



Equilibrium Studies of Fluoride Adsorption onto a Ferric Poly-mineral from Kenya

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ABSTRACT: African countries along the Great Rift Valley are among areas of the world where excess fluoride in water sources is a major public health problem. In this work, the removal of fluoride (F) from water solutions using a ferric poly-mineral (FPM) from Kenya was therefore studied using batch adsorption experiments. The effect of change in solution pH, temperature, initial concentration of F, mass of FPM, contact time and presence of various competing ions on F adsorption onto FPM was evaluated. Adsorption isotherms were then applied to the adsorption data to characterize and establish the adsorption capacity of the mineral. The adsorption of F onto FPM was found to be a fast process and, at 1000 mg/L initial F concentration at pH 3.32 and 293 K and using 0.2 g/mL adsorbent dosage, over 90% F removal from solution could be achieved in 30 min. Based on Giles system of classification of adsorption isotherms, F adsorption isotherm conformed to L4 Langmuir-type isotherms. This indicated that FPM is composed of a heterogeneous surface consisting of sites which, during adsorption, filled-up with F ions in succession. The adsorption data also correlated to Langmuir and Freundlich models indicating that F adsorption onto FPM was a mixed process involving chemisorption onto surface sites followed by gradual intra-particle penetration of F into mesoporous structure of the mineral. High mean Langmuir adsorption capacity of 10.8 mg/g, indicate that the mineral could be of use as an inexpensive substrate for the removal of F from aqueous streams.

KEYWORDS: Adsorption isotherms; Equilibrium analysis; Ferric poly-mineral; Fluoride adsorption; Water fluoride

Excessive fluoride (F) in water sources and its attendant hazards is a major public health problem in Sub-Saharan Countries along the Great Rift Valley (Steenbergen et al., 2011; Wambu and Muthakia, 2011; Vuhahula et al., 2011; Sajidu et al., 2008). Prolonged intake of excessive F through drinking water causes dental and skeletal fluorosis; it accumulates in bones causing skeletal deformities and 'has chronic effects on kidneys and the nervous system' (Chaturvedi et al., 1990; Wang and Reardon, 2001). The main source of F in natural water sources is solubilization from F-rich rocks (Wambu and Muthakia, 2011). However, wastes from bauxite and feldspar mining, phosphatic fertilizers, ceramics, glass, rubber, electronic and semiconductor industries contain high levels of F and may contribute significantly to F pollution in water sources (Arnesen et al., 1995).

Adsorption is the most popular method for treatment of F polluted water. However, commercial adsorbents which are expensive and require frequent regeneration, limits application of the technology in most developing countries (Haron and Yunus, 2001). Thus, more affordable and easy-to-use defluoridating media is therefore desired. Use of several low-cost adsorbents including: Alum Sludge (Sujana et al., 1998), Fly Ash (Chaturvedi et al., 1990), Charcoals (Bhargava and Killedar, 1992), Biomasses (Jamode et al., 2004), Montmorillonites (Karthikeyan et al., 2005), Attapulgit (Zhang et al., 2009), and Calcite (Min et al., 2009) continue to attract a lot of research interest at the moment. According to Coetzee et al. (2003) iron oxide-based geo-materials are among the most promising low-cost adsorbents for aqueous F.

However it still remains unclear whether the use of a certain ferric poly- mineral (FPM) from Kenya would be effective in the removal of F from aqueous solution.

In the study upon which this paper reports the capacity of FPM to sorb F from aqueous solutions was studied as function of different solution parameters. The Langmuir and the Freundlich equilibrium models were then applied to the adsorption data to characterize and evaluate the F adsorption capacity of the mineral..

METHODS

The adsorbent materials were collected from their natural deposits at Matili in Bungoma County, Kenya. They were dried and ground to pass through 2-mm sieves and dispersed by mechanical treatment to isolate < 1- μ m fractions by sedimentation in doubly de-ionized water (DDW). After sun-drying in air to a constant mass, separate portions of the material were agitated in 0.1 M HCl for selected time lengths (5-240 min). At the end of agitation period they were filtered and dried in an oven at 383 K and preserved in sealed polythene bags for subsequent tests. The chemical elements in treated samples were analyzed using spectrophotometric techniques in form of oxide percentage. For adsorption tests, unless otherwise specified, a known mass of FPM was mixed with 1000 mg/L F solution at 0.2 mg/mL FPM dosage in 100-mL Erlenmeyer flasks. The slurry was then shaken on a reciprocating shaker-bath at 293 K for selected time-length between 5 to 120 min. The supernatant solution was separated by centrifugation and analyzed for residual F using a Tx EDT Model

Equilibrium Studies of Fluoride Adsorption.....

