Fluoride Adsorption onto Sulphonated Polystyrene

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Abstract

Adequate fluoride (F⁻) taken in through food, soil and water is crucial for healthy bones and teeth building. Excess F⁻ results in dental, skeletal and soft tissue damage unless controlled by its removal. 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. In the present study, defluoridation has been applied using sulphonated polystyrene (SPS) investigated for fluoride adsorption. The material was collected from Eldoret dump site, sorted, ground, weighed, treated and tested for fluoride removal in water. The adsorbent was modified using solutions containing Ca^{2+}, Mg^{2+} and Al^{3+} ions. Fluoride adsorption properties for the adsorbent were then assessed with respect to changes in adsorbent dosage, contact time, agitation rate, solution pH, temperature and initial fluoride concentration. Fluoride adsorption from aqueous solutions using SPS was studied using batch experiments and the adsorbent was characterized by FTIR and SEM methods. F⁻ adsorption data correlated to the Freundlich and Langmuir models and could be classified as C-Type according to Giles classification of isotherms. The psueudo-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 streams.

Keywords: Adsorption, Defluoridation, Adsorbent, Isotherms, Kinetic Models, Sulphonated Polystyrene

INTRODUCTION

Fluoride is one of the most important elements in humans because of its role in bone and dentine mineralization (Grynpas *et al.,* 2000). F is the 13th most common element in nature, and it is extremely reactive and electronegative (Hem, 1989). Its availability in water in low concentration has a beneficial effect on teeth. Exposure to excessive amounts can cause irreversible demineralization of bone and tooth tissue, a condition known as fluorosis, and long-term damage to brain, liver, thyroid, and kidney (Barbier *et al.,* 2010: Gazzano *et al.,* 2010). For many years, native fluorosis has been a public health issue in Kenya, and today there is growing worry about the fate of fluoride (F-) in soil and groundwater sources, particularly in locations around the Great Rift Valley and the Central Highland. Moreover, in many parts of Kenya, fast population increase and changes in rainfall patterns have exacerbated the problem of water scarcity, pushing people to rely on low-quality water sources to meet their needs (Wambu & Muthakia, 2011). The standard and well-proven technique of providing clean water to communities is to remove fluoride from the water. Ion-exchange, precipitation, distillation, electro-chemical defluoridation, reverse osmosis, and adsorption are the main defluoridation processes (Piddennavar &Krishnappa, 2013: Kavita *et al.,* 2016). Adsorption is considered one of the most efficient technologies for fluoride removal in drinking water when compared to other technologies for fluoride removal based on initial cost, flexibility and simplicity of design, and ease of operation and maintenance forces

(Waheed *et al.,* 2009: Keerthi, 2015). The use locally available waste materials and modification of the materials which are adaptable to local needs would be ideal alternative to water defluoridation (Goswami & Purkait, 2012: Wambu, 2015).

Plastics are applied in a wide variety of tasks on a daily basis and are an essential. One of the most regularly used plastics is polystyrene (PS), which is quite useful in the packaging process (Choi & Ohama, 2004). It is a crucial plastic in our lives because of its mechanical resistance to compressive stress and heat non-conductive qualities (Eskander & Tawfik, 2011). Nevertheless, because it has a short usable life, it can readily be converted into solid waste and deposited in a variety of locations (Derraik, 2002), polluting natural resources such as water (Shin, 2006) and soil (Taguchi & Tanaka, 2001), and it has a serious pollutant effect due to its non-biodegradability (Kan &Demirboǧa, 2009). As a result, scientists have identified these polymers as resilient in marine environments (Browne *et al.,* 2008), as well as being a toxin in aquatic organisms (Gregory, 1991). On the other hand, external conditions such as sunlight, rain, and total solids can cause the monomer, styrene, to be freed from the primary polymer chain (Vodicka *et al.,* 2006); allowing for a possible carcinogenic effect in humans (Amianti & Botaro, 2008). As a result, researchers are seeking for strategies to limit PS contamination in the environment, which is why PS was used for water defluoridation in the current study. As a consequence, one of these methods could be recycling PS through physical modifications. As a result, PS has been blended with fibers to make filters and has been used in concrete to strengthen and reduce permeability (Gikunju *et al.,* 1995). In the current study PS was sulphonated and used as an adsorbent for fluoride ions.

