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# Fluoride Adsorption onto Soil Adsorbents: The Role of pH and Other Solution Parameters

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## Abstract

Soil adsorbents continue to attract increasingly high numbers of researchers in water defluoridation studies. An aspect of solution parameters, that is the aqueous adsorption of fluoride onto soil adsorbents in defluoridation studies, has been reviewed and reported. The pH was found to be the main factor controlling fluoride adsorption on the popular soil adsorbents including: aluminosilicates, iron (hydr)oxides, aluminum (hydr)oxides, apatites, carbonaceous minerals, calcareous soils and zeolites and the other key parameters being temperature, time of contact, and co-existent ions. Fluoride adsorption onto metal-exchanged zeolites and hydroxyapatites (optimum pH = 4–10), iron (hydro)oxide minerals (pH = 2–7), and carbonaceous minerals (pH = 4–12) is relatively pH-independent, and high amounts of fluoride are able to sorb upon the surfaces of these minerals in a wide range of pH values. However, montmorillonites (optimum pH = 5–6), aluminum (hydro)oxide minerals (pH = 5–7), and calcareous minerals (pH = 5–6) only sorb significant amount of fluoride in a narrow range of pH values. The fluoride adsorption onto the latter class of minerals, also generally occurring at slightly above room temperatures, appears to be highly specific and not strongly affected by the presence of coexistent anions including:  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ .

**Keywords:** adsorption, defluoridation, drinking water, fluoride, minerals, pH, soil

## 1. Introduction

Adequate dietary levels of fluoride are desired for good oral health and for the proper development of skeletal tissues [1]. Nonetheless, the excessive levels of fluoride in the environment pose major public health challenges in many regions of the world [2]. Dietary fluoride overexposure has been linked to a series of detrimental physiological effects [3] and it is known

to lead to serious mottling of teeth enamel and gross skeletal malformations [4]. Continued dependence on fluoride-enriched water by communities in high-fluoride areas is the principal conduit by which people get exposed to undue levels of fluoride from the environment. Problems linked to prolonged consumption of excessive fluoride through water and food are, for that reason, normally correlated to areas of high-fluoride-bearing rocks and fluoride-enriched soil minerals. Even so, the hydro-geological release of soil mineral fluoride and its bioavailability through food chains is dependent on the hydrogeochemical characteristics of the environment.

Because of its detrimental public health effects when consumed in excessive amounts, the World Health Organization (WHO) has set recommended levels of fluoride for drinking water at 0.7 ppm [5]. However, the set maximum permissible levels of 1.5 ppm are the most widely used fluoride standards of drinking water to guard against dental caries and ensure healthy development of teeth and bones [6]. The point-of-use treatment of contaminated drinking water, to remove excessive fluoride while allowing sufficient levels for good oral and skeletal health, is now an indispensable component in many domestic water treatment protocols around the world [7]. Because of the high costs involved, many studies have recently been devoted to investigating the capacity of different materials for fluoride removal from water with a view to device more affordable approaches to water defluoridation [8–10].

Soil adsorbents, in particular, have been among natural media that have been extensively explored by researchers as alternate affordable media in water defluoridation [11–14] as they are normally more readily available and, by and large, possess significant fluoride adsorption capabilities. Furthermore, they are relatively stable and usable in a wider range of water conditions than most other natural media. The soil adsorbents that have attracted highest attention of scientists for water defluoridation include montmorillonites, aluminosilicates, iron and aluminum (hydr)oxides, hydroxyapatites, carbonaceous minerals, calcareous soils, and zeolites [15]. The solution pH, fluoride concentration, temperature, and co-existent ions play a major role in controlling fluoride adsorption onto soil adsorbents. Understanding the influence of these parameters in fluoride removal from water by adsorption using soil adsorbents could present additional insight into the scope of applicability of the geomaterials in water defluoridation.

The present work was initiated to interrogate available literature on water defluoridation by adsorption using soil adsorbents with a view to divulge information that could inform subsequent strategies in water defluoridation-based soil mineral adsorbents.