3221 ion selective electrode (Wambu and Muthakia, 2011). The amount and percentage of F adsorbed were calculated according to a formula employed by Wambu et al. (2011).

RESULTS AND DISCUSSION

The results of spectrophotometric analysis indicated that FPM was predominantly an aluminosilicates (68.19%) mineral consisting of 5.89% iron oxyhydroxides, 10.19% combustibles and 2.73 % exchangeable alkalis. The percentage F uptake of acid-treated FPM increased with increasing adsorption time and reached equilibrium in just 30

min (Figure 1). Basing on this adsorption time, F adsorption increased with increasing time of acid activation from 40% for untreated FPM to 70% for 60 min acid-activated FPM. It then remained fairly constant thereon up to 240 min of acid activation. This showed that FPM is stable and could be utilized to treat F contaminated solutions even in strong acid conditions without significant chemical and surface degradation. A 30-min contact time with 0.1 M HCl, which was then employed in all subsequent pretreatment of the material, was found to be adequate for acid-activation of FPM for F adsorption.

Table 1 The Langmuir and Freundlich isothermal constants

Temp (K)	Langmuir			Freundlich		
	q_{max}	b	R^2	K_f	N	R^2
298	10.3	1.10	0.942	4.36	0.37	0.919
313	11.8	1.24	0.981	4.66	0.36	0.929
323	12.7	1.38	0.996	4.73	0.37	0.923
333	7.8	0.84	0.878	3.61	0.39	0.958

At very low pH (1.59), F adsorption increased rapidly with increasing adsorption contact time from just about 20% to 60% when the adsorption contact time was increased from 5 to 15 min (Figure 2). The %F removal then somehow slowed down before another rapid phase to a maximum of about 75% at 60 min. Similar trends could be observed with higher %F adsorptions over the same time interval when using adsorbate solutions at initial pH 3.32. The two-phase phenomenon was, however, not observed at pH 5.24 and 7.68; instead, a lower maximum adsorption percentage range of 70–80% was observed over

similar adsorption periods. Closer examination of adsorption data for 30-min adsorption contact time across different pH values reveals that %F uptake by FPM increased with increasing solution pH from about 65% at pH 1.59 to a peak of 85% at pH 5.24 and then decreased to 70% at pH 7.68. As expected, when adsorption contact time was increased from 30 to 60 min, %F adsorption increased to 90% at pH 3.32 (and 75% at pH 1.59) but suddenly decreased from 70–80% to 65–70% between pH 5.24 and 7.68. Highest F adsorption was recorded at an acidic medium pH~ 3.32 using 60 min contact time.

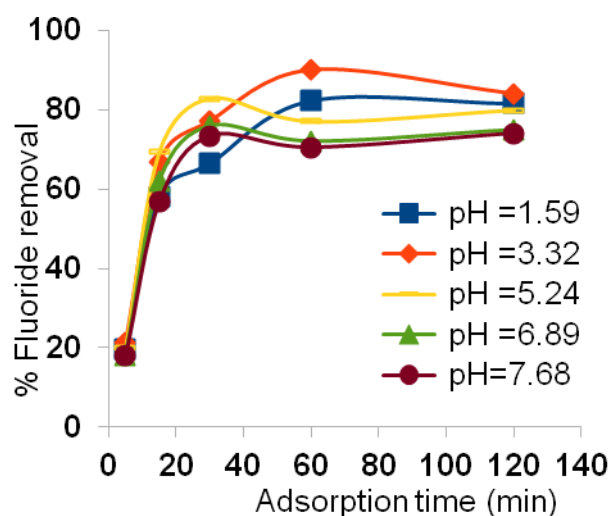


Fig 1 Effect of solution pH on F adsorption onto FPM from 1000 mg/L F solution using 0.2 g/mL adsorbent dosage at 293 K

