

**RESEARCH ARTICLE**

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## **Adsorption of Fluoride from Water by Use of Powdered Tilapia Fish Scales**

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### **Abstract**

*Ingestion of adequate fluoride ( $F^-$ ) necessary for healthy bones and teeth is realized through food, soil and water while its excess leads to dental, skeletal and soft tissue damage. Defluoridation is one of the conventional techniques used to protect against fluorosis. In the present study fluoride adsorption from water was done using fish scales collected from Eldoret. These materials were washed, dried, ground, weighed, treated and tested for fluoride removal in water and characterized by FTIR and SEM methods. The effect of  $F^-$  concentration, adsorbent dosage, contact time, temperature, and pH and agitation rate were also investigated. The results show that the % adsorption of  $F^-$  on to the powdered fish scales increased from 95% to 99% with corresponding adsorbent mass of 0.5 g/mL and 3 g/mL and a further increase in mass resulted in a constant % adsorption. Additionally, % removal of  $F^-$  initially increased from 96.7% and attained the highest % adsorption of 98.4 after 1 hour. Furthermore, % adsorption increased from 94.7 with agitation rate of 35 rpm to an optimum agitation rate of 400 rpm with % adsorption of 96. Moreover, fluoride adsorption increased from 94.1% to 96% with increased solution pH of 1 to 7 and then dropped beyond pH 9. Percentage adsorption increased from 95.5-96.4 between a temperature range of 288-313 K, and decreased there after between temperature of 323-353 K. The  $F^-$  removal increased from 82.6% to 99% between the initial fluoride concentration of 1-10 mg/L, after which the % adsorption remained constant. 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 be used as a low-cost adsorbent for adsorption of  $F^-$  ions from aqueous media.*

**Keywords:** Defluoridation, Adsorption

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### **INTRODUCTION**

Water is an essential natural resource for the preservation of life and the ecosystem, which we have thought to be a totally adequate supply and often taken for granted (Kumar *et al.*, 2019). However, one of the main factors on which the suitability of water for commercial, domestic or agricultural purposes depends is the chemical composition of the surface or

subsurface (Adhikari *et al.*, 1989). For the prevention of dental caries, small amounts of fluoride exposure have been found beneficial. For example, the presence of fluoride in the atmosphere, air, land and water is primarily due to certain natural and human activities (Singh *et al.*, 2018).

Disorders such as fluorosis, arthritis, hip fractures, infertility, osteoporosis and polydipsia are caused by the ingestion of

water containing  $\geq 1.5$  mg / L fluoride. In addition, it damages the teeth and skeleton and excessive fluoride exposure can also contribute to structural changes of the DNA (Ahamad *et al.*, 2019). When fluorine reacts with water as an element, it is slightly basic, and this is how fluoride moves between water, soil and rocks naturally (Alfredo *et al.*, 2014). In order to avoid health risks, there is also a need to decrease the fluoride content in water using different removal techniques.

The popular and commonly established process for providing clean water to the affected regions with fluorosis is defluoridation. Ion exchange, precipitation, distillation, electrochemical defluoridation, reverse osmosis and adsorption are the major techniques for fluoride removal (Piddennavar & Krishnappa, 2013). Particularly in comparison to several other fluoride removal techniques based on initial costs, versatility and due to its simple design, and convenience of operation and maintenance processes, adsorption has been found among the most effective fluoride removal technologies in drinking water (Kavita *et al.*, 2016). The appropriate solution to water defluoridation could include the use of low-cost adsorbents and other improved materials that are responsive to local needs (Waheed & Waghmare, 2009). The most common adsorbents employed include activated carbon, bone char, aluminium oxide, silicon dioxide, some adsorbents and several of natural and synthetic organic polymers (Piddennavar & Krishnappa, 2013). Consequently, as a low-cost adsorbent for water defluoridation, powdered tilapia fish scales were used because they are easily available and considered waste materials from the sites from which they were collected.

## MATERIALS AND METHODS

### Chemicals

Analytical grade reagents and chemicals were used throughout the tests. The reagents were obtained from Aldrich chemical Company and supplied by Kobian Laboratory, Nairobi, Kenya. A stock fluoride solution of  $50.0$  mg F L<sup>-1</sup> was prepared by dissolving  $110.5$  mg of reagent grade sodium fluoride in  $1.0$  L of glass-distilled water and a test fluoride solution of  $10$  mg F L<sup>-1</sup> was prepared fresh from stock fluoride solution by appropriate dilution.

