

Full Length Research Paper

Biosorption of fluoride ion from water using the seeds of the cabbage tree (*Moringa stenopetala*)

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Conventional water treatment technologies for the removal of fluoride ion may not be feasible for developing countries due to their high investment and operational costs. The aim of this study was therefore, to investigate the fluoride biosorption potential of the seeds of the cabbage tree (*Moringa stenopetala*). The influence of *Moringa* dosage, pH, contact time, and initial concentration of fluoride ion was investigated. The maximum fluoride sorption capacity was found to be 1.32 mg.g⁻¹ of dry weight of *Moringa* seeds at a biomass dosage of 2 g L⁻¹, pH 7.00, initial fluoride ion concentration of 10 mg.L⁻¹ and a contact time of 60 min. The fluoride level was reduced from 10 to 3.4 mg L⁻¹. The adsorption of fluoride ion onto *Moringa* powder was best described by the pseudo-second-order kinetic model ($R^2 = 0.99$). The adsorption equilibrium data have been fitted well to Langmuir as well as Freundlich adsorption models ($R^2 \geq 0.97$ for both models). The distribution constant (K_d) and maximum adsorption capacity (B_{max}) were significantly influenced by the amount of *Moringa* and equilibrium fluoride ion concentration ($p < 0.05$). The desorption tests indicated that only 20% of the initially bound fluoride ion was regenerated, while the remaining 80% were bounded with the *Moringa* powder. This suggests that chemisorption was the possible mechanism of fluoride removal.

Key words: Biosorption, chemisorption, desorption, fluoride, isotherm, *Moringa stenopetala*.

INTRODUCTION

Fluoride related health hazards are a major environmental problem in many regions of the world. Studies revealed that Ethiopia is among the 25 nations around the globe, where health problem occurs due to the consumption of fluoride contaminated water (Ayoob and Gupta, 2006). Out of 10 million people living in Rift Valley region of Ethiopia, 8.5 million people are exposed for high fluoride contamination. In the Ethiopian Rift

Valley, ground and surface water fluoride concentration varies from 0.5 to 264 mg.L⁻¹ (up to 26 mg.L⁻¹ in drinking water sources) (Tekle-Haimanot, 2006). As a result, over 80% of the children in the rift valley areas have developed varying degrees of dental fluorosis (Kebede et al., 2016). The public health and economic importance of fluorosis is significant in many endemic areas in view of the occurrence of debilitating skeletal fluorosis in humans

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and more recently, the discovery of pathology in cattle, sheep and other livestock. Crippling skeletal fluorosis is confined to tropical and sub tropical areas (WHO, 1984). Human sufferings due to dental and skeletal fluorosis, medical expenses to treat fluorosis, and untimely retirement of the productive members of the society can be prevented by defluoridating drinking water.

It is evident that there are different techniques available which have been found to be successful in defluoridation of drinking water containing excess fluoride. It is the only practicable option to overcome the problem of excessive fluoride in drinking water, where alternate sources are not available, and extensive research has been done on various methods for its removal. These methods are based on the principle of adsorption (Cengeloglu et al., 2002; Fan et al., 2003), ion-exchange (Wang et al., 2013), precipitation-coagulation (Roy and Dass, 2013), electrolytic defluoridation (Mameri et al., 2001) and electro dialysis (Hichour et al., 2000). However, conventional defluoridation technologies have high operational and maintenance costs, low fluoride removal capacity, a lack of selectivity for fluoride, undesirable effects on water quality, the generation of large amounts of sludge and complicated procedures involved in the treatment. Moreover, most defluoridation methods are unproven and unreliable under field condition in developing countries (Kloos and Tekle-haimanot, 1995; Kebede et al., 2016). In view of these serious drawbacks, there is a great need to develop an effective, efficient and eco-friendly adsorbent for the removal of fluoride from water.

To this end, a wide range of non-living biomass such as freshwater macrophytes such as *Eichhornia crassipes* (Sinha et al., 2003; Karmakar et al., 2016), fungi (Amin et al., 2015), algae (Mohan et al., 2007), yeast (Ramanaiah et al., 2007) and *Moringa olifera* (Bazanella et al., 2012; da Conceição et al., 2015) have been investigated as biosorbents. In the present work, seeds from the cabbage tree (*Moringa stenopetala*) were employed to remove fluoride ions from drinking water. *M. stenopetala* belongs to the family of the Moringaceae which is represented by a single genus, called *Moringa*. The water soluble *Moringa* seed proteins possess coagulating properties similar to those of aluminum sulphate and synthetic cationic polymers. *Moringa* seeds contain cationic polypeptides with various functional groups, particularly low molecular weight amino acids (Jose et al 1999). These amino acids are deprotonated to carboxylate ligands at pH range of 4 to 8, simultaneously protonating the amino group which facilitates the binding of negatively charged ions with the amino group.