These results indicate that at pH values less than 3.32, F ions are rapidly adsorbed at exposed sorptive sites in FPM; speedily saturating surface sites in the adsorbent. This is followed by gradual filling of less exposed sites in the adsorbent as the system approaches its maximum capacity at 60 min. Lower F adsorption capacity of FPM at pH 1.59 can be ascribed to competition for sorptive sites by Cl^- ions from HCl that was added during pH adjustments as well as to formation of low affinity molecular HF at low pH values. Thus, as solution pH was increased, concentration of Cl^- ions in solutions decreased because less HCl had been added and increasingly more HF molecules dissociated into more chemically active F. The %F adsorption therefore rapidly

increased with increasing pH to about pH 5 then decreased thereon. It can be assumed that at pH > 5, concentration of OH^- ions in solution sufficiently increase and somehow suppress %F uptake by FPM. It shows that, at pH > 5, OH^- ions from solution adsorb onto FPM surface increasing its surface negative charge and clogging adsorbent mesopores. These increases coulombic repulsions for F by FPM surfaces and lowers surface adsorption potential of FPM for F. The second rapid increase in adsorption after initial 15 min was therefore not observed at pH > 5. Clearly, this indicates that surface and intra-particle diffusion mechanisms govern F adsorption onto FPM at pH < 3.32 but only surface adsorption predominates at pH > 5.

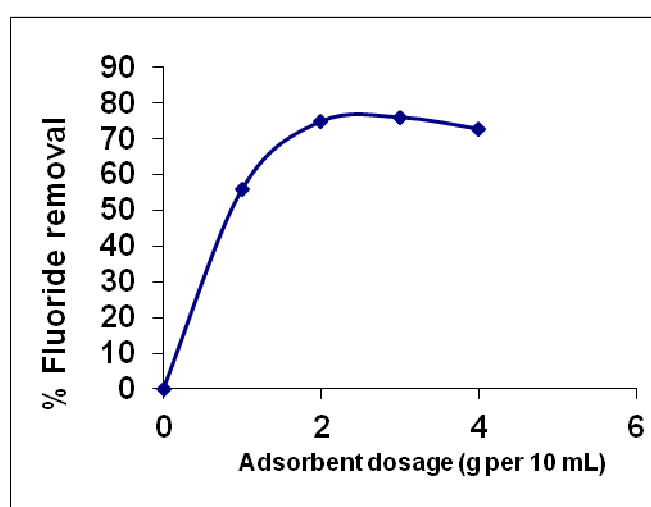


Fig 2 Effect of change in mass of FPM on its adsorption of F from 1000 mg/L F solution at pH 3.32 and 293 K

Figure 3 shows effect of change in mass of FPM on its adsorption of F. The %F adsorption increased steadily with increasing adsorbent mass to 70% at 0.2 g/mL FPM dosage and then remained constant. This shows that above 0.2 g/L adsorbent dosage, F uptake by FPM reaches a limiting value because the adsorbent particles get aggregated making it increasingly difficult for F ions from solution to access free sites in the colloid aggregates of adsorbent. Further increase in mass of FPM did not increase availability of sorptive sites in the system and F uptake FPM remained constant.

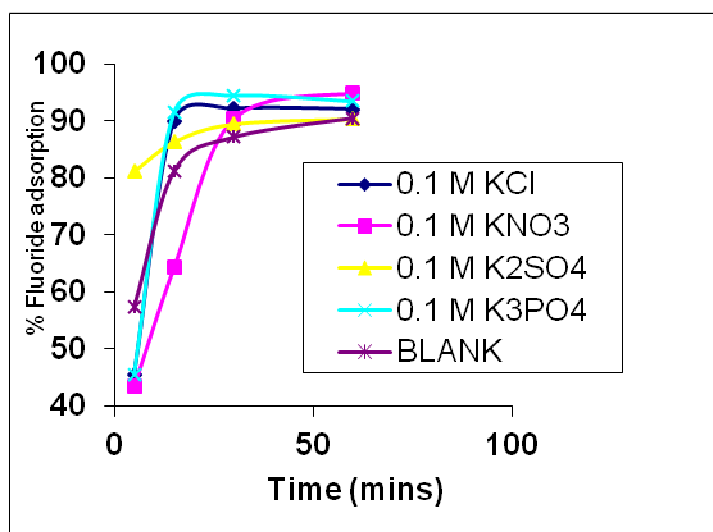


Fig 4 Effect of different anions on adsorption of F onto FPM from a 1000 mg/L F solution at 0.2 g/mL adsorbent dosage and 293 K