### Equipment

Samples of the adsorbent 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. The pH of the solutions was measured using a Hanna Instruments pH-211-microprocessor pH meter. The fluoride concentration was measured using Tx EDT Model 3221 direct fluoride ISE by addition of appropriate volume of TiSAB II (Wambu, 2015). For ISE meter calibration, standard solutions containing  $0.1$ ,  $1.0$ ,  $2.0$ ,  $2.5$ ,  $7.0$ , and  $10.0$  mg/L fluoride prepared by serial dilution of a  $1000$  mg/L fluoride stock solution with doubly de-ionized water (DDW) were employed. Phase separation during adsorption was done using a centrifuge (model U8V2A SER NO V 200559 and centurion 6000 series, London, Britain). The samples were analyzed in a Bruker Tensor 27 FTIR spectrophotometer for determination of functional groups.

### Preparation of the Materials

Fifty kilograms of tilapia fish scales were obtained from Eldoret town fish market, packed in polythene bags and transported to the laboratory where they were stored. They were washed several times with doubly distilled water and sun-dried for two days (Gikunju *et al.*, 1995). The dried scales were ground into fine powder in a mill Yanchieng Jiangsu China, model S11WP.

### Adsorbent Characterization

The infrared spectra of solid raw, chemically modified and combined adsorbents were obtained over the

wavelength region of 400-4000  $\text{cm}^{-1}$ . 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 raw, modified and combined 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.

### Batch Experiments

To optimize fluoride ion adsorption parameters on raw, modified and combined adsorbents, batch experiments were performed. The batch tests were carried out by agitating a pre-weighed volume of the adsorbent with 50 mL of fluoride solutions of known concentration in 250 mL stopper bottles. By centrifugation, the adsorbents were isolated. The fluoride concentration that remains 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:

$$q_e = \frac{v(C_i - C_f)}{m \cdot 1000} \quad 1$$

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:

$$\% \text{ adsorption} = \left(1 - \frac{C_f}{C_i}\right) \times 100 \quad 2$$

## RESULTS AND DISCUSSION

### Chemical Characterization of Adsorbents

To understand the nature of interactions that occurred between the reactive surface sites in the adsorbents and fluoride ions in water, infrared spectra of adsorbents laden with fluoride ions were obtained to check for the interactions between functional groups in the adsorbents and fluoride ions. SEM was done in order to observe surface morphology of the samples. The results for the FT-IR and SEM analyses are depicted in Figure 1 and 2, respectively.



Figure 1(a): Powdered fish scales FTIR spectra.

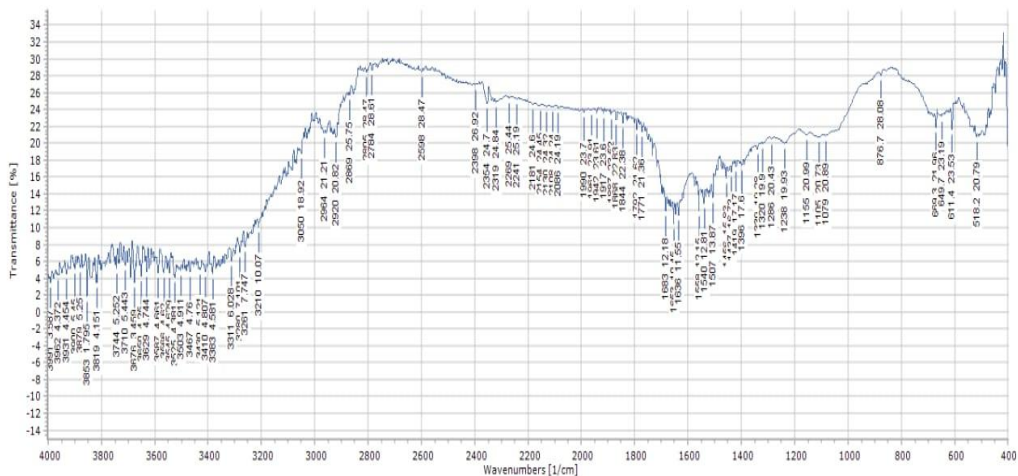


Figure 1(b): Powdered fish scales FTIR spectra after fluoride adsorption.

