

Water Defluoridation by Adsorption Using Aluminium Modified Chicken Feathers

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Abstract

Sufficient fluoride (F^-) ingestion through food, soil and water is necessary for the development of healthy bones and teeth while excess of it results in dental, skeletal and soft tissue damage. To protect people from fluorosis, it is therefore, important for the F^- to be removed from water. In the current study, F^- removal by adsorption method from aqueous solutions using chicken feathers modified by Al^{3+} was studied using batch experiments. The feathers collected from Kitale slaughter house were ground, weighed, treated and tested for defluoridation. The adsorbent was characterized by FTIR and SEM methods. The effect of F^- levels, adsorbent dosage, contact time, temperature, and pH and agitation rate were also investigated. The results showed that fluoride adsorption increased from around 48.5% to 88.9% with adsorbent mass increase from 0.1 g to 0.8 g. The percentage F^- uptake by the adsorbent then increased to nearly 94.6% when the adsorbent mass was further increased to 1.6 g, but a higher increase in mass resulted in a constant adsorption percentage. Additionally, the percentage removal of F^- increased from 71% at a period of 1 minute to a highest % of 95 after 60 minutes. Furthermore, the % adsorption increased from 66% with agitation rate of 35 rpm to an optimum agitation rate of 300 rpm with % adsorption of 90. Fluoride adsorption increased from 82% to 90% with rise in solution pH of 1 to 5 but dropped beyond pH 7. It was further observed that % adsorption increased from 87-94% between a temperature range of 293-313 K, and decreased between a higher temperature range of 313-353 K. The percentage adsorption removal increased from 76-99 % within the range of initial fluoride concentration of 2.5-40 mg/L, and there after decreased. However, the F^- adsorption data correlated to the Freundlich and Langmuir models and could be classified as C-Type according to Giles classification of isotherms. The pseudo-first and pseudo-second order kinetic models and the Weber and Morris intra particle diffusion model equation were applied onto the adsorbent. The adsorbent could thus be used as an inexpensive adsorbent for the removal of F^- ions from aqueous streams.

Key words: Adsorption, Defluoridation Aluminium modified feathers (AlF)

INTRODUCTION

Adequate fluoride intake is necessary in developing health bones and teeth and for the prevention of dental caries. Excessive fluoride intake, however, leads to dental, skeletal and soft tissue fluorosis (Piddennavar & Krishnappa, 2013). Since fluorosis is an irreversible condition and has no cure; prevention is the only remedy for this menace. Today fluorosis remains an important clinical and public health problem in many parts of the world. The global prevalence of fluorosis is reported to be about 32% (Kumar & Gopal, 2000). People get exposed to excessive fluoride through food, soil and water. However, drinking water with excessive fluoride remains the primary pathway of human exposure to hazardous levels of fluoride from the environment. Due to high toxicity of fluoride to mankind, there is an urgent need to treat fluoride-contaminated water to make it safe for human consumption. According to World Health Organization

(WHO), the maximum acceptable fluoride concentration in drinking water is 1.5 mg/L (Puthenveedu *et al.*, 2012). Providing water, with optimal fluoride concentration is, therefore one of the ways by which the future generation can be protected against the disease.

Defluoridation is the conventional and widely tested method for supplying safe water to the fluorosis affected communities. The main defluoridation techniques are based on; ion-exchange, precipitation, distillation, electro-chemical defluoridation, reverse osmosis and adsorption (Piddennavar & Krishnappa, 2013). The use of precipitation, distillation, ion exchange, membrane technologies, electro dialysis, and reverse osmosis to fluoride removal from water is limited by high costs and energy requirements and complexities of the techniques (Wambu *et al.*, 2011). Due to more simple design of adsorption unit, low sludge production and low investment costs, the adsorption process appears to have more advantages compared to other methods of removal of pollutants from water and wastewater. Its versatility and simplicity make adsorption to be widely accepted protocol to remove pollutants from water. The most common adsorbents employed include activated carbon, bone char, alumina, silica, some bio-sorbents and a number of natural and synthetic resins (Piddennavar & Krishnappa, 2013). Application of adsorption techniques to domestic defluoridation, based on activated alumina, was launched by UNICEF in rural India (Mariappan & Vasudevan, 2011). However, it was found that fluoride adsorption on alumina occurs only at specific pH range and requires pre-and frequent activation of alumina which makes the technique expensive (Piddennavar & Krishnappa, 2013; Mariappan & Vasudevan, 2011). Defluoridation by bone char is a process which involves the ion exchange and adsorption between fluoride in the solution and carbonate of the apatite comprising bone char. However, the bone char harbours bacteria and becomes unhygienic and without a regular fluoride analysis it is not possible to determine whether the material is exhausted and the fluoride uptake is ceased (Larsen & Pearce, 2002). Chicken feathers, in specific, are some of the natural adsorbents which could be used for water treatment. They constitute 4 to 6 % weight of mature chickens and are as a result, a byproduct provided by the commercial poultry sector in huge volumes. The use of chicken feathers to detoxify industrial waste water and drinking water is a very affordable practice. In addition, their high tensile strength, water insolubility, and durability over a wide range of pH, and structural resilience are the advantages of chicken feathers over similar sorbents (Rosa *et al.*, 2008). Currently chicken feathers can be used as low-cost adsorbents because they are easily available and safe. The effect of pH, F concentration, and time of contact, adsorbent dosage and temperature was studied and Freundlich, Langmuir and Weber-Morris isotherms used to validate the adsorption equilibrium.

Experimental

Preparation of the materials

Chicken feathers were collected from a chicken slaughterhouse in Kitale town and transported to the laboratory where they were washed several times with deionized water and sun-dried for 24 h. They were then ground to powder in a mill and chemically modified with Al^{3+} . This was done by adding 100 g of the ground feathers to 500 mL of 1000 mg/L of each of the Al^{3+} ions separately, transferring the solution to a mechanical shaker and shaking at 400 rpm for 12 hours. After which the filtration was done, then the chemically modified adsorbent was washed with distilled water and oven dried at 105°C before being used for fluoride uptake.