METHODOLOGY

Experimental procedures

Chemicals
Throughout the testing, are grade reagents and substances were employed. 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^{-1} 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^{-1} 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 using Tx EDT Model 3221 direct fluoride ISE by addition of appropriate volume of TiSAB II (Gregory, 1991). 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
Polystyrene waste (PS) which is used in packaging was collected from dump sites within Eldoret town, packed in polythene bags and transported to the University of Eldoret chemistry laboratory. 5 kilograms of the polystyrene was then grated, and heated at 100 ^{0}C for two hours to reduce its volume. A mass of 100 g of polystyrene particles was sulfonated by adding 600 mL concentrated sulfuric acid (98 wt %) in a 1000-mL flask, with 100 mL 1, 2-dichloroethane (DCE) as the swelling agent at 80^{0}C for 8 hours (Yinlin *et al.,* 2014). The product was washed 3-4 times with

100 mL distilled water then filtered and washed with diluted solution of sodium bicarbonate to ensure the removal of residual sulphuric acid (Hayat *et al.,* 2016).

Batch experiments
Batch experiments were carried out to optimize mass, time, pH, agitation rate, temperature and initial fluoride concentration on raw, modified and combined adsorbents. The batch experiments were carried out 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:

$$\% \, adsorption = \left(1 - \frac{c_{eq}}{c_i}\right) \times 100$$…………………………………………….2

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.

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 1.5 g 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 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.

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-µL pipettes.

Effect of change in solution temperature
The effect of change in solution temperature on fluoride adsorption onto SPS was carried out at different temperatures between 288 K - 353 K.

Effect of adsorbate concentration
The effect of change in fluoride concentration on its removal from water using the adsorbent was studied under conditions of 6 g/mL batch dosage, time of 30 minutes, agitation rate of 300 rpm, pH of 7 and constant temperature 323 K.

Data analysis
All tests were performed in triplicate. The data were analyzed by descriptive statistics by calculating the range, mean and standard deviation on replicate results. Causative relationships

were then analyzed by graphical regression of the variables and determination of correlation coefficients.

RESULTS AND DISCUSSION

Chemical characterization of adsorbents

The nature of interactions between reactive surface sites or functional groups in adsorbents 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 Figure 1 and 2, respectively.

Figure 1 (a) and (b), when PS is sulphonated (SPS), new absorption bands and the splitting of others, consistent with the presence of -SO$_3$H group on the aromatic ring are observed. New absorption bands at 3,340, 1,250, and 1,078 cm^{-1} were assigned to the stretching of the –OH in the -SO$_3$H group and to the asymmetric and symmetric stretching of the O=S=O group, respectively (Hayat *et al.,* 2016). According to Figure 1 (b), after fluoride adsorption, there was a reduction in the intensity of -SO$_3$H bands at 3885 and 520 cm^{-1} in fluoride treated SPS which may be due to fluoride adsorption/exchange.
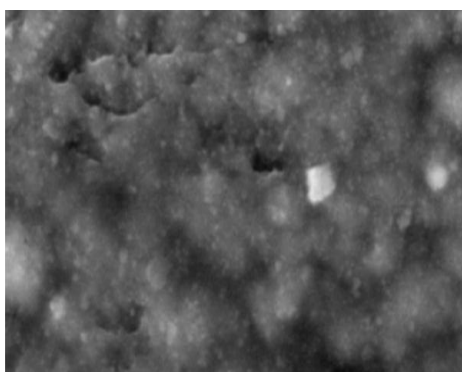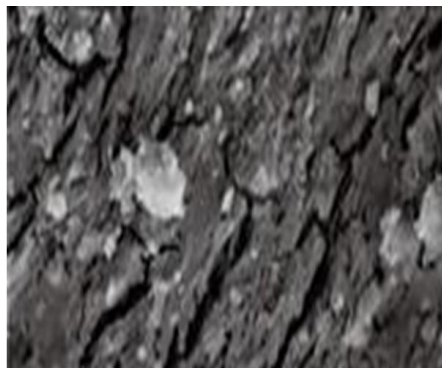

Figure 2(a): SEM image for SPS   **Figure 2 (b): SEM image for SPS after fluoride adsorption**