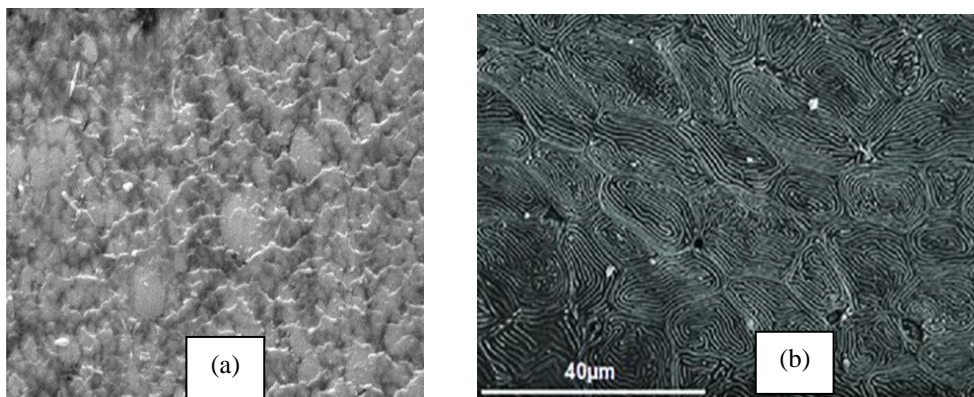


Figure 2: (a) SEM image for powder fish scales; (b) SEM image for powdered fish scales after fluoride adsorption.

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 higher implying the interactions and hence adsorption taking place.

Several findings on fluoride adsorption by various adsorbents have shown that surface sites and specific functional groups, in particular the hydroxyl group, are involved and directly engaged in adsorption (Xu *et al.*, 2017; Mohaptra *et al.*, 2011).

Furthermore, it was noted by Mondal *et al.* (2015) that fluoride reacts on the surface aluminum-impregnated coconut fiber surface with the OH and NH groups

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.

**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.

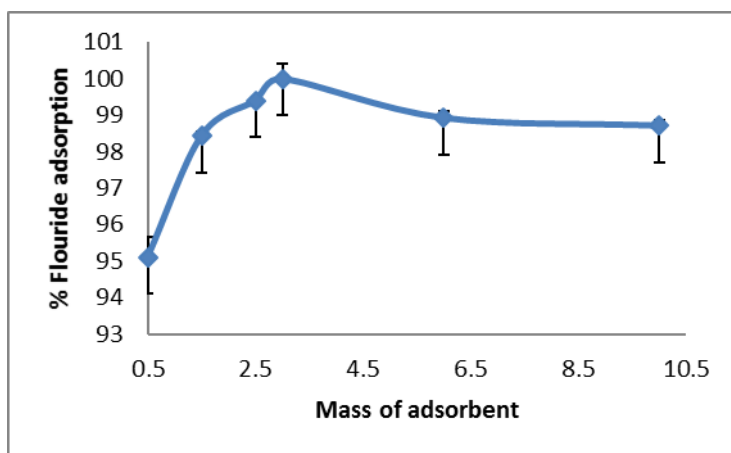


Figure 3: Effect of adsorbent dosage using 50 mL of the adsorbate solution containing 10 ppm of  $F^-$  being shaken at 400 rpm for 120 minutes at 298 K.

With a mass of 0.5 g/mL, the percentage adsorption of fluoride to the powdered fish scales increased from 95 percent to 99 percent with a mass of 3 g/mL. The rise in the sorptive surface area and the presence of more active adsorption sites is majorly attributable to this trend. A small drop in percentage removal with an increase in the adsorbent dose, is also shown in Figure 3, which may be attributable to the development of aggregates amongst particles of the powdered scale and the convergence of binding sites at high concentrations of adsorbent, minimizing the effective active site area (Alhussein *et al.*, 2019).

#### Effect of Change in Adsorption Contact Time

The influence of time variations on fluoride removal was investigated by applying

optimized adsorbent mass to 50 mL of 10 ppm fluoride and shaking at 400 rpm for 1, 2, 4, 8, 15, 30, 60 and 120 minutes at room temperature at different periods. The sorption process of fluoride ions by adsorbents often relies on the interactions between the solution and the surface of the adsorbent functional groups. When equilibrium is reached between the solute of the solution and the adsorbent, it can be inferred that adsorptions are successful. Nevertheless, to ensure that the adsorption process has been completed, specific time is required to maintain equilibrium interactions (Kavita *et al.*, 2016). The effect of change in contact time unto the adsorption of fluoride by the powdered fish scales is shown in Figure 4.