A batch experiment conducted by Sahilu (2010) revealed that a 2 g.L⁻¹ of *M. stenopetala* seed powder reduced 9 mg/L of fluoride ion from ground water to 2.2 mg/L. In addition studies have shown that the seeds of the cabbage tree (*M. stenopetala*) removes heavy metals

such as hexavalent chromium (Degefu and Dawit, 2013); cadmium (Mataka et al., 2010) and lead (Mataka et al., 2006) from water in batch experiments. The main objective of this study was to determine the fluoride sorption potential of seeds of *M. stenopetala* from aqueous solution. The influence of biomass dosage, initial fluoride ion concentration, pH and contact time were investigated.

MATERIALS AND METHODS

Preparation of biosorbent

M. stenopetala seeds were collected from the Chefe area, South Wello zone, Ethiopia. Seeds were de-shelled by hand and the de-shelled seeds were dried in an oven at 105°C for 72 h. The dried seeds were ground in a mortar and sieved through 1 mm mesh. No other chemical or physical treatments were used prior to the biosorption experiments.

Preparation of fluoride solutions

A stock solution of fluoride was prepared by dissolving 2.21 g anhydrous sodium fluoride in one litre of distilled water. The sodium fluoride was previously dried at 105°C to a constant weight and stored in a dessicator. The fluoride concentration in this stock solution was 1000 mg.L⁻¹. Other concentrations were prepared from this stock solution by dilution and varied between 1 and 40 mg.F.L⁻¹. Fresh dilutions were prepared for each experiment. All the chemicals used were of analytical grade. Total Ionic Strength Adjustment Buffer (TISAB) solution was prepared from 58 g of sodium chloride, 4 g CDTA, and 57 mL of glacial acetic acid for adjusting the pH. The TISAB solution regulates the ionic strength of samples and standard solutions and adjusts the pH and also avoids interferences by polyvalent cations.

Biosorption test

Sorption studies were carried out in batch experiments as a function of biomass dosage (2 to 20 g), contact time (5 to 120 min), pH (2 to 13) and fluoride ion concentration (1 to 40 mg.L⁻¹) at a water temperature of 20±1°C. The required amount of fluoride solution was taken in an Erlenmeyer flask, diluted to 250 ml with distilled water and the pH was adjusted to the desired value. Then, a known quantity of *Moringa* powder was added. These suspensions were placed on a shaker during a certain time. After shaking, the suspension was allowed to settle for 15 minutes. The suspension was filtered by using white band Whatman filter paper. The filtrate was collected and analyzed for Fluoride ion by means of Fluoride Ion Selective Electrode METTLER TOLEDO model. The fluoride ion concentrations before and after sorption were recorded. Percent removal by sorption to the sorbent was computed using the equation:

$$\text{Removal efficiency}(\%) = \frac{C_o - C_e}{C_o} \times 100$$

where C_o is the initial fluoride ion concentration in the solution and C_e is the final fluoride ion concentration in the solution.

Adsorption kinetics

In order to evaluate the kinetic parameters, pseudo first-order and second-order models were tested to analyze the adsorption kinetics. Kinetic studies are important in determining the optimal contact time required to reach equilibrium (Ghorai and Pant, 2005).

The pseudo-first-order equation is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

where q_e and q_t are the amounts of fluoride adsorbed (mg/g) at equilibrium and at any time t (min), respectively. Where q_e and q_t are the amounts of fluoride adsorbed (mg/g) at equilibrium and at any time, t (min), respectively. K_1 is the pseudo first-order reaction rate constant of adsorption (min^{-1}) and K_2 the pseudo-second-order rate constant of adsorption (mg/g, min). The value of K_1 and q_e were calculated from the slope and intercept of the plot of $\log(q_e - q_t)$ versus t , while the value of K_2 and q_e were calculated from the intercept and slope of a plot of t/q_t versus t , respectively (Ghorai and Pant, 2005).

Intra-particle diffusion of fluoride

Weber–Morris model was used to understand the possible contribution of intra-particle diffusion for the removal of fluoride on an adsorbent. The linear form of intra particle diffusion model given by Weber–Morris is:

$$q_t = k_p t^{0.5}$$

where q_t is the amount of fluoride adsorbed per unit mass of adsorbent (mg/g) at a given time t , k_p is the rate constant of intra-particle diffusion ($\text{min}^{-1/2}$) and t is contact time (min). The uptake is proportional to the square root of contact time during the course of adsorption:

$$q_t = k_p \sqrt{t}$$

where q_t is the amount adsorbed at equilibrium (mg/g), k_p is the rate constant of intra-particle transport ($\text{mg g}^{-1} \text{min}^{-1/2}$). The intra-particle diffusion rate constant (k_p) value estimated from the slope of plot of q_t versus square root of time (Weber and Morris, 1963).