From Figure 2 (b) the SEM images after defluoridation show morphological defects, irregular shape and in some coarse surfaces. This may be as a result of fluoride adsorption by the adsorbents.
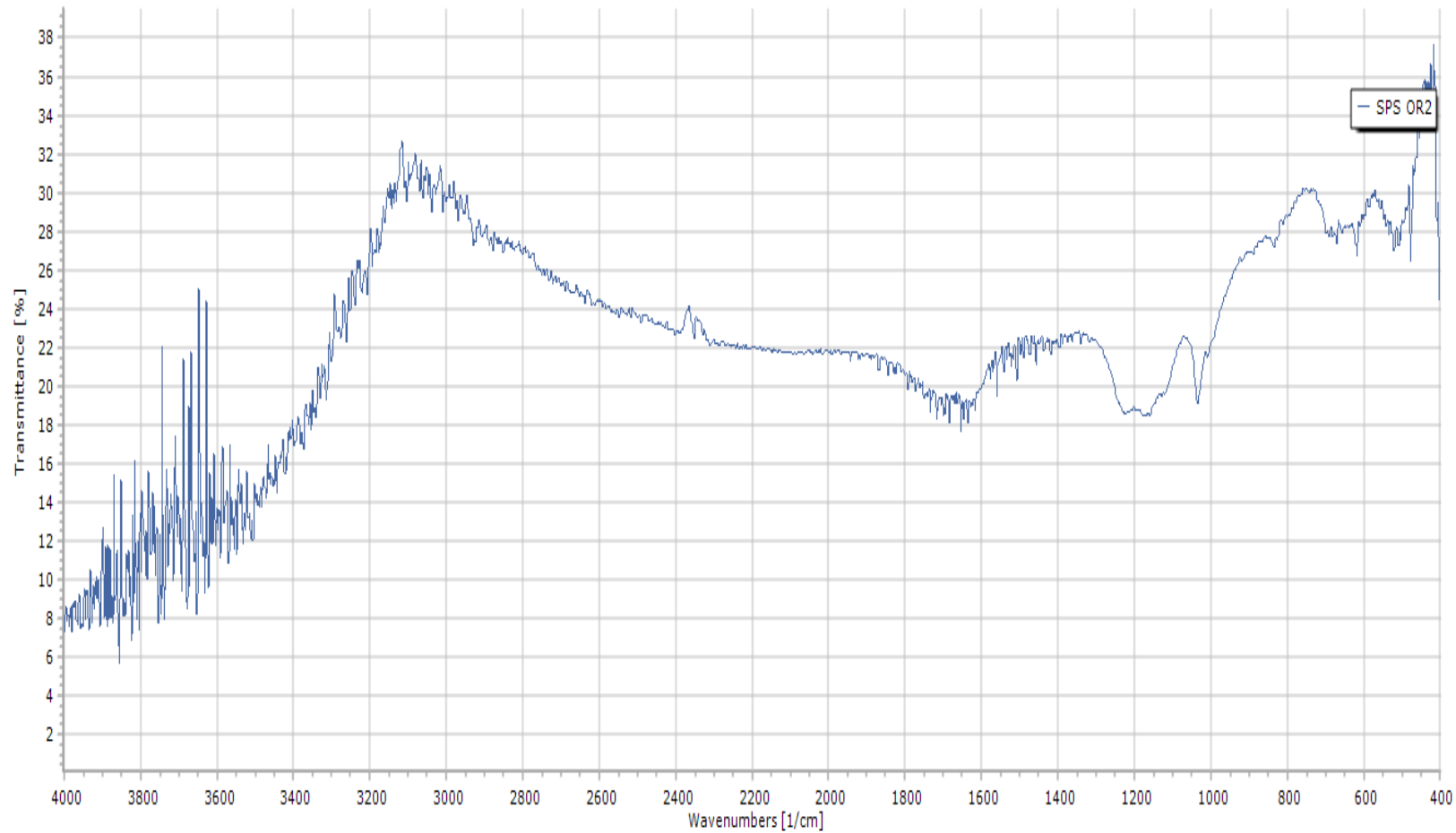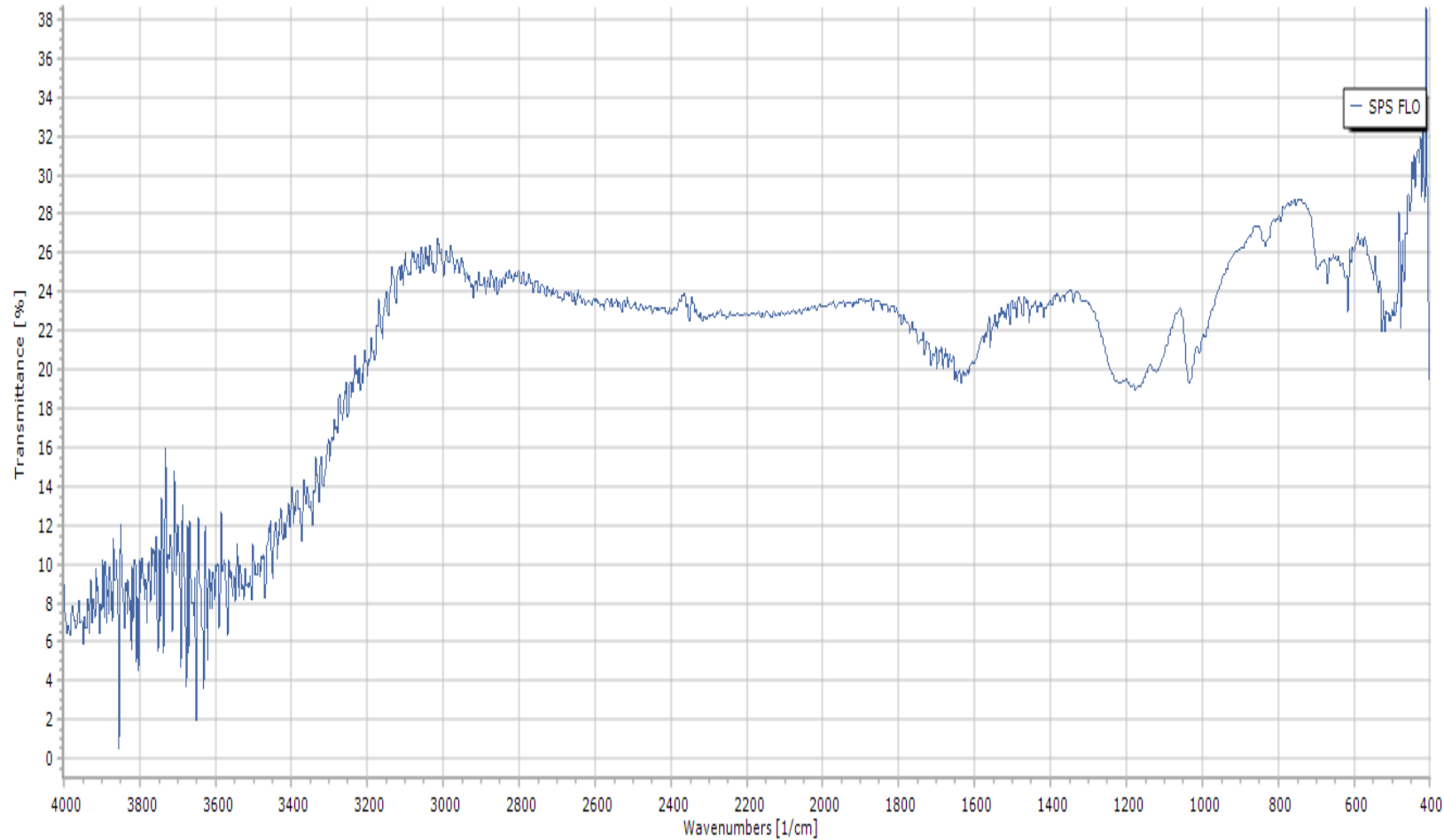
Figure 1 (a): SPS FTIR spectra