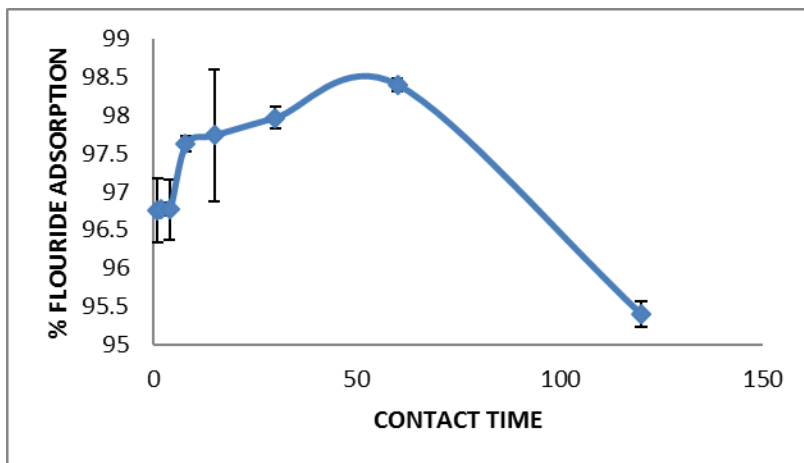


Figure 4: Effect of contact time using 50 mL of the adsorbate solution containing 10 ppm of F, 3 g mass, being shaken at 400 rpm at 298 K.

The percentage adsorption of flouride unto the the adsorbent increased form 96.7% when time was 1 minute to a highest % of 98.4 when time was 60 minutes as illustrated by Figure 4. This time was adopted as optimum time for the subsequent batch experiments. This observation may be as a result of adsorption sites having been exhausted. A significant factor in the fluoride removal is the contact time between adsorbing material and aqueous solution. Studies have shown that at the start of the remediation process, the rate of removal of contaminants from water using biomaterials was higher (Waheed &

Waghmare, 2009). It is because reaction sites are depleted as activity progresses resulting in lower pollutant absorption rate.

**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. The effect of agitation rate increases up to a certain level after which the rate of sorption remains constant (Puthenveedu *et al.*, 2012). How the agitation rate affected the adsorption of flouride unto the adsorbent is shown by Figure 5.

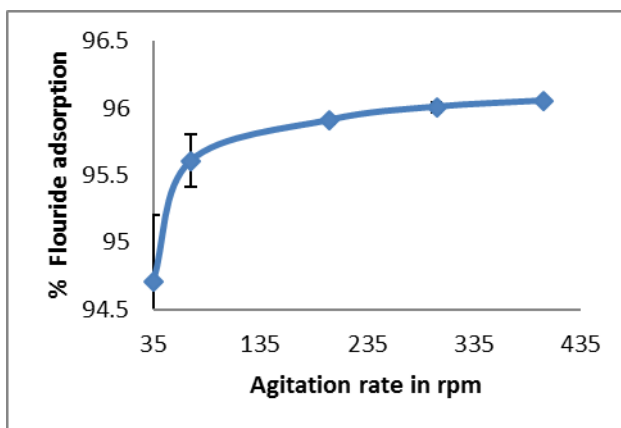


Figure 5: Effect of agitation rate using 50 mL of the adsorbate solution containing 10 ppm of F 3 g mass, 60 minutes at 298 K.

From Figure 5, the effect of agitation rate on adsorption had values of 95-96% with agitation rate between 35-435 rpm, initially percentage adsorption increased steadily then remained constant. Agitation rate increased the % adsorption. The optimum agitation rate for powdered fish scales was 400 rpm with a % adsorption of 96.05%. This agrees with information reported in literature (Hugo *et al.*, 2013). Reduction of the thickness of the boundary layer around the adsorbent particles as a result of stirring or agitation increases adsorption efficacy. Hence the concentrations of fluoride ions near the adsorbent surface may be increased

with increasing stirring intensity. Also, increased agitation results to enhanced mass transfer of fluoride ions from bulk solution to the adsorbent surface reducing the adsorption equilibrium time (Hanafiah *et al.*, 2009).

#### Effect of Change in Fluoride Solution pH

The impact of pH on the adsorption of fluoride to the adsorbent was examined at pH values between 1-13. The pH of the adsorbate was changed using 50- $\mu$ L pipettes by adding a few drops of 1 M NaOH or 1 M HCl. The percentage of fluoride adsorption was plotted against initial solution pH and the results shown in Figure 6.