Adsorption isotherms

The adsorption of fluoride ion was tested with 2 g *Moringa* and varying fluoride ion concentrations (from 1 to 40 mg L^{-1}) at $\text{pH} \pm 7.0$. The contact time was 60 min. The volume of test solution was 250 ml. The biosorption equilibrium uptake capacity for each sample was calculated based on a mass balance.

$$S = \frac{V(C_0 - C_e)}{M}$$

where V is the sample volume (L), C_0 is the initial fluoride ion concentration (mg.L^{-1}), C_e is the final fluoride ion concentration (mg.L^{-1}), M is the amount of biomass (g dry matter), S is the amount of fluoride ion sorbed to the *Moringa* (mg.g^{-1}).

Freundlich isotherm

The Freundlich isotherm can be described as follows:

$$S = K_f \cdot C_e^{1/n}$$

where C_e is the equilibrium fluoride ion concentration (mg.L^{-1}), S is the amount of fluoride ion sorbed to the *Moringa* (mg.g^{-1}), K_f is the Freundlich constant denoting the adsorption capacity (mg.g^{-1}), n is the empirical constant, indicating adsorption intensity (L.g^{-1}). K_f and n denote, respectively the adsorption capacity (mg.g^{-1}) and adsorption intensity (L.g^{-1}) of the *Moringa*.

The logarithmic form of the equation is given as follows:

$$\log S = \log K_f + 1/n \log C_e$$

The Langmuir model

The Langmuir model can be described as follows:

$$C_e/S = 1/(k \cdot b) + C_e/k$$

where C_e is the equilibrium fluoride ion concentration (mg.L^{-1}), S is the amount of fluoride ion sorbed to the *Moringa* (mg.g^{-1}), K is the adsorption maximum (mg.g^{-1}), b is the constant (L.g^{-1}). The constant b represents the binding strength of the adsorption place for the ion.

Ligand binding model

The adsorption of fluoride ion to the biomass was fitted to a ligand binding model with one site saturation. This can be described as follows:

$$S = B_{\max} \times C_e / (K_d + C_e)$$

where S is the amount of fluoride sorbed to the *Moringa* (mg.kg^{-1}), B_{\max} is the maximum binding capacity (mg.g^{-1}), C_e is the equilibrium fluoride concentration (mg.L^{-1}), and K_d is the equilibrium distribution constant.

Desorption and reusability studies

In order to determine the reusability of the biosorbent, adsorption-desorption experiment were performed. A 250 ml test solution containing 20 mg.L^{-1} of fluoride ion was transferred into 250 ml Erlenmeyer flask. The pH of the solution was adjusted at around 7 using 0.2 M HCl or 0.2 M NaOH. After addition of 10 g of *Moringa* powder the mixture was shaken on a mechanically for 2 h. The suspension was filtered using Whatman filter paper and the residue left after filtration was subjected to desorption. Fluoride ion concentrations present in the filtrate were determined. Desorption

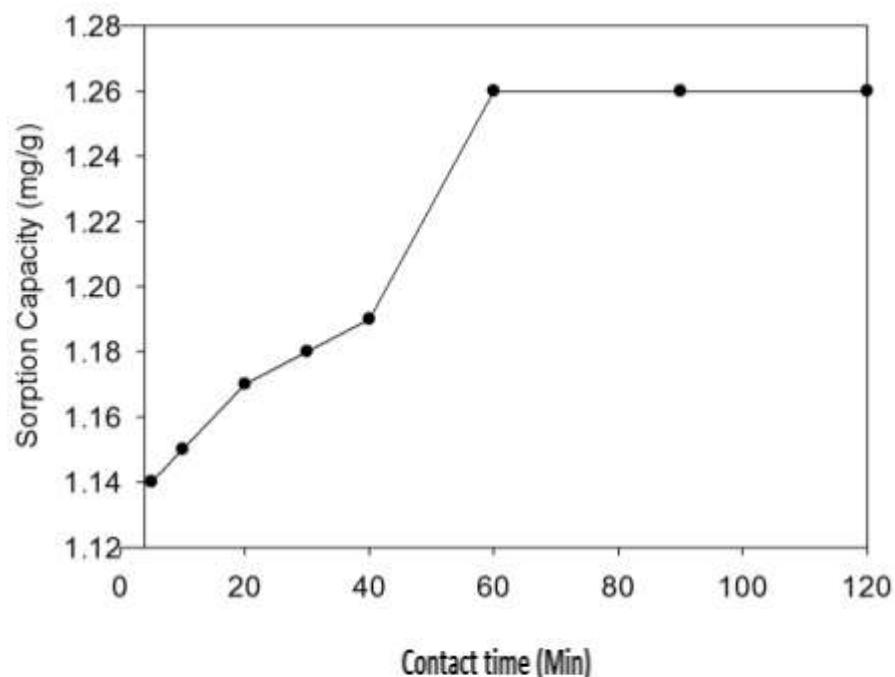


Figure 1. Sorption of Fluoride ion as a function of contact time initial F^- concentration of 20 mg.L^{-1} , *Moringa* dosage of 2 g, volume of test solution 250 ml, pH ± 7 and contact time 5 to 120 min.

