between studies shouldbe within the same type of alumina and using similar hydration protocol. However, Yang et al.showed that as hydration time increases, the surfaces of alumina minerals tend to becomemore similar. It is possible that at longer hydration

times, differences in surface morphometryare less significant and comparisons between studies may be more relevant.

P^H variation

The impact of P^H on the sorption of fluoride to alumina is significant in that it not only controls the maximum uptake capacity of the sorbant, but that it also controls the solubility of various fluoride complexes that form during the sorption process. Thus,P^Hmust be considered when trying to optimize fluoride uptake as well as when attempting to minimize dissolution that could release both fluoride and aluminum into treated drinking water. Although the mechanistic details of fluoride sorption are not clear, sorption of fluoride anions to alumina sorbants is often reported as a result of electrostatic interactions with positive, and even neutral, surface charge. However, studies have failed to specify whether interactions between fluoride and alumina surfaces form inner or outer-sphere complexes. Possible surface-exchange reactions can be expressed as

$$AlOH_2^+{}_{surface} + F^-AlF_{surface} \leftrightarrow H_2O$$
$$AlOH_{surface} + F^-AlF_{surface} \leftrightarrow OH^-$$

If aluminum is released from the sorbant, the formation of several different fluoride-aluminum complexes can occur, whose solubility varies with pH, as shown in Figure 2. At circum-neutral pH the dominant species are AlF_3 and F^-.

The influence of pH on removal of fluoride studied employing test solutions adjusted to initial pH values of 9.00 ± 0.10, 8.00 ± 0.10, 7.00 ± 0.10, 6.00 ± 0.10, 5.00 ± 0.10, 4.00 ± 0.10 and 3.00 ± 0.10 shows the effect of pH on removal of fluoride by AA. As the pH of the test fluoride solution is increased from 3.00 to 9.00, removal of fluoride remains more or lessconstant at around 92 – 94% upto a pH of 7.00 but drastically reduces to 35% at a pH 9.00. This drastic reduction is removal with increasing pH is characteristic of anion sorption with a distinctive pH-sorption edge The pH sorption edge is a narrow pH region often about 2 pH units wide in which sorptionbehaviour changes rather dramatically. In the present case, the decrease in sorption withincreasing pH, i.e. pH-sorption edge is characteristic of anionic sorption i.e. nearly complete removal at low pH to no removal at higher pH values and indicates formation of ligand-like complexes whose tendency to sorb decreases with increasing pH.

P^H values	The % removal of fluoride
9.00 ± 0.10	35
8.00 ± 0.10	55
7.00 ± 0.10	62
6.00 ± 0.10	74
5.00 ± 0.10	81
4.00 ± 0.10	92-94

Effect of Temperature on physiorption

Temperature plays a double role in the fluoride sorption process. Temperature canimpact the physical binding processes of fluoride to a sorbant. However, temperature also canhave a direct impact on the physical properties of a sorbant, if thermally treated prior to exposure, so that sorption capacities can be significantly altered. Most sorption studies areconducted at room temperature in laboratory settings. However, because many cases of fluorosisare found in arid regions where temperatures are well above 25 °C, it is important to understandwhat impact temperature has on the sorption of fluoride to alumina sorbants.showed that temperature appears to play a slight role in the optimal pH for sorption in that by increasing temperature from 10 °C to 40 °C the pH decreased from8 to 6.1. This change suggests that increased temperatures either favor desorption of protonsfrom the surface or hydroxide sorption to the surface, shifting protonation constants to lowervalues as shown in the following surface equilibria