## 2. Adsorption surface enhancement for soil adsorbents

The potential soil adsorbents for fluoride sequestration from water are as diverse as the natural soil systems on earth. However, a glimpse through recent literature reveals that only few minerals have been repeatedly been studied for their potential to sorb fluoride from water over the last few decades. The selection of a soil adsorbent for water defluoridation studies is usually informed by, among other factors, the already known sorption capacities of

the mineral for fluoride or for related adsorbates; the ease of availability of the mineral, its procurement, preparation, and applicability under given conditions; as well as by its user and environmental safety considerations. Based on approximate fluoride adsorption capacities of the minerals frequently revealed in the literature, the minerals that have exhibited the most promising potential for water defluoridation in the most recent studies include palygorskite (with a mean fluoride adsorption capacity of 57.97 mg/g), pumice (18.27 mg/g), zeolites (15.65 mg/g), hydroxyapatite (13.27 mg/g), iron-enriched laterites (9.39 mg/g), bauxite (7.53 mg/g), and montmorillonites (4.82 mg/g). The other minerals including kaolinites, ceramics, and quartz normally have mean fluoride adsorption capacities of less than 3.0 mg/g and do not constitute prospective robust fluoride adsorbents [15].

The capacity of soil media to sorb large amounts of fluoride is controlled by the predominant surface chemistry of the soil systems. The primary fluoride sorptive sites of clay colloids in the soil minerals comprise mainly the protonated or non-protonated silanol groups and the cationic positive centers provided by prevalent soil cations such as  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Si}^{4+}$ . Natural soil systems are, however, generally associated with low ion-exchange capacities because the soil surfaces are normally saturated with replaceable counter groups, which mask and neutralize intrinsic surface charge so as to maintain mineral surface stability. The ion-exchange properties of the soil minerals can, however, be enhanced by pre-treatments that are aimed at dislodging the masking ions from the soil surfaces so as to increase the reactivity of the soil surfaces toward the target adsorbate ion and unblock the pores into the crystal lattice structure of the soil systems [16]. This is more so for soil surfaces that possess net charges that repel the adsorbate ions as is usually the case of fluoride adsorption onto clay systems, which are normally characterized by high density of electronegative oxygen groups in their structures that induce a net negative charge in the adsorbent soil surfaces. These surface charges make such soil to naturally repel and keep fluoride in the solution. This necessitates pretreatment to produce soil surface charge reversal in order to enhance their fluoride adsorption affinities and capacities.

The surface charge reversal for negatively charged soil adsorbents, which is aimed at enhancing electro-activity of their colloid surfaces towards aqueous fluoride particles, may be achieved by impregnating the adsorbent soil structure with multivalent metal ions or by grafting and intercalating the soil adsorbents with charged reactive groups. Hydrothermal activation of soil adsorbents in dilute acids is also a common practice that is not only simpler to apply but also more cost-effective [17, 18]. The latter procedure results in partial dealumination of the clay structure, which increases the proportion of silica and the density of acid silanol groups on soil adsorbent surface leading to increased overall positive charge of the clay surfaces [19, 20].

### 3. Effect of selected solution parameters

The effects of adsorption solution parameters on the adsorption process spring from their influence on the adsorbents soil surface chemistry and on the flux transport of adsorbate

solutes from the bulk solution through the aqueous matrix to the adsorbent surface. The principal solution parameters that control fluoride sequestration onto soil surfaces include the pH, temperature, contact time, fluoride concentration, and co-existing ions. Other contributing factors comprise: adsorbent dosage, adsorbent particle size, and the rate of agitation. The effect of adsorbent dosage and particle size and those of the adsorbate concentration mirrors each other. This is because both adsorbent dosage and particle size and those of the adsorbate concentration control the availability of reacting “particles” that drive the thermodynamic adsorption equilibrium on either side of the adsorption interface. Increase in the adsorbent dosage and in the adsorbate concentration results in high rates of adsorption as a result of more intensified solute fluxes through aqueous media to the soil surfaces. This influence is, however, extensively discussed elsewhere in the literature [15].

### 3.1. Effects of pH

Speciation and aqueous availability of fluoride in water is the function of pH, concentration, and the presence of cations such as:  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  [21]. At low pH values of 4 and less, for example, the molecular HF fluoride species predominates aqueous fluoride speciation in solution. The formation of HF, which favors solubility and aqueous availability of fluoride, increases with decreasing pH of the media [22]. The fluoro-aluminum complexes that include  $\text{AlF}_2^+$ ,  $\text{AlF}_2^+$ , and  $\text{AlF}_3^0$  and other metallo-fluoro complex species involving other multivalent cations such as  $\text{Fe}^{3+}$ , emerge in the pH range of 4–6 and the concentration of free fluoride ions in this pH range is only 21.35% [23]. At higher pH values, the stability of metallo-fluoro complexes decreases and the free fluoride anions,  $\text{F}^-$ , predominate. All fluorides exist as free anions,  $\text{F}^-$ , at pH values of 8–9, where all forms of aluminum species form the aluminate,  $[\text{Al}(\text{OH})_4]^-$ , complexes in the presence of excess  $\text{OH}^-$  species [24].