of fluoride ions was performed by 0.02 M KCl solution. Biomass loaded with fluoride ions was placed in the desorption medium (250 ml 0.02 M KCl solution) and shake mechanically for 120 min. Then, the suspension was filtered by means of a Buchner filter. Fluoride

Ion Selective Electrode METTLER TOLEDO model was used to determine the fluoride ion concentration. The desorption efficiency of fluoride ion was calculated from the following equation:

$$\text{Desorption efficiency (\%)} = \frac{\text{Amount of Fluoride-ion desorbed (mg.L}^{-1}\text{)}}{\text{Amount of Fluoride-ion adsorbed (mg.L}^{-1}\text{)}} \times 100$$

pH of *M. stenopetala*

The pH of *M. stenopetala* in 1M KCl solution and water was determined using pH electrode.

Data analysis

The obtained data were fitted by means of Sigma Plot version 13 onto a ligand binding model with one site saturation. The binding rate coefficient of Fluoride ion on half of the binding sites of *Moringa* biomass (K_d) and the maximum adsorption capacity (B_{max}) was obtained from the curve. Significance was considered at $p < 0.05$.

RESULTS

Effect of contact time on fluoride biosorption

The amount fluoride ion sorbed increases with time and

reached its steady state in 60 min at which maximum sorption capacity (1.26 mg.g^{-1}) were achieved (Figure 1). This is due to the fact that initially a large number of vacant surface sites are available for adsorption. With increasing time, the remaining vacant surface sites may be difficult to occupy due to repulsive forces between the molecules of the solid and bulk phase (Saravanane et al., 2002; Kebede et al., 2016). However, increase in contact time beyond 60 min did not increase the sorption efficiency, which might be due to the presence of fewer adsorption sites.

Effect of pH on fluoride biosorption

The fluoride sorption capacity progressively increased as the pH of the solution increased from 2 to 7 (Figure 2). At pH below 7, the decrease in fluoride adsorption efficiency

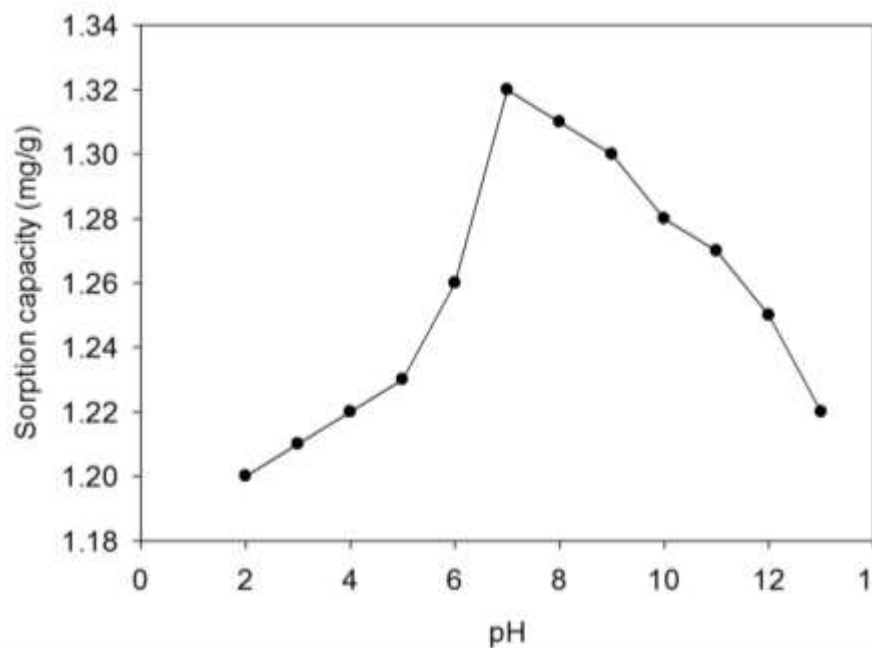


Figure 2. Effects of pH on fluoride ion sorption capacity of *M. stenopetala* seeds , initial fluoride ion concentration of 10 mg.L⁻¹, *Moringa* dosage 2 g, volume of test solution 250 ml, contact time 60 min.

and fluoride adsorption capacity might be due to the formation of hydrofluoric acid, which would reduce the coulombic attraction between adsorbent surface and the fluoride ion (Kagne et al., 2009). *Moringa* seeds contain cationic polypeptides with various functional groups, particularly low molecular weight amino acids (Jose et al 1999). The carboxylic group of the amino acids would progressively be deprotonated as carboxylate ligands at pH range of 4 to 8, simultaneously protonating the amino group. Such positively charged NH₃⁺ groups facilitate the *Moringa*-fluoride binding. As the pH rises above 7, sorption capacity dramatically decreased. This is due to the stronger competition for active sites between fluoride and hydroxide ions (Tembhurkar and Dongre, 2006). As hydroxyl ion concentration increases the overall charge on the biomass surface becomes negative. This causes a hindrance to the biosorption of the negatively charged Fluoride ion, resulting in a decrease of biosorption of fluoride at higher pH levels (Kebede et al., 2016).