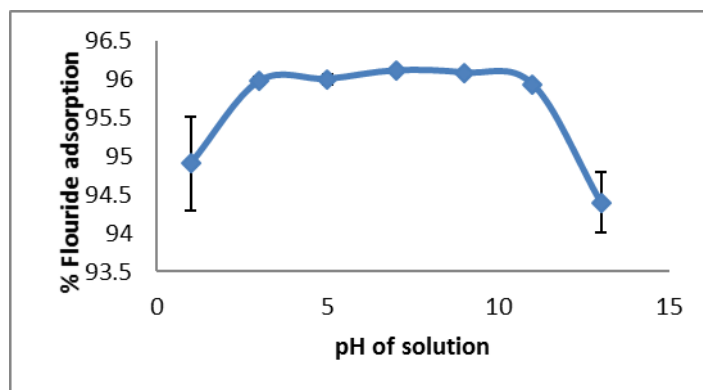


Figure 6: Effect of solution pH using 50 mL of the adsorbate solution containing 10 ppm of F<sup>-</sup> 3 g mass, 60 minutes, 400 rpm at 298 K.

Fluoride adsorption by fish scales at different pH values presented in Figure 6 showed that the adsorption percentage increased from about 94.5% to 96%, which, however, remained almost constant between pH 4-11 and dropped beyond pH values of 10. The optimum pH of the adsorbent solution was 7. Fluoride adsorption depends on pH. The efficacy of adsorbent removal improves with a rise in pH value (Keerthi, 2015). Because the protonated surface is responsible for the adsorption of anions, the highest adsorption of fluoride happens at acidic pH for several adsorbents (Goswami & Purkait, 2012) and reduces at higher pH values.

#### Effect of Change in Solution Temperature

Temperature may affect the physical binding processes of fluoride to a sorbent and, if thermally treated prior to exposure, could also have a significant effect on the physical characteristics of a sorbent, such that sorption capacities may be dramatically changed. The majority of sorption experiments are performed at room temperature in laboratory environments. As temperature rose, most likely due to increased deprotonation or surface hydroxylation triggering increasingly negatively charged sorbent surfaces, sorption was seen to be less preferred. When trying to implement defluoridation procedures on site in hot climates, this is a significant point to remember, for sorption



capacities obtained under room temperature conditions can be greater than in the field as a result of increased temperatures (Kavita *et al.*, 2016). The influence of the change in solution temperature on the adsorption of

fluoride on the scales of powdered fish was assessed at different temperatures between 288 K-353 K and the results are shown in Figure 7.

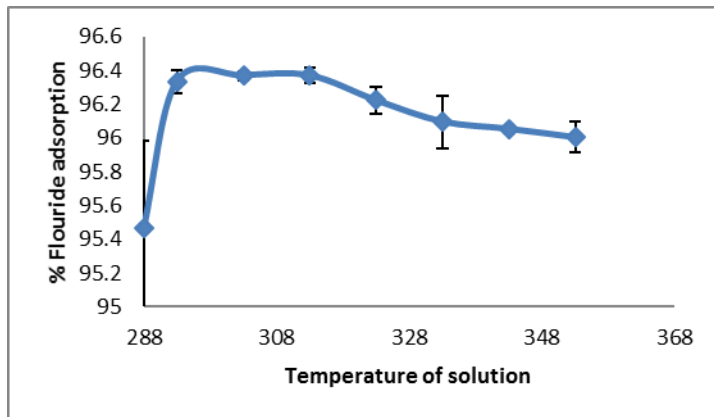


Figure 7: Effect of temperature using 50 mL of the adsorbate solution containing 10 ppm of F<sup>-</sup> 3 g mass, 60 minutes, 400 rpm, pH 7.

The effect of thermal change from Figure 7 revealed that adsorption was between 95-96% across the different temperatures within the range, the optimum temperature being 303 K with adsorption of 96.37%. The current results, therefore, showed that fluoride adsorption onto fish scales was 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 3 g/mL batch dosage, time of 60 minutes, agitation rate of 400 rpm, pH of 7 and constant temperature 303 K and the results presented in Figures 8.