The effect of other ions is presented in Figure 4. The anions did not reduce F uptake by FPM. Somewhat, F adsorption increased in presence of potassium salts in solutions. This shows that electronic and geometrical dimensions of F ion favor its adsorption onto FPM over other anions. Additional K^+ counter ions must have adsorbed at FPM surface increasing its potential for F adsorptions. The %F adsorption in presence of the anions decreased with increasing electronegativity of central atoms in oxo-anions: $NO_3^- > PO_4^{3-} > Cl^- > SO_4^{2-}$. It can be assumed that SO_4^{2-} ions with more electronegative sulphur centers

draws electrons from the oxygen atoms more strongly making them poorer Lewis acids than the oxygen atoms in PO_4^{3-} and NO_3^- . The SO_4^{2-} ion therefore has greater mobility in solution because it experiences less viscous drag through solution and through electrical double layer close to FPM surface. More so, the SO_4^{2-} with more electronegative oxide centres and greater overall negative charge than univalent Cl^- has stronger coulombic attraction to positive centres in FPM. The SO_4^{2-} is therefore a better competitor for positive adsorbent surface than the other anions; it therefore tends to reduce F adsorption more strongly.

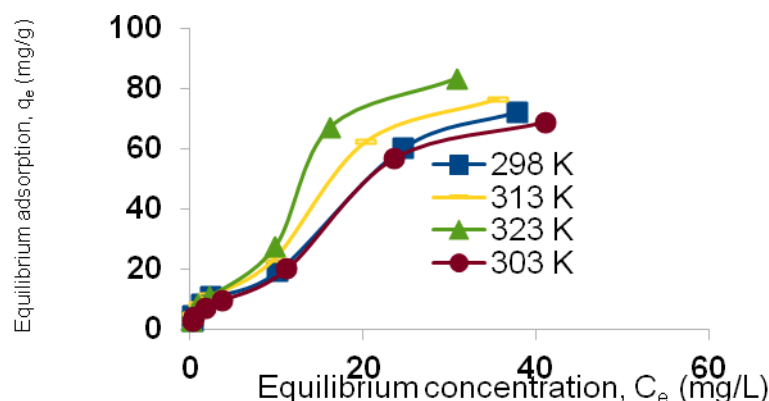
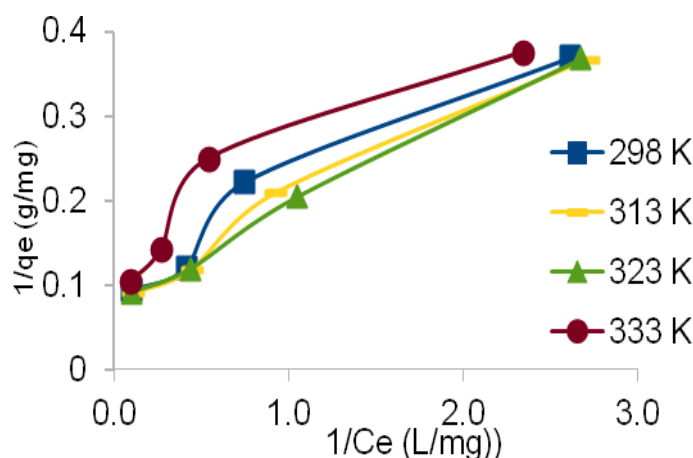
**Fig 5** Adsorption isotherms for F uptake by FPM from 1000 mg/L F solution using 0.2 g/mL adsorbent dosage at 293 K