Effect of initial fluoride ion concentrations

As illustrated in Figure 3, by changing the initial concentration of fluoride ion concentration from 2 to 40 mg.L⁻¹, removal efficiency was reduced from 54 to 26%. A reduction in percent removal at higher fluoride ion concentrations may be due to the increase in the number of fluoride ions competing for the available binding sites

on the biomass and the lack of binding sites available for binding of fluoride ions at higher concentration. Similarly, it has been found that fluoride removal using iron ore was smaller at higher fluoride ion concentration (Kebede et al., 2016). In contrast, sorption capacity increases from 0.07 to 1.32 mg.g⁻¹ as the initial fluoride ion concentration increased from 2 to 40 mg.L⁻¹. This finding is consistent with the results of Kebede et al. (2016), who found that the activity of fluoride ion increase as its concentration increases.

Effects of *Moringa* dosage on fluoride removal

As shown in Figure 4, fluoride sorption capacity decreased from 5 to 0.05 mg.g⁻¹ when the biomass dosage increased from 2 to 20 g.L⁻¹. The reason might be attributed to the high biomass concentration which could make a “screen” effect on the dense outer layer shielding the binding sites from fluoride ion in the solution and thereby lowering the specific uptake at higher biomass loadings (Kebede et al., 2016).

Adsorption kinetics studies

The derived parameters such as, q_e, k₂, and K_p, for the kinetic models are presented in Table 1. The coefficient

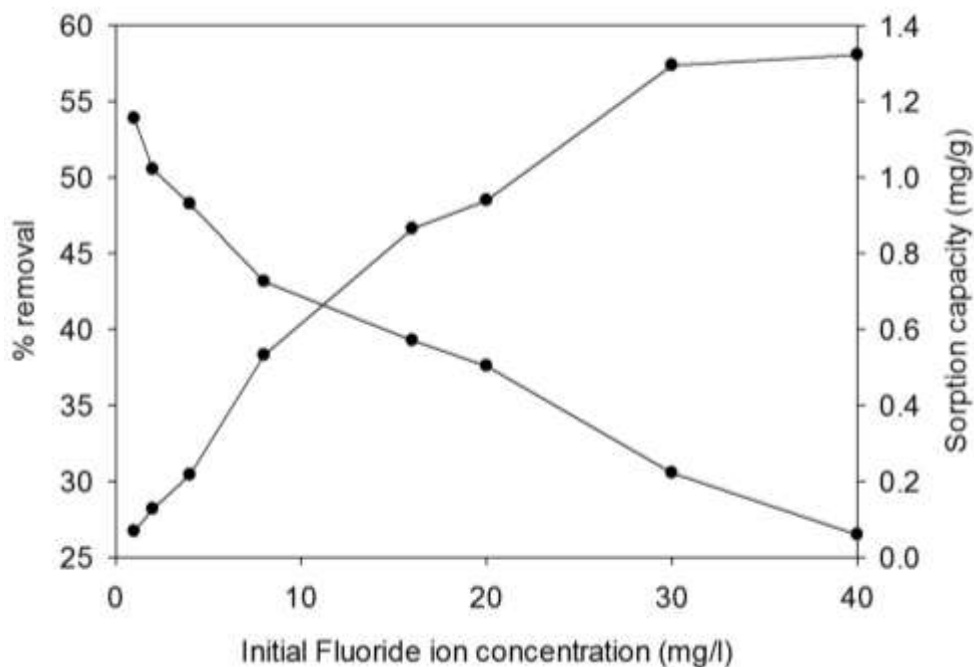


Figure 3. Effects of initial Fluoride ion concentration on biosorption by *M. stenopetala*, initial fluoride ion concentration 0 to 40 mg. L⁻¹, *Moringa* dosage 2 g, volume of test solution 250 ml, pH ±7, contact time 60 min.