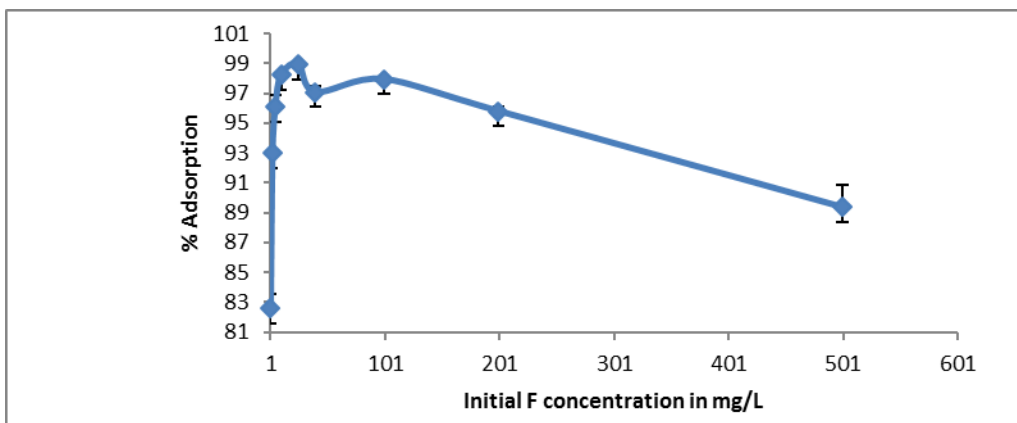


Figure 8: Effect of change in initial adsorbate concentration on fluoride adsorption onto powdered fish scales.



With rising initial fluoride concentration for a constant adsorbent dosage and contact time, fluoride removal percentage declined. At higher initial fluoride concentrations, the drop in percentage removal is attributable to the exhaustion of the adsorbent's active sites. Even so, when the initial fluoride concentration was raised, the overall potential of the adsorbents increased. This could be due to the use of less available or less active sites due to a rise in fluoride ion diffusivity and activity after a rise in initial fluoride concentration. The porous adsorbents' interiors comprise more sites than the external ones. Nevertheless, the sites on the inner surface of a pore may not be as readily accessible as the sites on the exterior surface due to resistance to the pore diffusion (Kefyalew *et al.*, 2012). As per

Figure 8, at 25 mg/L initial fluoride concentration, adsorption increased to 98 percent and then decreased.

**Equilibrium Analysis**

Adsorption isotherms are helpful in explaining how the adsorbate particles interact at equilibrium with adsorbent sites and are important to adsorption protocol optimization. Probably the most appropriate models for specifying the extraction of adsorbates from aqueous systems are the Langmuir and Freundlich isotherms (Wambu, 2015). The Giles, Langmuir and Freundlich Isotherms were applied in this study and the results shown in Figure 9 and Langmuir and Freundlich isotherm constants for the adsorption of fluoride onto the adsorbent are shown in Tables 1 and 2, respectively.