Adsorbent characterization

The infrared spectra of solid chemically modified adsorbents were obtained over the wavelength region of 400-4000 cm^{-1} . Infrared spectra of adsorbents laden with fluoride ions were obtained to check for the interactions between functional groups in the adsorbents and fluoride ions. Samples of modified adsorbents were analyzed using a JEOL JMS-6400 scanning electron microscope/Bruker X FLASH 4010 SEM microanalysis detector, in order to observe surface morphology of the samples. In all the experiments analytical grade reagents were used.

Batch experiments

Batch experiments were carried out to optimize fluoride ion adsorption parameters on raw and modified feathers. The batch experiments were carried out in triplicates in 250 mL stoppered bottles by agitating a pre-weighed amount of the adsorbent with 50 mL of fluoride solutions of known concentration. The adsorbents were separated by centrifugation. The concentration of fluoride remaining in the filtrate was analyzed potentiometrically using a fluoride ion-selective electrode.

After equilibration the final concentration, C , (mg/L), of the adsorbate solution was determined and the amount of adsorption, q_e (mg/g), calculated from the mass balance equation as:

$$q_e = \frac{v(C_i - C_e)}{m1000}$$

1

where, v is the volume of the solution (mL) and m is the mass of the adsorbent (g) used. The percentage adsorption can then be obtained as:

$$\% \text{ adsorption} = \left(1 - \frac{C_{eq}}{C_i}\right) \times 100$$

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RESULTS AND DISCUSSION

Chemical characterization of adsorbents

The nature of interactions between reactive surface sites or functional groups in the adsorbent and fluoride ions in water led to their infrared spectra and SEM showing surface morphology. The results for the FT-IR and SEM analyses are depicted in Figures 1 and 2, respectively.

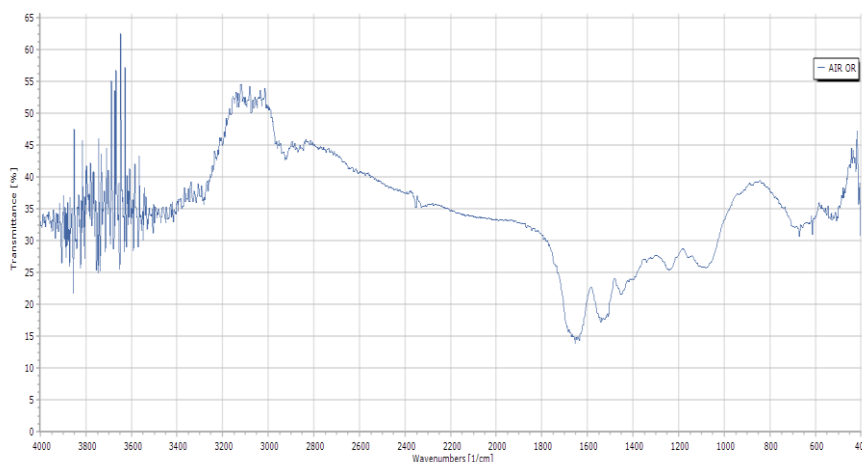


Figure 1: Aluminium modified Feather FTIR spectra before fluoride adsorption

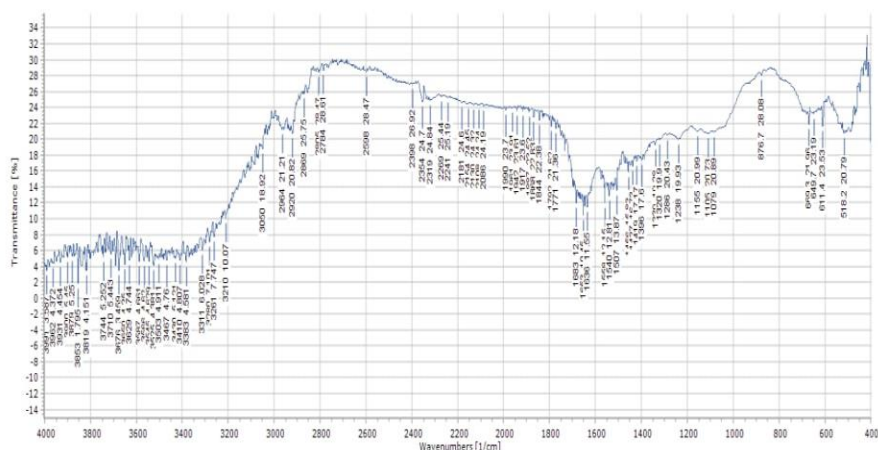


Figure 1: Aluminum modified Feathers FTIR spectra after fluoride adsorption

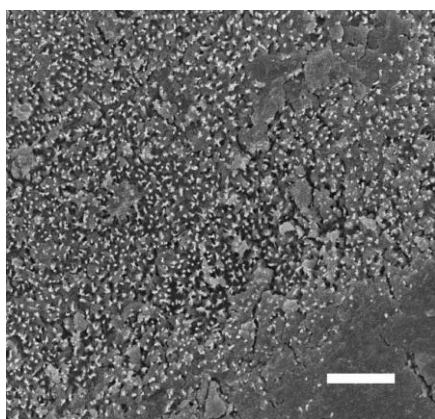


Figure 2(a) SEM image for AIF

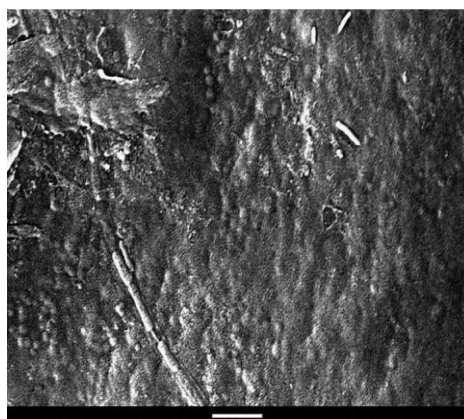


Figure 2 (b) SEM image for AIF after fluoride adsorption

From Figures 1 (a) and (b), the observed changes in peaks and intensities indicated that interactions leading to the adsorption actually occurred between the AIF and fluoride ions. The peaks in Figure 1 (a) generally shifted slightly to lower absorption values in Figure 1 (b). Intensity changes giving the peaks were noticeably much high implying the interactions and hence adsorption taking place. According to Egwuatu *et al.*, (2014), the chicken feather IR spectrum has shown a range of absorption peaks that demonstrate the chicken feather's complex existence. One of the keys to understanding the mechanism of the fluoride ion binding to chicken feathers is the functional groups. Table 1 displays the absorbance peaks and their corresponding intensities for the specified groups.