Figure 5 shows effect of initial F concentration on its adsorption onto FPM. At all concentrations, F adsorption onto FPM increased with increasing temperature from 293 to 323 K and dropped sharply when the equilibrium temperature was raised to 333 K. In all cases the reaction was reversible at low temperatures indicating an endothermic adsorption mechanism. The F adsorption isotherm was an L4 Langmuir plot. This indicates heterogeneity in FPM

sorptive surfaces; presence of two types of sites that fill up successively (Giles et al., 1960). It also shows that F ions experience little competition from similar species in solution for sorptive sites in FPM and that once adsorbed onto FPM F particles do not interact. The initial curvature of the isotherms indicates that as more sites in FPM were filled-up it became increasingly difficult for incoming F particles from bulk solution to find vacant sites.

**Figure 6** Langmuir adsorption isotherms for F adsorption onto FPM at pH 3.32

To further clarify the adsorption equilibrium, F adsorption data was appropriated to Langmuir and

Freundlich isotherms. The Langmuir isotherm was applied in the form:

$$\frac{1}{q_{eq}} = \frac{1}{bq_{max}C_{eq}} + \frac{1}{q_{max}} \quad 1$$

where, q_{eq} is equilibrium adsorption (mg/g) and C_{eq} is equilibrium concentration (mg/L), q_{max} is maximum adsorption capacity and b is a Langmuir constant. The Freundlich isotherm on the other hand was employed in the form:

$$\log q_{eq} = \log K_f + n \log C_{eq} \quad 2$$

where K_f and n are Freundlich constants. Figures 6 and 7 show representative Langmuir and Freundlich plots and corresponding isothermal constants for all experimental temperatures are presented in the Table. The data fitted both models with R^2 values greater than 0.92 although data fit to Langmuir model were somehow better. Simultaneous conformity of adsorption data to Langmuir and Freundlich models

indicates that F sorption onto FPM is mixed adsorption involving chemisorption of adsorbate particles and physical absorption of adsorbate ions in mesoporous phases of adsorbent. It can be seen that the number of adsorption sites tended to increase with increase in temperature showing that chemisorption was the more dominant mechanism. The q_{max} averaged at 10.8 mg/g and values of b indicated higher affinity for F by FPM sites at 323 K as compared to those at other temperatures employed in this study. The Langmuir constant, b , and Freundlich constants, K_f and n , were consistent with effective binding of F particles by FPM. It can be seen that FPM has got a high F sorptive capacity compared to similar low-cost adsorbents including: montmorillonites (1.5–1.9 mg/g) (Karthikeyan et al., 2005), activated carbons (4.6 mg/g) (Alagumuthu et al., 2010) and alumina (7.7 mg/g) (Munavali et al., 2009). Moreover the adsorbent, can be obtained cheaply from its natural resource for easy and safe use for the removal of F from aqueous streams.

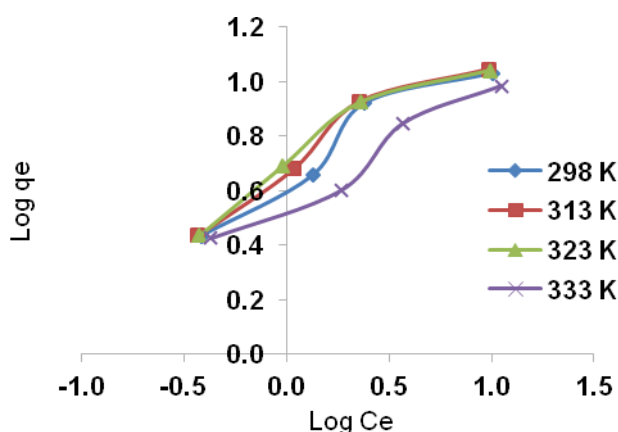


Fig 7 Freundlich adsorption isotherms for F adsorption onto FPM at pH 3.32 K

Conclusions: It has been found that acid treatment of a ferric polymineral (FPM) from Kenya produces highly adsorbent material which could be used for inexpensive removal of fluoride from water. The adsorption process required only 30 min and was controlled by solution temperature, pH and adsorbent dosage. It was however less strongly influenced by other anions in solution. Up to 90% F removal from 1000 mg/L F solution could be achieved at pH 3.32 using 0.2 g/mL adsorbent dosage at 293 K. The adsorption data could be described by Langmuir and Freundlich isotherms and the general adsorption isotherm was an L4 Langmuir type. So, a mixed adsorption mechanism involving surface chemisorption and mesoporous physical absorption of adsorbate has been proposed. The mean Langmuir maximum adsorption capacity was 10.8 mg/g which compared favorably with those of other low-cost F adsorbent. Thus, FPM can be recommended for used as a safe and inexpensive treatment for F

contaminated water because of its robust adsorption characteristics and surface stability