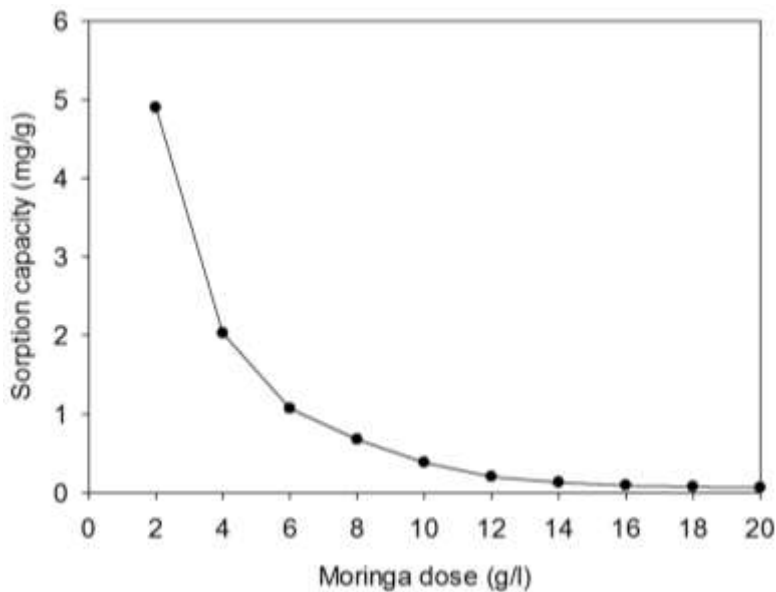


Figure 4. Sorption capacity of Fluoride ion at different dosage of *Moringa*, initial concentration 10 mg.L⁻¹, pH ±7, volume of test solution 250 ml, contact time 60 min.

of determination (R^2) for the pseudo second-order kinetic model (Figure 5a) was found to be high (0.99). The

estimated equilibrium adsorption capacity (q_e) with a value of 1.27 mg/g is approximately similar with the

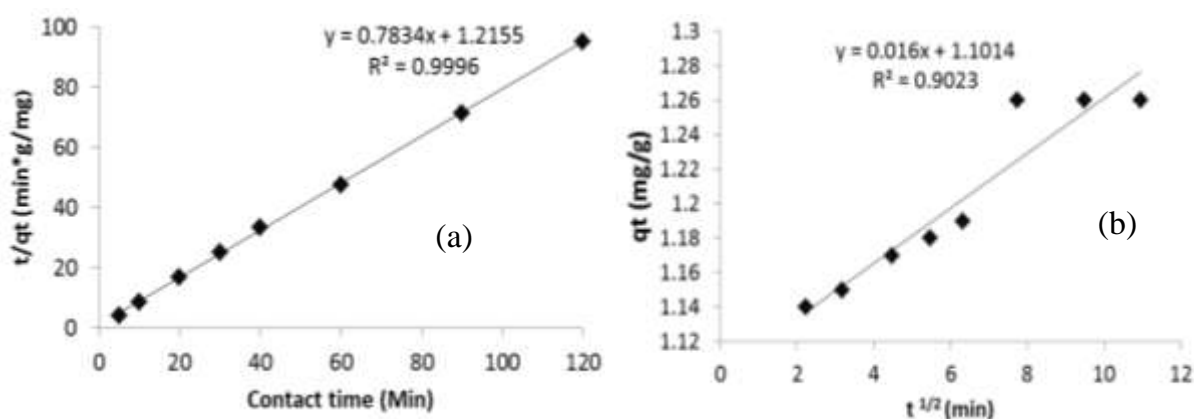


Figure 5. Plot of pseudo-second-order model (a) and Intraparticle diffusion model (b) for fluoride ion adsorption onto *Moringa* powder. Initial Fluoride ion concentration 20 mg. L⁻¹, *Moringa* dosage 2 g, volume of test solution 250 ml, pH ±7.

Table 1. Kinetics parameters for the adsorption of fluoride ion on seeds of cabbage tree (*M.stenopetala*).

Kinetics	Parameter	Values
Pseudo second order	qe experimental (mg/g)	1.26
	qe calculated (mg/g)	1.27
	K ²	1.67
	R ²	0.9996
Intraparticle diffusion	Kp (min ^{1/2})	0.163
	R ²	0.9023

experimental value of 1.26 mg/g (Table 1). Therefore, the adsorption of fluoride ion onto *Moringa* powder is best described by the pseudo-second-order kinetic model suggest that fluoride should be adsorbed by chemisorption, which involves the sharing of electrons between fluoride and the adsorbent (Bhaumik and Mondal, 2015). However, the adsorption of fluoride did not follow the pseudo-first order equation (results not shown).

The plot of qt versus t^{1/2} for intra-particle diffusion in the adsorption of fluoride ion onto *Moringa* powder was used to obtain the diffusion rate parameters. As presented in Figure 5b, the intra-particle diffusion rate constant (kp) value estimated from the slope of plot of qt versus square root of time was found to be 0.163 min^{1/2} for the initial fluoride concentration of 20 mg/L. If intra-particle diffusion is a rate-controlling step, then the plots should be linear and pass through the origin (Weber and Morris, 1963). However, in this study, the plot does not pass through the origin. This suggested that fluoride removal is a complex process and the intra-particle diffusion was not the only

rate controlling step which is similar with the findings of Kebede et al. (2016).

Adsorption isotherm of fluoride

A graphical representation of Freundlich and Langmuir adsorption isotherm is presented in Figures 6 and 7, respectively. Higher values of correlation coefficients indicate that adsorption data are good fitted for both the Freundlich and Langmuir model (R² = 0.97 and 0.98 for Freundlich and Langmuir model, respectively). Freundlich constants Kf and n, that is, 1.07 mg.g⁻¹ and 0.36 L.mg⁻¹, indicate good adsorption capacities. Kf is defined as the adsorbate adsorbed per unit weight of adsorbent (Chen et al., 2010). The Langmuir isotherms show a k value of 0.92 mg.g⁻¹ and a value for constant b of 0.16 L.mg⁻¹. Again, these data indicate the high affinity of fluoride for sorption with *M. stenopetala* seeds. The constant k in the Langmuir equation indicates the adsorption maximum.