$$Al(OH)^+{}_{2surface} AlOH_{surface} \leftrightarrow + H^+$$
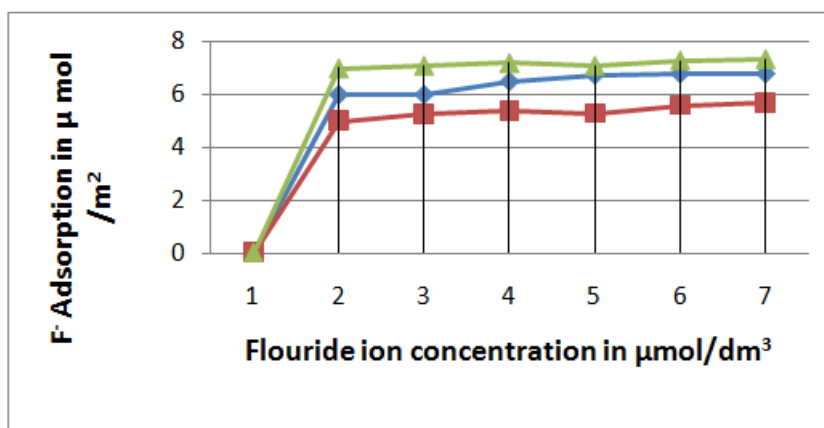$$AlOH_{surface} + OH^- \leftrightarrow AlO^-{}_{surface} + H_2O$$

As temperature increased, sorption was shown to be less favored most likely due to increaseddeprotonation or hydroxylation of the surface causing more negatively charges sorbant surfaces. This is an important observation to note when attempting to apply defluoridation methodson site in hot climates, for sorption capacities attained under room temperature conditions may be higher than in the field as a result of increased temperatures.

Effect of Fluoride Concentration
Specific Sorption

Not only do surface structure, pH, and temperature play roles in influencing the sorptionof fluoride, but fluoride concentration itself significantly impacts specific sorption as well as thedissolution of fluoride-

aluminum complexes. Sorption processes are typically characterized by adsorption curves and adsorption isotherms, the most commonly used being the Langmuir andFreundlich isotherms. A typical adsorption curve and isotherm are shown in Figures 5 and 6,respectively.

Release of Aluminum from Alumina Sorbants

Dissolution of fluoride-aluminum complexes are, in part, related to increased solubility at lower pH values. However, fluoride-promoted dissolution of alumina has been observed inseveral studies. It is important to understand the dissolution of these complexes to prevent therelease of not only fluoride, but also aluminum into treated water.

Studied possible mechanisms for the dissolution of fluoride-aluminum complexes by specifically looking at bayerite and boehmite. The study showed an increasingdissolution rate with decreasing pH when observing pH below the pH. Yet, dissolution alsoincreased with increasing sorption of fluoride, varying nonexponentially with fluoride loading concluded that the sorption of fluoride to both terminal and bridging sites inthe sorbants increase dissolution rates. Proposed mechanisms for dissolution includedlabialization of oxygen bridges in the inner-coordination aluminum complex by stable ligands,displacement of terminal water molecules by fluoride or hydroxides, and at high concentrationsof fluoride, the exchanging of bridging hydroxl groups for fluoride. From Table given below , it appearsthat δ-Al_2O_3 has dissolution rate an order of magnitude faster than α- Al_2O_3 at pH 4. AlthoughpH levels of treated water do not reach this low pH, it is still significant to know that different alumina polymorphs may have different fluoride-promoted dissolution rates, which could impactthe quality of treated drinking water.

Dissolution rates of aluminum oxides at pH=4, I=0.1M and 25ºC

Mineral	Rate R_H[moles m^{-2}s^{-1}]	K_m[s^{-2}]	$T_{1/2}$[days]
δ- Al_2O_3	1.1×10^{-12}	1.22×10^{-8}	606
γ- Al_2O_3	1.5×10^{-10}	1.83×10^{-7}	38
Corundum	2.0×10^{-12}	3.4×10^{-6}	222
Bayerite	3.0×10^{-12}	9.1×10^{-7}	8.9
Boehmite	5.9×10^{-13}	9.2×10^{-7}	0.90