In the same way, the solution pH controls the ionization of reactive surface groups in the colloid soil surfaces and determines the nature and the intensity of the soil surface charge and the adsorption potential at the soil surfaces [25]. Calcareous minerals, for instance, facilitate pH-dependent fluoride solubility according to the mass balance Eq. (1) as follows [26]:



This equation relates calcite and fluorite in the natural soil environments when both salts are in contact with the water. Accordingly, the increase in pH and in the concentrations of  $\text{HCO}_3^-$  increases water fluoride concentrations and vice versa.

In addition, anionic adsorption onto soil adsorbents can proceed through specific or non-specific adsorption. The former is based on ligand-exchange reactions where the anions displace  $\text{OH}^-$  and  $\text{H}_2\text{O}$  from the soil surfaces, whereas the latter involves electrostatic coulombic forces and mainly depends on the pH of zero net charge (pHpzc) of the adsorbent soil surface. Above pHpzc, the soil surface assumes positive charge, whereas below net positive surface charge persists [27]. The specific adsorption of fluoride by metal oxyhydroxide surface sites, for example, occurs by ligand exchange according to Eqs. (2) and (3) for protonated and non-protonated sites, respectively, as follows:



The pH of the aqueous media is, therefore, the prime factor that controls fluoride uptake by soil surfaces.

However, the solution pH of maximum fluoride adsorption varies from one type of soil adsorbent to the other. For iron-enriched laterites [27–29], kaolinites [22, 30–33] and, to a limited extent, for certain hydroxyapatites [34, 35], the maximum fluoride adsorption capacities occur in acidic media at pH values of 5 or less. Fluoride uptake in low pH (3–5) can be attributed to the formation of weak hydrofluoric acid [27]. It, therefore, shows that the adsorbent surfaces for these minerals have affinity for HF aqueous species.

The maximum fluoride adsorption capacities for montmorillonite clays [22, 36, 37], aluminum (hydrox)oxide minerals [38–44] and calcareous minerals [11, 12] are, however, restricted to pH values of 5–6. Montmorillonites,  $\text{Mx}[(\text{Mg}, \text{Al}, \text{Fe})_2(\text{OH})_2(\text{Si}_4\text{O}_{10})] \cdot n\text{H}_2\text{O}$ , are a group of expanding smectite clays comprising octahedral sheets of alumina sandwiched between two tetrahedral sheets of silica. The tripartite sheets are then loosely held together by weak oxygen-oxygen and oxygen-cation bonds [22]. The principal fluoride binding sites in montmorillonites are the cationic  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  centers. At pH of 4 and less, the capacity of montmorillonites to sorb large amounts of fluoride is greatly compromised due to their disruptive dissolution of the mineral structure with release of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{SiO}_2$ . A major part of fluoride in a montmorillonite-water system exists in the form of aqueous iron and aluminum complexes, and only a small fraction is able to sorb onto the clay surface.

Conversely, certain soil sorbents, which include pumice [45, 46]; palygorskites [47]; and particular ferric oxide minerals such as hematite [48, 49] are able to sorb high amounts of fluoride over an entire range of pH values from 2 to about 8. Furthermore, fluoride adsorption onto natural and metal-exchanged zeolites [50] and onto a class of carbonaceous adsorbents including lignite [51, 52] and coal [52, 53] appear to be quite pH-independent and high amounts of fluoride adsorption based on this class of adsorbents occur over the wide range of pH values of 4–12.