Table 1: IR data for chicken feathers

Wave number (cm^{-1})	Assigned functional group
3,379.1	OH, NH
2,919.4	C-C
1,541.08	C=C
1,031.35	PO_4^{3-} band
870.73	CO_3^{2-} band
561.79	Ca^{2+} band

The presence of NH, C=O and S=O groups on the surface of chicken feathers makes it an active sight for adsorption.

According to Figure 2 the SEM images after defluoridation show morphological defects, irregular shape and coarse surfaces. This may be as a result of fluoride adsorption by the adsorbents. This may be as a result of fluoride adsorption by the adsorbent. When Khosa *et al.*, (2013), utilized chicken feathers as adsorbents for arsenic, the SEM results have showed that the untreated feathers have long shafts and barbs and a smooth surface while the surface of modified feathers shows shiny patches leading to a completely amorphous structure where the shafts and barbs of the feathers have disappeared and the original structure of the feather could not be identified.

Effect of change in mass of adsorbent

To study the effect of an increase in the dose of adsorbent on removal of fluoride, experiments were conducted by adding varying doses of 0.5, 1.5, 2.5, 3, 6 and 10 g to 50 mL of a test solution containing initial fluoride concentration of 10 ppm and shaking at 400 rpm for 120 minutes at room temperature. The percentage F^- removal was determined and plotted against the mass of the adsorbent and the results presented in Figure 3.

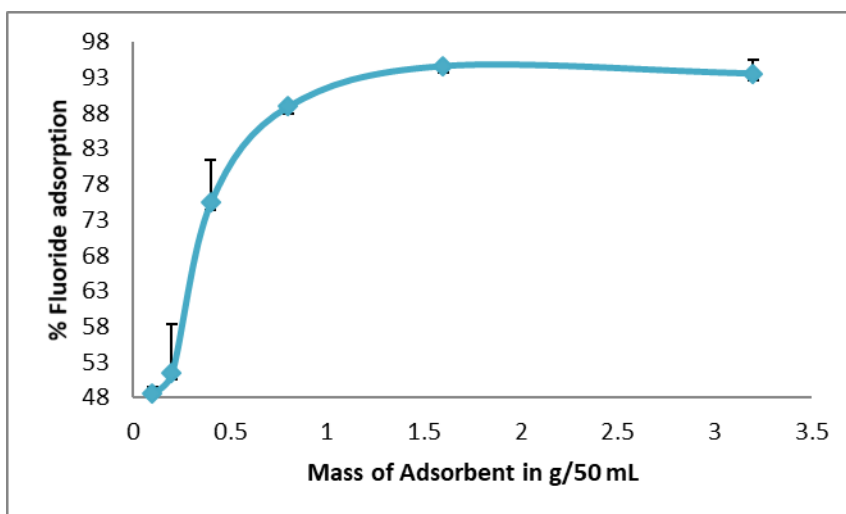


Figure 3: Effect of adsorbent dosage on fluoride adsorption onto the AIF

[Experimental conditions: using 50 mL of the adsorbate solution containing 10 ppm of F being shaken at 400 rpm for 120 min at 298 K].

The fluoride adsorption by Al modified feathers increased from around 48.5% to 88.9% when the mass of the Al modified feathers was increased from 0.1 g to 0.8 g. The percentage of fluoride uptake by Al modified feathers then further increased to about 94.6% when the adsorbent mass was further increased to 1.6 g. When the mass was increased the percentage, adsorption remained almost constant. This rise in F⁻ removal efficiency with increasing adsorbent dosage was ascribed to increased availability of adsorptive surface in the solution. Further increase in doses did not result in the considerable increase in defluoridation. This is due to the overlapping of the active sites at higher concentrations of the adsorbents, thus reducing the net surface area (Piyush *et al.*, 2012), and also due to non-adsorbability of fluoride ion as a result of sorbent-sorbate interaction (Puthenveedu *et al.*, 2012). The highest fluoride adsorption percentage by Al feathers was observed at a mass of 1.6 g of adsorbent. Adsorbent doses of 1.6 g/mL were, therefore, adopted in all subsequent fluoride uptake tests using feathers.

Effect of change in adsorption contact time

The effect of increase in time on the removal of fluoride was studied by adding optimized mass of adsorbent to 50 mL of 10 ppm fluoride and shaking at 400 rpm for varying times of 1, 2, 4, 8, 15, 30, 60 and 120 minutes at room temperature. The adsorption of fluoride ion by adsorbent also depends on the interactions of functional groups between the solution and the surface of adsorbent. Adsorptions can be assumed to be complete when equilibrium is achieved between the solute of solution and the adsorbent. However, specific time is needed to maintain the equilibrium interactions to ensure that the adsorption process is complete (Kavita *et al.*, 2016). The effect of change in contact time unto the adsorption of fluoride by the Al feathers is shown in Figure 4.