Influence of Major Ions on Fluoride Adsorption

The majority of fluoride sorption studies conducted make use of DDW water containingan electrolyte background, but do not take into account the affects of other major ions present innatural waters. However, a small number of studies have observed the impacts of specific ions on defluoridation, an effect that is important to understand when attempting to applydefluoridation techniques developed in the laboratory to the field. showed thatthe presence of silicon (64 mg/L) appears to compete with fluoride sorption, however thepresence of sulfate (2.25 g/L) does not seem to impact sorption. However, contrary to thesefindings, determined that the presence of sulfate (0.05 M) at acidic conditions significantly decreases the fluoride removal capacity as well as enhances the dissolution ofaluminum species. Percent removal at pH 6 dropped from approximately 95% to 75% with thepresence of sulfate. Although natural groundwater with high fluoride concentrations tend to bemore alkaline , this is still an important factor that should considered if treating more acidicwaters with elevated levels of sulfate. Yet showed that the presence of carbonate and bi-carbonates (100-500 mg/L) in elevated concentrations decreased the sorption offluoride to filter material produced from aluminum sulfate wastes primarily through competitionas well as the change in pH associated with the presence of these anions.Sorption efficiencydecrease from 82% to 68% in the presence of 500 mg/L bicarbonate. However, anions

likechloride, sulfate, phosphate and nitrate had virtually no impact on fluoride sorption. Thus, defluoridation of highly alkaline groundwater could potentially be a challenge.

II. Conclusions

Alumina sorbants clearly seem to be a viable option for defluoridation methods due to their significant specific sorption. However, in light of the complex interactions of differentvariables during the sorption process, one finds a wide range of sorption values in the literature., studies conducted with DDW containing only a background electrolyteand alumina polymorphs report specific sorption capacities (mg/g) ranging between 2.4 and 11.9,with a mean of 6.3 ± 5 and a median of 4.38 . Studies conducted using aluminum hydroxides as sorbants showed a greater spread of specific sorption capacities rangingfrom 0.8 mg/g to 98 mg/g.

It is clear that pH plays a critical role in maximizing sorption and that when deviationsfrom optimal ranges occur significant drops in fluoride removal are observed, whether it bebecause of ion competition, change in surface charge, or dissolution of the sorbant. Yet, as discussed above, these processes can be altered by environmental conditions such astemperature, fluoride concentration, and presence of other major ions in solution.

Based on the above analysis, it is clear that there lies a significant gap between researchbeing conducted in the laboratory and the conditions found in fluoride contaminated naturalwaters. Although there are a number of field studies that have been conducted utilizing alumina packed columns for the treatment of fluoride contaminated drinking waters in regions of Chikkballapur rural areas, more emphasis should be placed on understanding the factors that influence the sorptionprocess in natural waters in a controlled laboratory setting using fully hydrated sorbants. Indoing so, knowledge can be attained to enhance defluoridation methods, making them moreeffective and cost efficient when used in the field.

References

[1].   Ku, Y.; Chiou, H.-M., The Adsorption of Fluoride Ion from Aqueous Solution byActivated Alumina Water, Air, & Soil Pollution **2001,** 133, 349-360.
[2].   Choi, W.-W.; Chen, K. Y., The removal of fluoride from waters by adsorption. WaterTechnology **1979**, 562-569.
[3].   Ghorai, S.; Pant, K. K., Investigations on the column performance of fluoride adsorptionby activated alumina in a fixed-bed. Chemical Engineering Journal **2004,** 98, (1-2), 165-173.
[4].   Karthikeyan, G.; Meenakshi, S.; Apparao, B. V., Defluoridation technology based onactivated alumina. In 20th WEDC Conference, Colombo, Sri Lanka, 1994.
[5].   Zewge, F., Solution to the Fluoride Problem in the Rift Valley Region of Ethiopia.Solutions 2006, pp 15-22.
[6].   Karthikeyan, G.; Muthulakshmi, A.; Saravana, G. S., J. Indian Water Works Association**1999**, 7, 291.
[7].   Stumm, M., Morgan, J., And Aquatic Chemistry: Chemical Equilibria and Rates in NaturalWaters. John Wiley & Sons, Inc.: New York, 1996.
[8].   EPA, U. S. National Secondary Drinking Water Regulations. (16.12.08)
[9].   Handa, B. K., Geochemistry and genesis of fluoride-containing ground waters in India.Ground Water **1975,** 13, (3), 275-281.