In general, therefore, montmorillonites normally tend to solubilize in low pH media and get poisoned by excessive  $\text{OH}^-$  ions in alkaline media. For this reason, montmorillonites usually have narrow fluoride sorption edge within the neutral pH values. Like for montmorillonites, the usual pH for effective fluoride removal from water using metal-enhanced palygorskite is usually in the range of 2–8. Fluoride adsorption onto metal-exchanged zeolites and onto certain synthetic hydroxyapatites is, however, relatively independent of pH, and the adsorbents are able to take up high fluoride adsorption over a wide choice of pH values of 4–10. Aluminum oxide minerals usually have a narrower fluoride sorption edge in the pH range of 5.5–6.5 as is maximum fluoride adsorption onto Ca-based minerals, which occurs within the pH values of 5–6. On the other hand, high fluoride uptakes by hematite occur over a wider range of acidic pH values of 2–7. In the same way, optimum fluoride removal using carbonaceous adsorbents can be achieved at room temperature in the pH range of 4–12.

Differences in pH of maximum fluoride uptake for various soil systems arise principally from the differences in the surface chemistry of the mineral adsorbents, which control the affinity of soil surfaces towards different fluoride species in soil surfaces. It can be assumed that soils that have high fluoride adsorptions in strongly acidic media of pH 5 or less have higher affinity for molecular HF species, which are dominant in this range of medium pH. The HF particles adsorb by forming continuous hydrogen bonds with electronegative centers in the soil surfaces. Certain soils that preferentially sorb fluoride in the near-neutral acidic pH values of 5–6 have affinity for  $F^-$  species, and the mode of fluoride adsorption is mainly complexation with positive cationic centers in the soil colloid structure, which include  $Al^{3+}$ ,  $Fe^{3+}$  and  $Si^{4+}$  among others. Soil adsorbent that sorb high fluoride levels over a wide range of pH values contains heterogeneous surfaces, which have attraction to several different fluoride species in solution.

### 3.2. Adsorption temperature

The effect of temperature on fluoride adsorption onto soil surfaces arise from its influence on the adsorption energy balance, on the kinetics of adsorbate particles, and on the chemical activation of reacting species. Higher temperatures enhance increased rates of adsorption by enhancement of faster solute transport from the bulk solution towards the adsorbent surfaces. Higher temperatures also raise the average energy of the particles allowing a higher number of particles to attain necessary activation energy to enable them to react. Very high temperatures may, however, counter the adsorption fluxes leading to reduced rates and magnitude of uptake of the adsorbate by the adsorbents.

As for the effects of solution pH, however, the effect of temperature on fluoride adsorption on popular soil adsorbents is varied. The peak fluoride adsorption by natural montmorillonites [22, 36, 37, 54], Fe(III)-modified montmorillonite [55], pumice [56] and lignite [51, 52] occur within a range of temperatures close to room temperature (298 K). Nevertheless, the highest fluoride uptake by both aniline-modified montmorillonites and pyrole-modified montmorillonites [57] as well as by coal [52, 53] is favored by above room temperatures close to 303 K. It has been found that fluoride-exchange reactions for hydroxyapatites [58–60] and for certain ferric oxide minerals such as hematite [48, 49] can occur over a wide range of temperatures of 298–323 K. Fluoride adsorption onto  $Mg^{2+}$  and  $Al^{3+}$  [47],  $Fe^{3+}$  [61] and  $ZrO^{2+}$  [62] loaded palygorskite minerals; synthetic hydroxyapatites [63, 64]; calcareous minerals [65] and onto magnesia-loaded fly ash cenospheres (MLC) is favored by higher temperatures in the range of 303–323 K. This indicates the existence of endothermic chemical surface reactions. The efficacies of bauxite to sorb fluoride has, however, been found to decrease with increasing temperature indicating the existence of exothermic fluoride immobilization in bauxite surfaces [39, 44].

### 3.3. Contact time

The resident time required for equilibration in an adsorption process depends mainly on the adsorbent structure and on the nature of reactions that occur between the adsorbate particles and reactive sites at the adsorbent surface. Adsorbents with compact crystalline structures and characteristically surface exposed reactive sites tend to have rapid rates of adsorption

than porous media with intraparticle sorptive sites. This is because in the latter case, the adsorbate particles have to be transported by diffusion into the inner adsorbent structures in order to access the reactive adsorbent sites. Fluoride adsorption onto pulverized crystalline calcareous minerals tends to occur rapidly by surface precipitation of fluorite,  $\text{CaF}_2$ , over the entire mineral surface [66, 67]. Water defluoridation using calcareous materials is, as a result, normally characterized by fast adsorption rates and the adsorption equilibrium lies within the range of 30–60 min [11, 68].