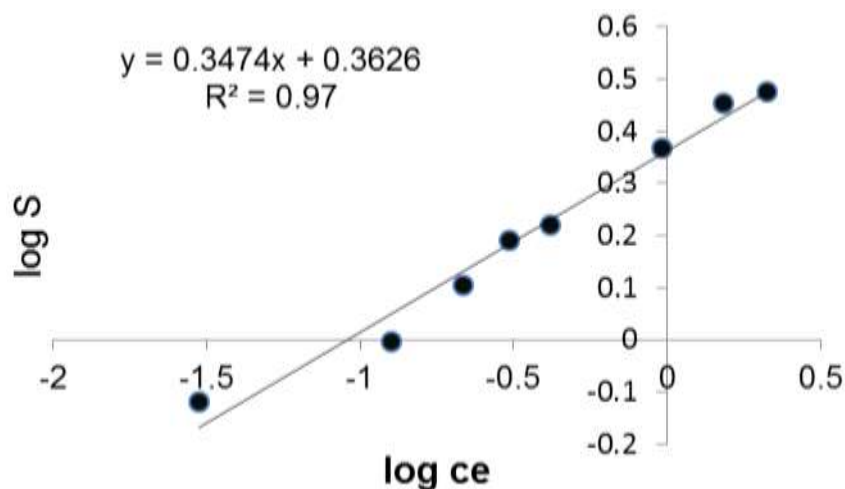


Figure 6. Freundlich isotherm for adsorption of Fluoride ion, initial Fluoride ion concentration 0 to 40 mg. L⁻¹, *Moringa* dosage 2 g, volume of test solution 250 ml, pH \pm 7, contact time 60 min.

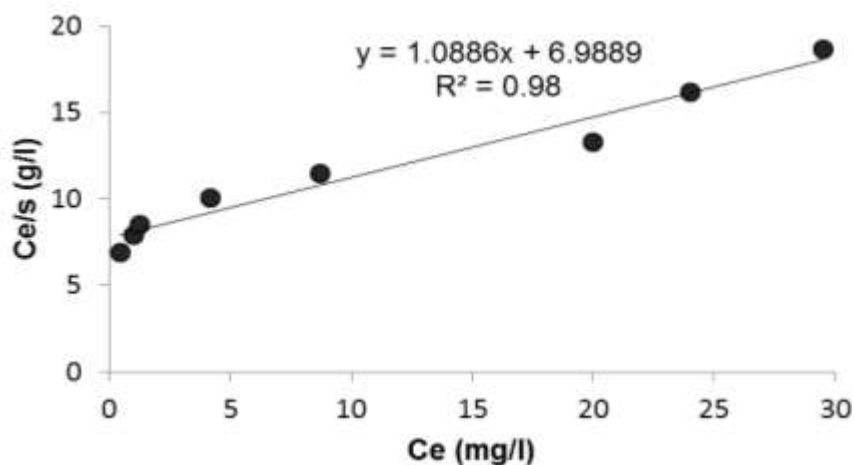


Figure 7. Langmuir Isotherm for adsorption of fluoride ion, initial Fluoride concentration 0 to 40 mg. L⁻¹, *Moringa* dosage 2 g, pH \pm 7, volume of test solution 250 ml, contact time 60 min.

Ligand binding model

Figure 8 shows ligand binding model of fluoride ion on *Moringa* seed powder. The maximum binding capacity (Bmax) of fluoride on the target biomass was 15.5 mg.g⁻¹, which is greater than the theoretical maximum adsorption capacity ($K = 0.92$ mg.g⁻¹) obtained from Langmuir isotherm. Both the distribution constant (K_d) and maximum adsorption capacity (Bmax) were significantly influenced by the amount of adsorbent and equilibrium fluoride concentration ($P < 0.05$).

Desorption test

In this study, desorption tests were employed to elucidate the nature of adsorption processes. A 10 mg.L⁻¹ fluoride solution was allowed to adsorb onto 2 g.L⁻¹ of *Moringa* seed powder. After 2 h of this sorption experiment, the concentration of fluoride in the filtrate was found to be 3.4 mg.L⁻¹, which means 7.6 mg.L⁻¹ of fluoride ion was adsorbed on *Moringa* seeds (Table 2). Attempts were made to desorb fluoride ion from these fluoride ion loaded *Moringa* seeds using a 0.02 M KCl solution (pH 6.03).