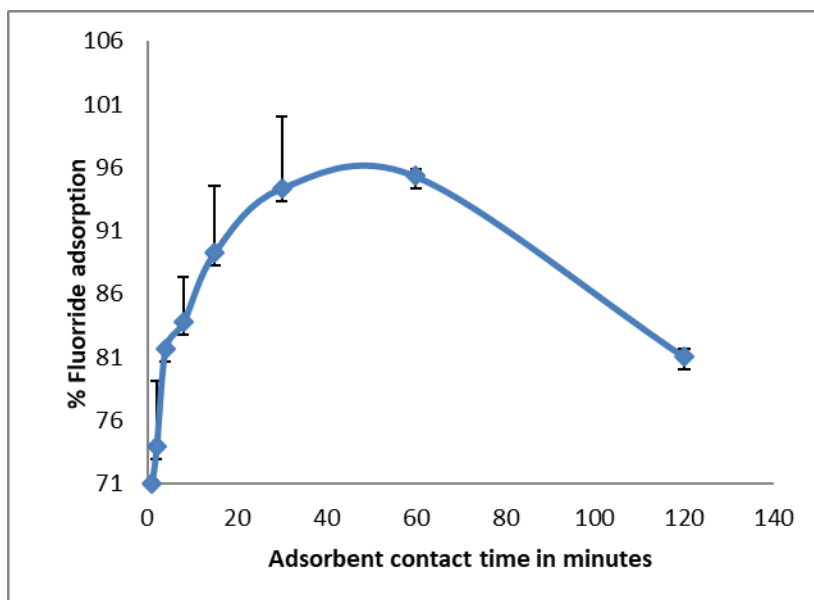


Figure 4: Effect of contact time on fluoride adsorption onto the AlF

[Experimental conditions: using 50 mL of the adsorbate solution containing 10 ppm of F 1.6 g mass, being shaken at 400 rpm at 298 K].

The percentage adsorption of fluoride onto the feathers increased from 71% when time was 1 minute to a highest % of 95 when time was 60 minutes beyond this time adsorption percentage decreased sharply as illustrated by Figure 4. This time was adopted as optimum time for the subsequent batch experiments. Studies have shown that the rate of removal of pollutants from water using biomaterials is higher at the beginning of the remediation process. This is because as interaction progresses reaction sites become exhausted resulting in lower uptake rate of the pollutant (Mbugua *et al.*, 2014).

The effect of change of agitation rate on adsorption

Using optimized mass, time and 50 mL of 10 ppm fluoride the agitation rate was optimized by varying rates of 35, 70, 200, 300, 350 and 400 rpm at room temperature. How the agitation rate affected the adsorption of fluoride onto the adsorbent is shown by Figure 5.

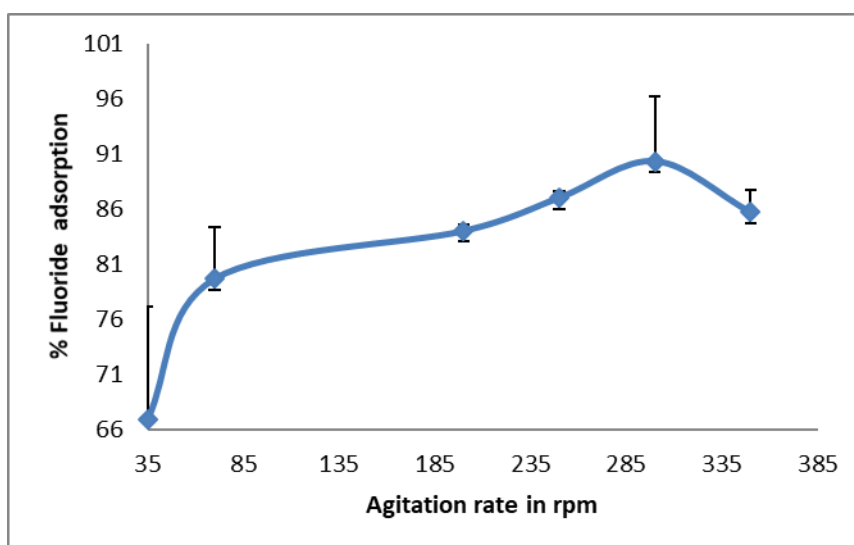


Figure 5: Effect of agitation rate on fluoride adsorption onto the AIF

[Experimental conditions: using 50 mL of the adsorbate solution containing 10 ppm of F 1.6 g mass, 60 minutes at 298 K].

From Figure 5 the percentage adsorption increased steadily from 66-90% with agitation rate of 35-300 rpm, thereafter a decrease in the adsorption percentage was observed as the agitation rate increased. The optimum agitation rate for Al feathers was 300 rpm with % adsorption of 90. This agrees with what others found (Puthenveedu *et al.*, 2012). Decrease in adsorption could be due to increased turbulence and as a consequence, decreased boundary layer thickness around the adsorbent particles as a result of increasing the degree of mixing. Increase in adsorption capacity with increase in agitation rate could be explained in terms of the reduction of boundary layer thickness around the adsorbent particles (Hanafiah *et al.*, 2009). Therefore, with increasing stirring rate, the concentrations of fluoride ions near the adsorbent surface could be increased. A higher stirring rate also encouraged a better mass transfer of

fluoride ions from bulk solution to the surface of the adsorbent and shortened the adsorption equilibrium time.

Effect of change in fluoride solution pH

The effect of pH on fluoride adsorption onto the adsorbent was studied at pH values of 1-13. The adsorbate pH was adjusted by addition of small amounts of 1 M NaOH or 1 M HCl using 50- μ L pipettes. The percentage of fluoride adsorption was plotted as a function of initial solution pH and the results presented in Figure 6.

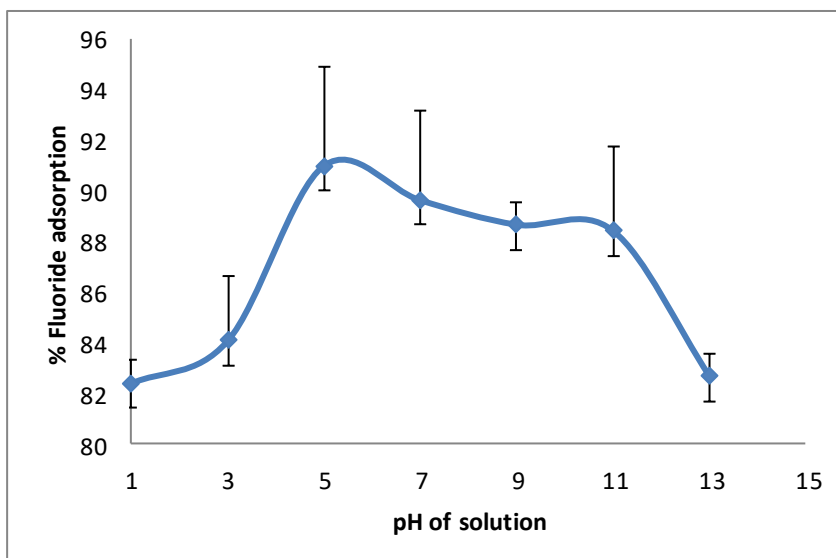


Figure 6: Effect of solution pH on fluoride adsorption onto the AlF

[Experimental conditions: using 50 mL of the adsorbate solution containing 10 ppm of F 1.6 g mass, 60 minutes, 300 rpm at 298 K].