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REFERENCES

- Alagumuthu, G, Veeraputhiran, V, Venkataraman, R (2010). Adsorption isotherms on fluoride removal: Batch techniques. Arch Appl Sci Res 2: 170-185.
- Arnesen, AKM, Abrahamsen, G, Sandvik, G, Krogstad, T (1995). Aluminium-smelters and fluoride

Equilibrium Studies of Fluoride Adsorption.....

pollution of soil and soil solution in Norway. *Sci Total Environ* 163:39–53.

Wang, Y, Reardon, E (2001). Activation and regeneration of a soil sorbent for defluoridation of drinking water. *J Appl Geochem* 16: 531-539.

Bhargava, DS, Killedar, DJ (1992). Fluoride adsorption on fishbone charcoal through a moving media absorber. *Water Res* 26: 781–788.

Chaturvedi, AK, Yadava, KP, Pathak, KC, Singh, VN (1990). Defluoridation of water by adsorption on fly ash. *Water Air Soil Pollut* 49: 51–61.

Coetzee, PP, Coetzee, LL, Puka, R, Mubenga, S (2003). Characterisation of selected South African clays for Defluoridation of natural waters. *Water SA* 29(3): 331-339.

Giles, CH, Macewans, TH, Nakhwa, N, Smith, D (1960). Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J Che Soc* 60: 3973–3993.

Haron, MJ, Yunus, WMZW (2001). Removal of fluoride ion from aqueous solution by a cerium-poly (hydroxamic acid) resin complex. *J Environ Sci Health Part A-Toxic/Hazard Subst Environ Eng* 36: 727–734

Karthikeyan, G, Pius, A, Alagumuthu, G (2005). Fluoride adsorption studies of montmorillonite clay. *Indian J Chem Technol* 12: 263–272.

Min, Y, Takayuki, H, Nobuyuki, H, Haruki, M (1999). Fluoride removal in a fixed bed packed

with granular calcite. *Water Res* 33: 3395–3402.

Munavalli, GR, Patki, VK (2009). A comparative study of defluoridation techniques. *J IPHE, India* 10:35-34.

Sajidu, SMI, Masamba, WRL, Thole, B, Mwatseteza, JF (2008). Groundwater fluoride levels in villages of Southern Malawi and removal studies using bauxite. *Inter J Phys Sci* 3(1):1-11.

Steenbergen, FV, Haimanot, RT, Sidelil, A (2011). High fluoride, modest fluorosis: Investigation in drinking water supply in Halaba (SNNPR, Ethiopia). *J Water Resour Prot* 3: 120-126.

Sujana, MG, Thakur, RS, Rao, SB (1998). Removal of fluoride from aqueous solution using alum sludge. *J Colloid Interface Sci* 206: 94–101.

Vuhahula, EAM, Masalu, JRP, Mabelya, L, Wandwi, WBC (2009). Dental fluorosis in Tanzania Great Rift Valley in relation to fluoride levels in water and in ‘Magadi’ (Trona). *Desalination* 248 (1-3): 610-615.

Wambu, EW, Muthakia, GK (2011). High fluoride water in the Gilgil area of Nakuru County, Kenya. *Fluoride* 44(1): 37–41.

Wambu, EW, Muthakia, GK, wa-Thiong’o, JK, Shiundu, PM (2011). Kinetics and thermodynamics of aqueous Cu(II) adsorption on heat regenerated spent bleaching earth. *Bull Chem Soc Ethiop* 25(2): 1–10.

Zhang, J, Xie, S, Ho, YS J (2009). Removal of fluoride ions from aqueous solution using modified attapulgite as adsorbent. *Hazard Mater* 165: 218–222.