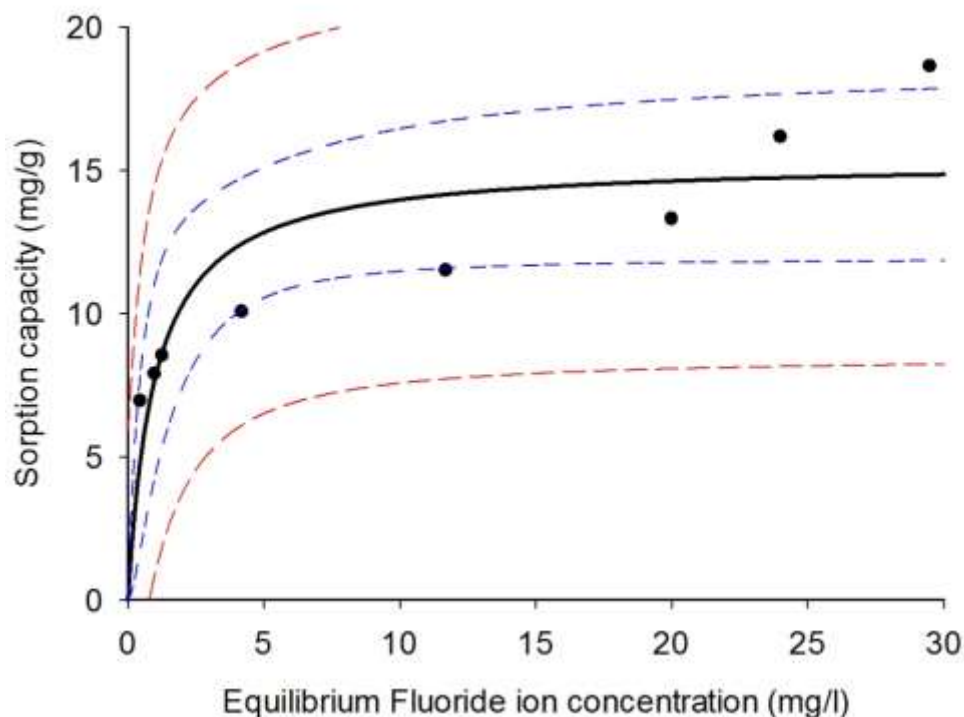


Figure 8. Binding of fluoride ion on *Moringa stenopetala* powder, initial fluoride ion concentration 0 to 40 mg. L⁻¹, *Moringa* dosage 2 g, pH \pm 7, volume of test solution 250 ml, contact time 60 minutes. Solid line = Sorption capacity vs. Equilibrium fluoride ion concentration; black dots = Sorption capacity vs. Equilibrium fluoride ion concentration; Short-Short line = 95% confidence band; Medium dash line = 95% prediction band.

Table 2. Adsorption-desorption Fluoride concentration, initial concentration 10 mg.L⁻¹, *Moringa* dosage 2 g.L⁻¹.

Fluoride ion	Values
Residual (filtrate) (mg.L ⁻¹)	3.4 \pm 0.6
Removed by <i>Moringa</i> (mg.L ⁻¹)	7.6 \pm 0.8
Regenerated from <i>Moringa</i> (mg.L ⁻¹)	1.5 \pm 0.2
% of regeneration	20 \pm 2.2

After 2 h of desorption, only 20% of the initially bound fluoride ion was regenerated, while the remaining 80% remained bound with the *Moringa* powder, which indicates that most of the fluoride ions are able to form strong bonds with the positively charged functional group (NH₃⁺) of *Moringa* powder. The negligible desorption of fluoride ion with 0.02 M KCl indicates the predominance of chemical bonding between *Moringa* powder and fluoride ion. This implies that physical adsorption is not playing a significant role in fluoride removal by *Moringa* powder.

Conclusions

The results of this study revealed that application of *M. stenopetala* seeds as a biosorbent introduces a less expensive and environmentally friendly method for removal of fluoride ion from aqueous media. The removal of this pollutant was found to be depending on biomass dosage, pH, initial concentration and contact time. The adsorption capacity of *Moringa* for fluoride was 1.32 mg.g⁻¹ of dry weight of *Moringa* seeds. The adsorption equilibrium data has been fitted very well to Langmuir as

well as Freundlich adsorption models ($r^2 \geq 0.97$). The desorption tests indicated that only 20% of the initially bound fluoride ion was regenerated, while the remaining 80% were bounded with the *Moringa* powder. This suggests that chemisorption was the proposed mechanism for fluoride removal. *Moringa* seeds powder could be applicable for the removal of fluoride ion from water, but could not bring fluoride concentration to permissible level. Hence, chemical activation or impregnation would increase the efficiency of this biosorbent. Further studies are required to determine functional groups of *Moringa* seeds which are responsible for fluoride fixation. Moreover, the surface morphology of the biosorbent and mechanism of fluoride–biosorbent interaction should be determined using scanning electron microscope (SEM) and/or Fourier transform infrared (FTIR).

Conflicts of interests

The authors have not declared any conflict of interests.

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