Fluoride adsorption onto Al feathers increased from 82% to 90% when the solution pH was increased from 1 to 5 and it dropped beyond pH 7. This shows that highest fluoride uptake by feathers occurred at pH 5.

It has been found that removal efficiency of adsorbent increases with increased pH values (Keerthi, 2015). Since the protonated surface is accountable for anions adsorption, the maximum fluoride adsorption for many adsorbents occurs at acidic pH (Goswami & Purkait, 2012) and decreases at higher pH values.

Effect of change in solution temperature

The effect of change in solution temperature on fluoride adsorption onto Al feathers was carried out at different temperatures between 288 K - 353 K and the results are shown in Figure 7.

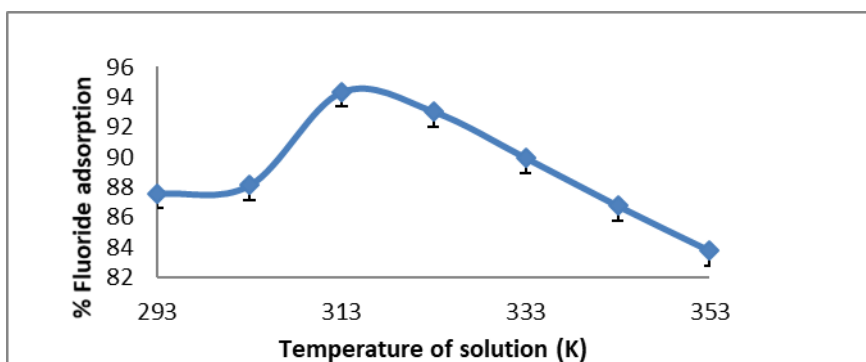


Figure 7: Effect of temperature on fluoride adsorption onto the AlF

[Experimental conditions: using 50 mL of the adsorbate solution containing 10 ppm of F^- 1.6 g mass, 60 minutes, 300 rpm, pH 5].

From Figure 7 the adsorption of fluoride increased from 87-94% between temperature of 293-313 K, the adsorption decreased thereafter between temperature of 313-353 K. Temperature plays a double role in the fluoride sorption process. Temperature can impact the physical binding processes of fluoride to a sorbent. However, temperature also can have a direct impact on the physical properties of a sorbent, if thermally treated prior to exposure, so that sorption capacities can be significantly altered. Most sorption studies are conducted at room temperature in laboratory settings. As temperature increased, sorption was shown to be less favoured most likely due to increased deprotonation or hydroxylation of the surface causing more negatively charged sorbent surfaces. This is an important observation to note when attempting to apply defluoridation methods on 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 (Kavita *et al.*, 2016). The current results, therefore, showed that fluoride adsorption onto the adsorbent is typically an exothermic process as also postulated elsewhere in the literature (Sujana *et al.*, 2009).

Effect of adsorbate concentration

The effect of change in fluoride concentration on its removal from water using the adsorbent was studied under conditions of 1.6 g/mL batch dosage, time of 60 minutes, agitation rate of 300 rpm, pH of 5 and constant temperature 313 K and the results presented in Figures 8.

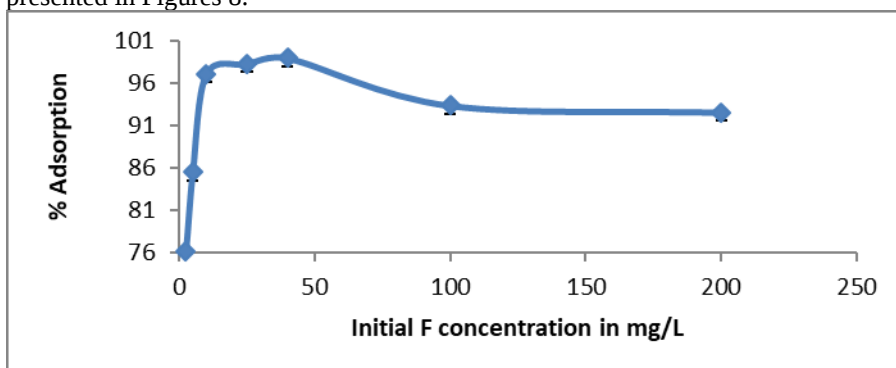
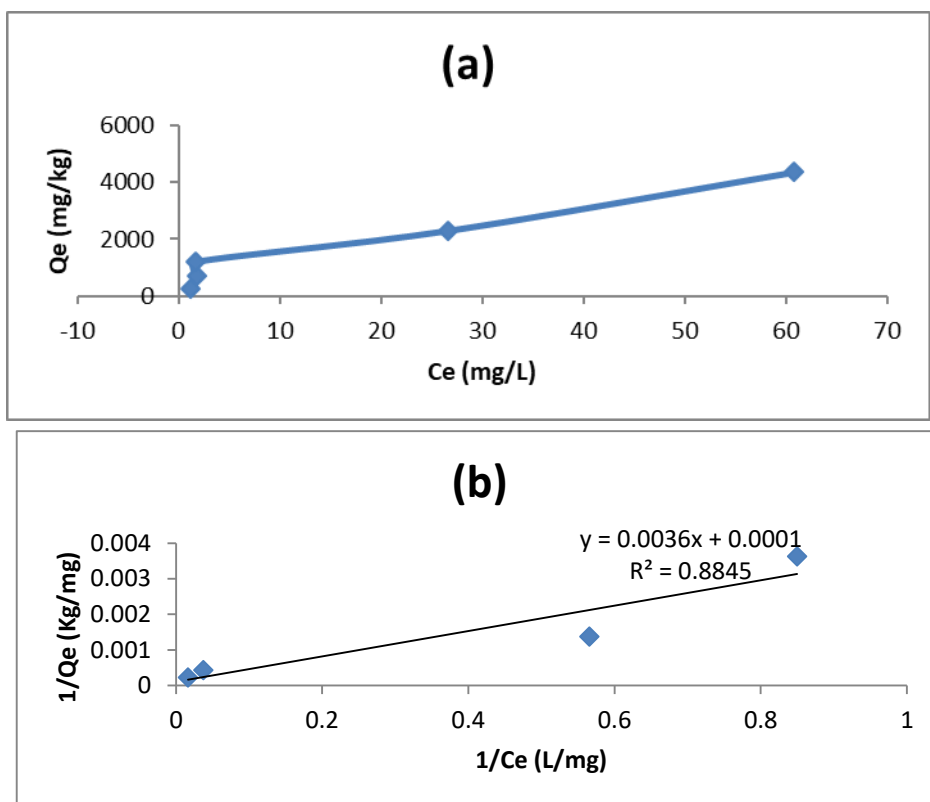