In less crystalline adsorbents such as lignite, more than 90% fluoride adsorption occurs within the initial 10 min. It, however, takes up to 150 min to saturate the less exposed sites inside the adsorbent structure with the latter 10% of the process [51, 52]. Such trends are also observed in the case of fluoride adsorption onto coal with shorter equilibration periods of 60–90 min for the latter phase of adsorption [52, 53], which shows that coal is more crystalline and less porous than lignite.

Equilibration periods required for fluoride adsorption onto pumice have been reported to lie within the range of 20–30 min but pumice adsorbents have not generally been associated with the two-phase adsorption phenomenon. This indicates the presence of limited porosity in the mineral structure of these adsorbents [46, 56]. Although some authors have linked fluoride adsorption onto natural montmorillonites to rapid sorption rates associated with the short adsorption equilibrium periods of just 20–30 min [22, 37], several natural montmorillonites [36, 54] and Fe(III)-modified montmorillonites [55] appear to have consistent fluoride adsorption equilibrium time intervals in the range of 110–180 min. In the same way, a number of mineral adsorbents including metal-intercalated palygorskites [47] and certain aluminum oxide minerals [39, 44] appear to have equilibrium intervals within the same range of periods. This signifies that these minerals possess structural porosities that are comparable.

As in the case of fluoride adsorption onto calcareous and carbonaceous soil adsorbents, the immobilization of fluoride into adsorbent zeolites [50, 69, 70], hydroxyapatites [60, 63, 64], iron oxide minerals [49] as well as into certain classes of aluminum oxide minerals [41] is characterized by initial rapid phases of adsorption characterized typically by short equilibration intervals of just 10–30 min, which are then followed by prolonged equilibration that could extend to 10–48 h. The final slow phase of equilibration can be ascribed to high structural porosity as in the case of zeolites or to slow valence exchange reaction mechanisms characteristic of fluoride immobilization upon hydroxyapatite, hydr(oxide) aluminum and iron minerals.

### 3.4. Co-existent ions

Natural water systems contain dissolved species across the organic-inorganic chemical continuum. Co-existent ions in water control the adsorption of fluoride by their competitive effect for the sorptive space on the adsorbent soil surfaces and by their influence on the adsorbate flux from the bulk solution to the sorbent surface. Co-ions tend to lower the rates and magnitude of adsorption, but the extent of these influence largely depend on the chemical and geometric dimensions of the ions, relative concentrations and affinities of the individual ions for the adsorbent surface. The influence of interfering ion, however, varies from one soil adsorbent to the other.

The soil adsorbents whose fluoride uptake is most affected by co-existent anions include iron oxide minerals [27–29] and certain carbonaceous mineral adsorbents. The suppression of fluoride immobilization upon ferric oxide minerals in the presence of common anions follows the order:  $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$  [29]. Fluoride adsorption onto zeolites [50], HAps [59, 63, 64], bauxite [39, 40] and calcareous mineral adsorbents [11, 12, 58, 66, 67, 71, 72] is, however, site specific, and it is not normally affected by competing anions in solution. For that reason, the adsorbents are able to sorb relatively high amounts of fluoride independent of co-existing anions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{PO}_4^{3-}$  ions.

## 4. Conclusions

Soil adsorbents that have attracted the highest interest as possible adsorbents for the removal of fluoride from water include: aluminosilicates, iron and aluminum (hydr)oxides, apatites, carbonaceous minerals, calcareous soils and zeolites. It is found that the pH is the main solution factor controlling fluoride adsorption onto soil surface. The other contributing parameters include temperature, time of contact and co-existent ions. The montmorillonite clays, generally, solubilize in low pH media and get poisoned by excess  $\text{OH}^-$  ions in alkaline media. They are generally characterized by small fluoride sorption edge within the neutral pH values. The usual pH for efficient fluoride removal from water using metal-enhanced palygorskite is in the range of 3–2. Fluoride adsorption onto metal-exchanged zeolites and onto synthetic HAps is, however, independent of pH, and high fluoride adsorption occurs in the pH range of 4–10. Aluminum oxide minerals, on the other hand, usually have a narrow sorption edge in the pH range of 5.5–6.5. In the same way, maximum fluoride adsorptions onto most of the calcareous minerals occur within the pH values of 5–6. High fluoride uptakes by hematite occur over a wide range of pH (2–7) but optimum fluoride removal using carbonaceous adsorbents can be achieved at room temperature in the pH range of 4–12.

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