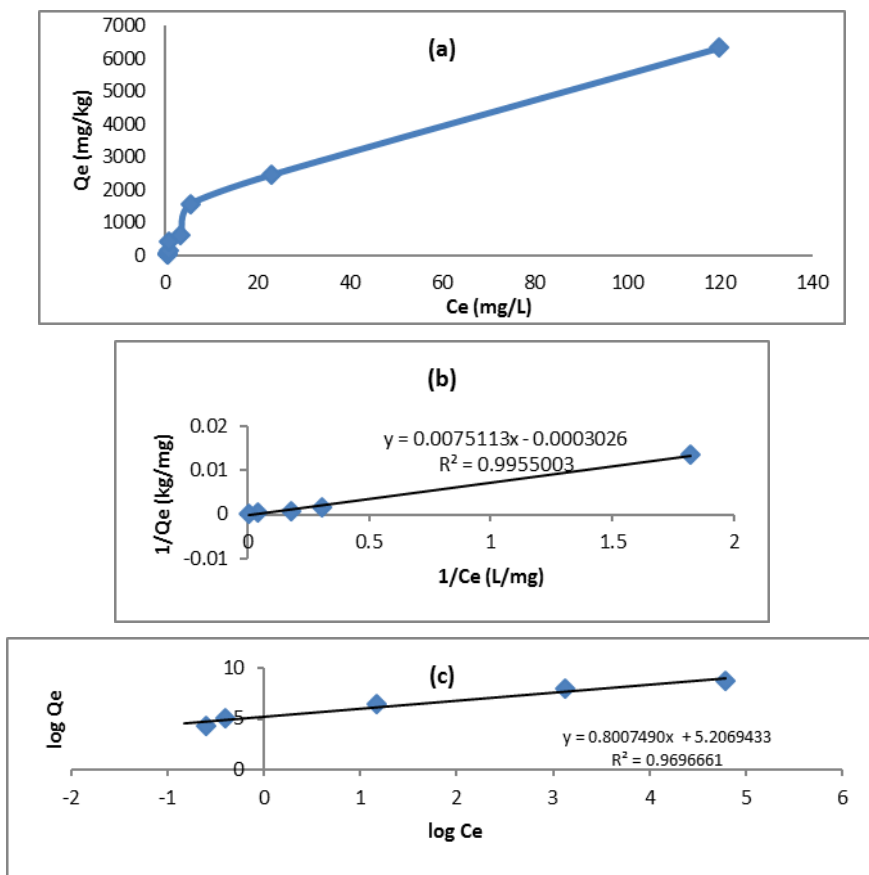


Figure 9: Equilibrium isotherm plots onto the powdered fish scales - (a) Giles, (b) (Langmuir and (c) Freundlich.

The adsorbent showed a correlation with the description of C isotherms by Giles from Figure 9. The key pattern of these systems is a microporous substrate and a solute that is supposed to have greater affinity for the substrate than the solvent for general chemical considerations (Hinz, 2001). Consequently, a linear isotherm is compatible with the constraints under which the number of sites (not necessarily equal in energy) stays unchanged over the entire spectrum of concentrations of the solute until the substrate is exhausted. This implies that the available surface for adsorption

increases proportionally with y, the quantity of adsorbed solute (Hayat et al., 2016). The equilibrium data for fluoride adsorption onto the adsorbent were fitted by the Langmuir and Freundlich isotherms with R<sup>2</sup> values of 0.9955 and 0.9696, respectively. The monolayer coverage of fluoride ions on the adsorbent was predicted by the best fit of equilibrium data in the Langmuir isotherm expression (Uddin et al., 2007). The findings therefore imply that on the surface of the adsorbent, a monolayer of fluoride ions was adsorbed at homogeneous adsorption sites (Mourabet et al., 2017).

Table 1: Langmuir Isotherm Constants for the Adsorption of Fluoride onto the Adsorbents

Adsorbent	pH	Temperature (K)	k <sub>l</sub> (mg/kg)	b	R
Fish scales	7	323	133.1327	0.00000229	0.995503

Table 2: Freundlich Isotherm Constants for the adsorption of fluoride onto the adsorbents

Adsorbent	pH	Temperarure (K)	k <sub>f</sub>	n	R
Fish scales	7	323	133.1327	0.00000229	0.969666

From Tables 1 and 2 the values of the Langmuir constants, k<sub>l</sub> 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 (133.1327) indicated the rate of adsorbate removal was high.

**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 adsorbent (Wambu, 2015). The psueudo-first and pseudo-second order kinetic models 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.