Figure 8: Effect of change in initial adsorbate concentration on fluoride adsorption onto Al feathers

Fluoride removal efficiency decreased with increasing initial fluoride concentration for a constant adsorbent dose and contact time. The decrease in removal efficiency at higher initial fluoride concentrations is due to the saturation of the active sites of the adsorbent. However, the total capacity of the adsorbents increased when the initial fluoride concentration was increased. This can be attributed to the utilization of the less accessible or energetically less active sites because of increase in diffusivity and activity of fluoride ion upon increasing initial fluoride concentration. The interiors of the porous adsorbents contained more sites than exteriors. However, the sites present on the interior surface of a pore may not be as easily available as the sites on the exterior surface because of the resistance to the pore diffusion (Kefyalew *et al.*, 2012). The results from Figure 8 indicate that the percentage removal for feathers increased between 2.5-40 mg/L initial fluoride concentration where the adsorption percentage ranged from 76-99 %, there after the adsorption decreased.

Equilibrium Analysis

Adsorption isotherms are useful in describing how the adsorbate particles interact with adsorbent sites at equilibrium and they are relevant in optimization of adsorption protocol. The Langmuir and the Freundlich isotherms are perhaps the most satisfactory models for describing the removal of adsorbates from aqueous systems (Wambu, 2015). The Giles, Langmuir and the Freundlich Isotherms were applied in this study and the results shown in Figure 9 and the Langmuir and Freundlich isotherm constants for the adsorption of fluoride onto the adsorbent shown in Tables 1 and 2, respectively.



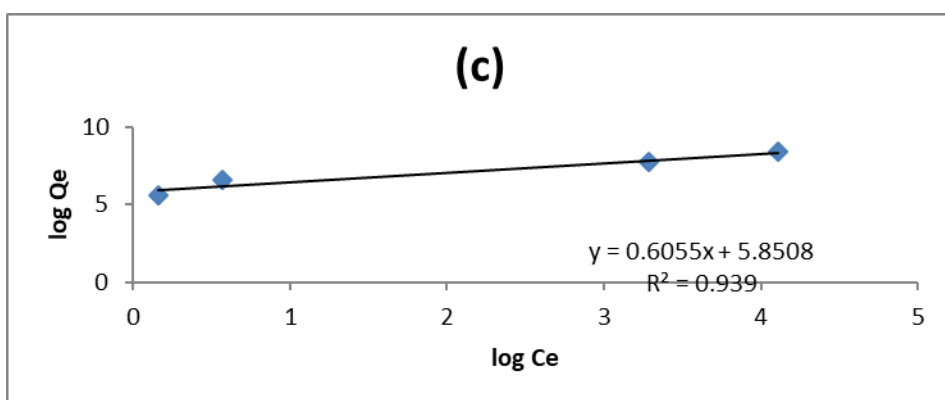


Figure 9: Equilibrium isotherm plots onto the AlF (a) Giles, (b) Langmuir and (c) Freundlich.

According to Figure 9 (a) the Al feathers showed a similarity with the C isotherm classification by Giles. The feature common to these systems is a substrate which is microporous and a solute which on general chemical considerations is expected to have higher affinity for the substrate than has the solvent. A linear isotherm is therefore consistent with conditions in which the number of sites (not necessarily of equal energy) remains constant throughout the whole range of solute concentrations up to saturation of the substrate. This means that the surface available for adsorption expands proportionally with y , the amount of solute adsorbed. The equilibrium data for fluoride adsorption onto the adsorbent were fitted by the Langmuir and Freundlich isotherms with R^2 values of 0.8845 and 0.939, respectively. The best fit of equilibrium data in the Langmuir isotherm expression predicted the monolayer coverage of fluoride ions onto the adsorbents (Uddin *et al.*, 2007). Therefore, the results suggest that a monolayer of fluoride ions is adsorbed on homogeneous adsorption sites on the surface of the adsorbents (Mourabet *et al.*, 2017). The values of the Langmuir constants, k_l and b , indicated efficient fluoride binding onto the adsorbent, while for Freundlich the value of the constant n (adsorption intensity) was less than unity, indicating favourable adsorption. The higher value of k (347.5123) indicated rate of adsorbate removal was high.

Table 2: Langmuir and Freundlich isotherm constants for the adsorption of fluoride onto the adsorbent

	pH	Temperature (K)	K_l (mg/Kg)	b	R
Langmuir	5	313	285.7143	0.00000035	0.8845
Freundlich	pH	Temperature(K)	K_f	N	R
	5	313	347.5123	1.651528	0.939

Adsorption kinetics

Fluoride adsorption onto surfaces consist of the transfer of adsorbate fluoride particles from the bulk adsorbate solution to the surface of the adsorbent. The adsorbate particles then interact with reactive sites in the adsorbent surface or penetrate into the inner adsorbent sites in the crystalline lattice of the soil adsorbents (Wambu, 2015). The pseudo-first order kinetic model, pseudo-second order kinetic model and the Weber and Morris intra particle diffusion model equation were applied onto the adsorbent. This was done to test the influence of external diffusions on fluoride adsorption onto the adsorbents, to investigate the nature of interactions between fluoride particles and the adsorbent sites and to assess existence of intraparticle diffusion of fluoride into inner pores of the adsorbents. The linear plots for the laws were constructed and the derived kinetics constants presented in Figure 10 and in Tables 3,4 and 5, respectively.

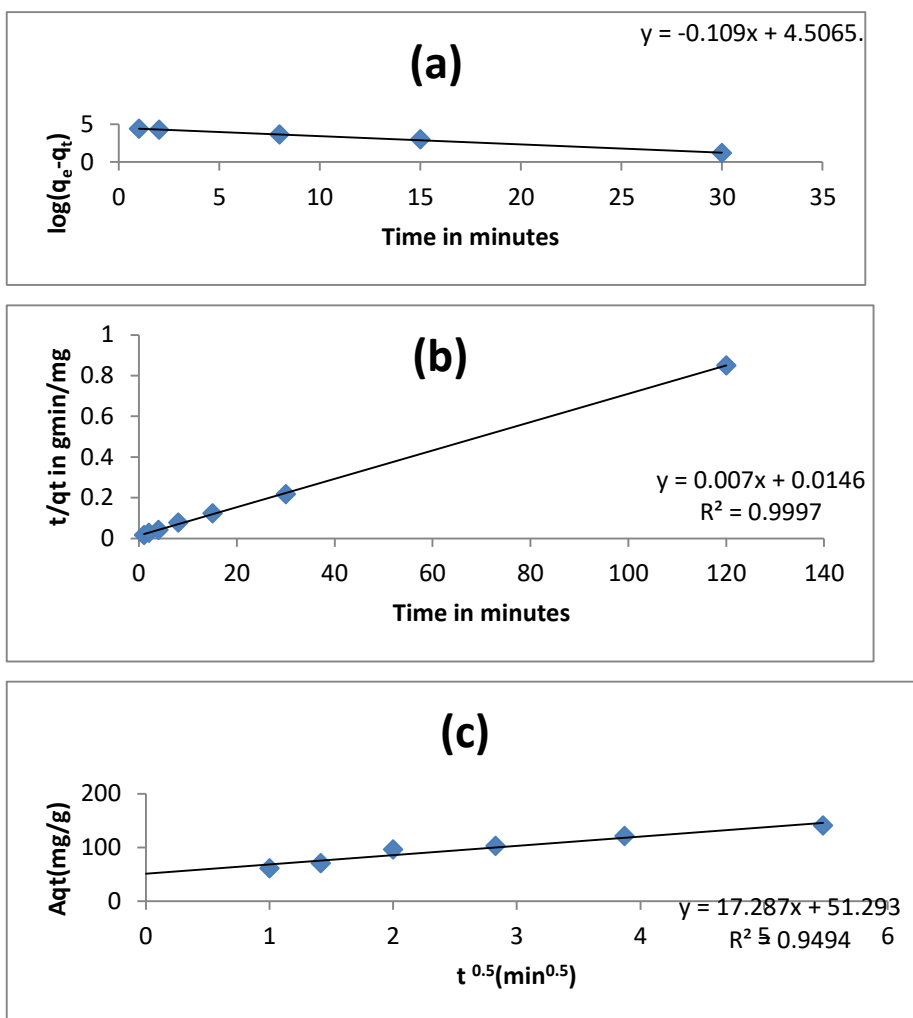


Figure 10: Time profile for fluoride adsorption onto adsorbents

Showing (a) Pseudo-first order, (b) Pseudo-second order and (c) Weber- Morris intraparticle diffusion plot.

According to Figure 10 (a), the plots were found linear with good correlation coefficient (0.9972) indicating the applicability of pseudo first-order model in this study. The correlation coefficient (R^2) values for pseudo second-order adsorption model had a higher value, that is, 0.9997. Comparatively, in this case, the R^2 value was higher than that of pseudo first-order model. This indicates that the adsorption kinetics of fluoride onto Al feathers can be better described by pseudo second order model. A similar phenomenon has been observed by others for the adsorption of fluoride on various adsorbent (Tej & Majumder, 2016). This showed that the rate of fluoride adsorption onto the adsorbent was controlled more strongly by surface reactions between the adsorbent sites and adsorbate fluoride particles than by external transfer processes.

According to the Weber Morris model, the plot of uptake, q_t , versus the square root of time ($t^{0.5}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate-controlling step (Yakout & Elsherif, 2010). For this study from Figure 10 (c), the plots did not pass through the origin therefore there was some level of boundary layer control hence the intra-particle diffusion is not the only rate-limiting step. The linear plots show that nearly 50% of fluoride was rapidly taken up by adsorbent. This is attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surfaces. The fluoride adsorption by adsorbent may be governed by the initial intra-particle transport of fluoride controlled by surface diffusion process.

Table 3: Kinetics constants for Pseudo-first order, Pseudo-second order and Weber and Morris Intra-particle Diffusion Model fluoride adsorption onto the adsorbent

	$K_{1,ads}(\text{min}^{-1})$	$q_e(\text{mg/Kg})$	R^2	
Pseudo-first order	2.412	32099.63	0.9972	
	$h_o=k_{2,ads} q_e^2$ (mg/g/min)	$k_{2,ads}$ (g/mg/min)	$q_e(\text{mg/g})$	R^2
Pseudo-second order	68.49315	0.47945	142.8571	0.9997
	$k_p(\text{mg/Kg/min}^2)$	C	R^2	
Weber and Morris Intra-particle Diffusion	17.287	51.293	0.9494	

Conditions: T (K): 303; C_o (mg/L): 1000; pH: 7; M (g/100 mL): 293-40].