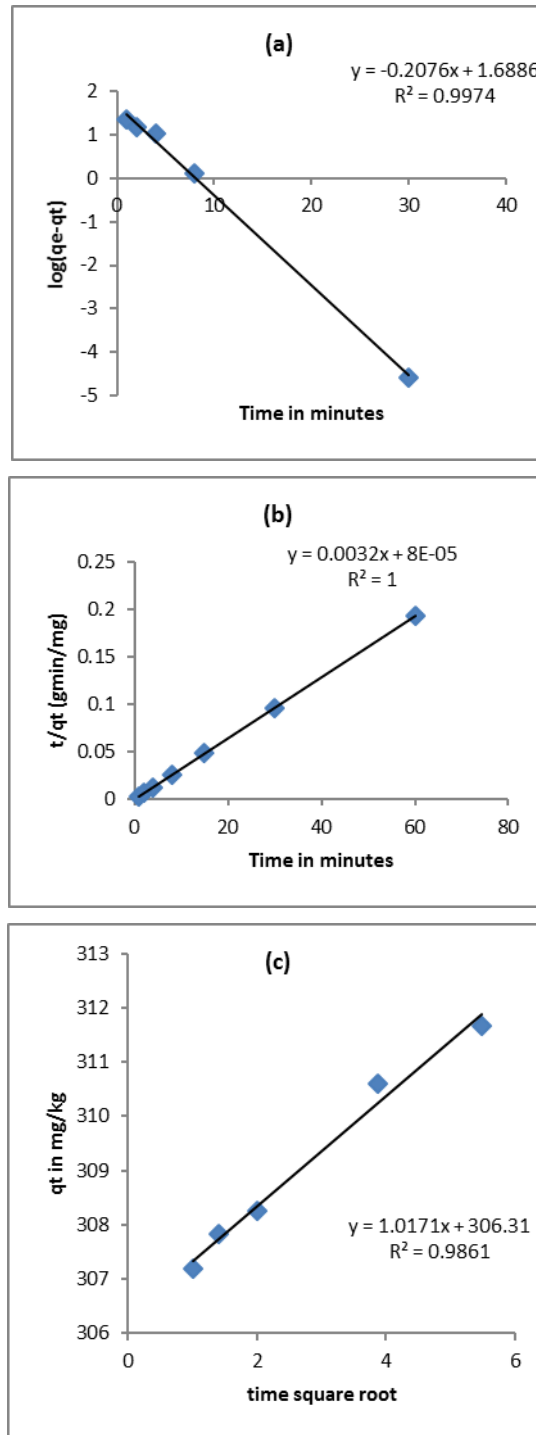


Figure 10: Time profile for F<sup>-</sup> adsorption onto powdered fish scales adsorbent showing (a) Pseudo-First Order, (b) Pseudo-Second Order and (c) Weber-Morris Intraparticle Diffusion plots.

Table 3: Kinetics constants for Pseudo-First Order fluoride adsorption onto the adsorbents T (K): 303; Co (mg/L): 1000; pH: 7; M (g/100 mL): 293-40]

Adsorbent	$K_{1,ads}(\text{min}^{-1})$	$q_e$ (mg/kg)	$R^2$
Fish scales	0.478103	1.001842	0.9974

Table 4: Kinetics constants for Pseudo-Second Order fluoride adsorption onto the adsorbents T (K): 303; C<sub>o</sub> (mg/L): 1000; pH: 7; M (g/100 mL): 293-40]

Adsorbent	$h_0=k_2 \cdot q_e^2$ (mg/g/min)	$k_{2,ads}$ (g/mg/min)	$q_e$ (mg/g)	$R^2$
Fish scales	12500	40	312.5	1

Table 5: Kinetics constants for Weber and Morris Intra-particle Diffusion Model fluoride adsorption onto the adsorbents T (K): 303; Co (mg/L): 1000; pH: 7; M (g/100 mL): 293-40]

Adsorbent	$k_p(\text{mg/kg/min}^{0.5})$	C	$R^2$
Fish scales	1.0171	306.31	0.9861

From Figure 10 (a), the plot was found to be linear with a good correlation coefficient (0.9974) indicating the applicability of pseudo first-order model in this study. The correlation coefficient ( $R^2$ ) value for pseudo second-order adsorption model had a higher value, that is, 1. Comparatively in this case, the  $R^2$  value is higher than that of pseudo first-order model. This indicates that the adsorption kinetics of fluoride onto the fish scales can be better described by pseudo second order model. A similar phenomenon has been observed by others for the adsorption of fluoride on various adsorbents (Tej & Majumder, 2016). This shows 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 and from Figure 10 (c), the plot 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 plot shows that nearly 50% of fluoride was rapidly taken up by the adsorbent. This would be due to the rapid

use of the most readily available adsorbing sites on adsorbent surfaces. Adsorption of fluoride by an adsorbent could be controlled by the initial intra-particle transport of fluoride guided by the surface diffusion process.

## CONCLUSIONS

The adsorbent was successfully synthesized and this was confirmed by FTIR analysis which indicated the presence of the anchored functional groups. From the SEM analysis the images showed morphological defects, irregular shape and coarse surfaces. According to the batch simulation tests the adsorbent had high fluoride adsorption capacity of 58.65 mg/g. The fluoride adsorption capacities of the adsorbent was, however, strongly controlled by solution parameters including the pH, temperature, adsorbent mass, contact time and agitation time. Optimum fluoride adsorption by the adsorbents would best be conducted in neutral pH of 7 at temperatures between 288 -313 K. The F<sup>-</sup> adsorption equilibrium data for the adsorbents were fitted by the Giles, the Langmuir and the Freundlich isotherms. The pseudo first-order, pseudo second-order plots and Weber-Morris intraparticle diffusion model were found linear with good correlation coefficients of > 0.9. Tilapia fish scales could be used as a low-cost adsorbent for fluoride water adsorption.

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