CONCLUSION

From the FTIR analysis, the observed changes in peaks and intensities showed that interactions leading to the adsorption actually occurred between the adsorbent and fluoride ions. FTIR studies on fluoride removal by the adsorbent showed the involvement and the participation of the surface sites and potential functional groups in the adsorption. From the SEM analysis the images showed morphological defects, irregular shape and coarse surfaces. Chemical modification by Al^{3+} on the chicken feathers improved their fluoride adsorption capacity up to 95 %. Fluoride adsorption capacities of the adsorbent were strongly controlled by solution parameters including the pH, temperature, adsorbent mass, contact time and agitation time. Fluoride

adsorption equilibrium data for the adsorbents were fitted by the Giles, the Langmuir and the Freundlich isotherms. The adsorbent, showed a similarity with the C isotherm classification by Giles. Adsorption kinetics of fluoride onto Al feathers can be better described by pseudo second order model. Fluoride adsorption onto the adsorbent described by Weber-Moris intraparticle diffusion model, controlled fluoride adsorption onto the adsorbent. Aluminium modified chicken feathers are promising low cost adsorbent that could be used for water defluoridation adsorption.

REFERENCES

- Egwuatu, C. I., Umedum, N. I., Anarado, C.J.O. and Eboatu, A.N. (2014). Chicken feathers as a sequestrant for lead ions in aqueous solution, *International Journal of modern Analytical and Separation Science*, 3 (1): 51-66.
- Goswami, A. and Purkait, M.K. (2012). The defluoridation of water by acidic alumina. *Chemical Engineering Research and Design*, 90 (12): 2316–2324.
- Hanafiah, M., Zakaria, H. and Wan N.W.S. (2009). Preparation, characterization, and adsorption behavior of Cu (II) ions on to alkali-treated weed (*Imperata cylindrica*) leaf powder. *Water Air Soil Pollut*, 201(1–4):43–53.
- Kavita, P.; Sarita, S.; Ashok, S. and Sanjay, V. (2016). Defluoridation of contaminated water by using low cost adsorbents: A review. *International Journal of Advanced Science and Research* 1 (6): 28-32.
- Keerthi, B. G. (2015). Adsorption on fluoride removal by using batch techniques. *Proceeding of NCRIET-2015 & Indian J.Sci.Res.* 12(1): 209-213.
- Kefyalew, G., Feleke, Z., Bernd, H. and Negussie, M. (2012). Fluoride removal by adsorption on thermally treated lateritic soils. *Chemical Society of Ethiopia* 26(3): 361-372.
- Khosa, A.M., Wu, J. and Ullah, A. (2013). Chemical modification, characterization, and application of chicken feathers as novel biosorbents. *Royal society of chemistry*, 3: 20800-20810.
- Kumar, S. and Gopal, K. (2000). A Review on Fluorosis and its Preventive Strategies. *Indian J. Environmental Protection* 20 (6):430-6.
- Larsen, M.J. and Pearce, E.I.F. (2002). Defluoridation of Drinking Water by Boiling with Brushite and Calcite. *Caries Research* 36:341-346.
- Mariappan, P. and Vasudevan, T. (2011). Domestic defluoridation techniques and sector approach for fluorosis mitigation. Pages 1-11. Available from: URL: www.twadboard.gov.in.
- Mbugua, G., Mbuvi, H. and Muthengia, J. (2014). Rice husk ash derived zeolite blended with water hyacinth ash for enhanced adsorption of cadmium ions. *Current World Environment*, 9: 280-286.
- Mourabet, M., El Rhilassi, A., El Boujaady, H., Bennani-Ziatni, M. and Taitai, A. (2017). Use of response surface methodology for optimization of fluoride adsorption in an aqueous solution by Brushite. *Arabian Journal of Chemistry*, 10: S3292–S3302.
- Piddennavar, R. and Krishnappa, P. (2013). Review on Defluoridation Techniques of Water. The *International Journal of Engineering and Science*, 2 (3):86-94.
- Puthenveedu, S., Pillai, H., Chonattu, J. and Tharayil, M. (2012). Defluoridation of water using biosorbents. *Natural science*, 4 (4): 245-251.
- Piyush, K. P., Madhurima, P. and Rekha, S. (2012). Defluoridation of Water by a Biomass: *Tinosporacordifolia*. *Journal of Environmental Protection*, 3: 610-616.
- Rosa, G., Reynel-Avila, H. E., Bonilla-Petriciolet, A., Cano-Rodríguez, I., Velasco-Santos, C. and Martínez-Hernández, A. L. (2008). Recycling Poultry Feathers for Pb Removal from Wastewater: Kinetic and Equilibrium Studies. *World Academy of Science, Engineering and Technology*, 47.
- Sujana, M.G., Pradhan, H.K. and Anand, S. (2009). Studies on sorption of some geomaterials for fluoride removal from aqueous solutions. 1. *Hazard. Mater*, 161: 120-5.
- Tej, P. S. and Majumder, C.B. (2016). Comparing fluoride removal kinetics of adsorption process from aqueous solution by biosorbents. Department of Chemical Engineering, IIT Roorkee, Roorkee 247: 667, Uttarakhand, India.
- Uddin, M. T., Islam, M. S. and Abedin, M. Z. (2007). Adsorption of phenol from aqueous solution by water hyacinth ash. *ARPJ Journal of Engineering and Applied Sciences*, 2:2.
- Wambu, E.W., Onindo, C.O.; Willis J. A. and Muthakia, G.K. (2011). Fluoride Adsorption onto Acid-Treated Diatomaceous Mineral from Kenya. *Materials Sciences and Applications* 2: 1654-1660.
- Wambu, E.W. (2015). Fluoride levels in water sources of Gilgil area in Kenya. Defluoridation using locally available geomaterials, PHD. Thesis, Kenyatta University.
- Yakout, S. M. and Elsherif, E. (2010). Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons. *Carbon Science and Technology* 1 (2010): 144 – 153.