Figure 1 (b): SPS FTIR spectra after fluoride adsorption

Effect of change in mass of adsorbent

The percentage F⁻ removal was determined and plotted against the mass of the adsorbent and the results presented in Figure 3.
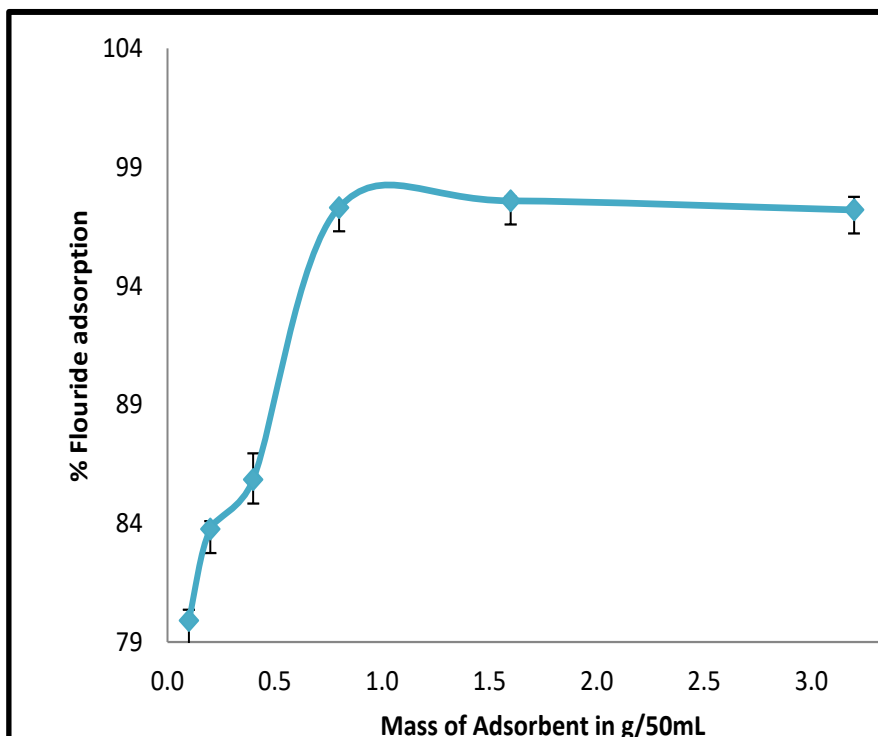

Figure 3: Effect of adsorbent dosage using 50 mL of the adsorbate solution containing 10 ppm of F⁻ being shaken at 400 rpm for 120 min at 298 K.

Fluoride uptake by sulphonated polystyrene (SPS) increased with increasing mass of adsorbent. Fluoride removal from solution could be achieved at 1.5 g/mL doses. The adsorbent ratio of 1.5 g/mL which was maintained in all the subsequent tests was adequate for over 95% fluoride adsorption from water under the conditions of these tests. This shows that sulphonated polystyrene can be used as a low-cost adsorbent for water defluoridation.

Effect of change in adsorption contact time

The adsorption of fluoride ion by adsorbent also depends on the interactions of functional groups between the solution and the surface of adsorbent. Adsorption 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 the completion of adsorption process (Kavita *et al.,* 2016). The effect of change in contact time on adsorption of fluoride by the SPS is shown in Figure 4.
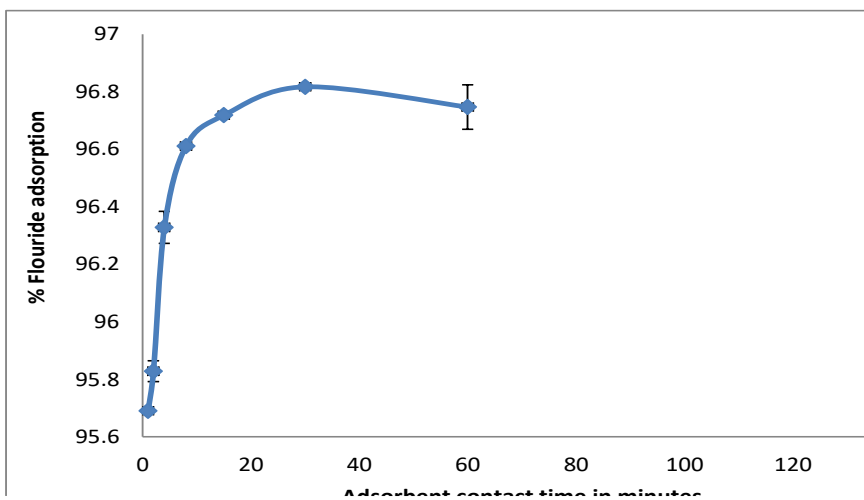
Figure 4: Effect of contact time using 50 mL of the adsorbate solution containing 10 ppm of F⁻, 6 g mass, being shaken at 400 rpm at 298 K.

The % adsorption of flouride on to the adsorbent increased from 95.7% within a period of 1 minute to the highest % of 96.8 and after a period of 30 minutes an equilibrium was attained as illustrated by Figure 4. This time was adopted to be optimum for subsequent batch experiments. 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 chemical materials was higher (Waheed &Waghmare, 2009).

The effect of change of agitation rate on adsorption
It was shown that agitation rate increased the % adsorption, after which the % adsorption decreased. The optimum agitation rate for SPS was 300 rpm with a % adsorption of 58%. From literature it has been recorded that the effect of agitation rate increases up to a certain level after which the rate of sorption remains constant (Yinlin *et al.,* 2014: Puthenveedu *et al.,* 2012). The effect of agitation rate on the adsorption of flouride unto the adsorbent is shown by Figure 5.
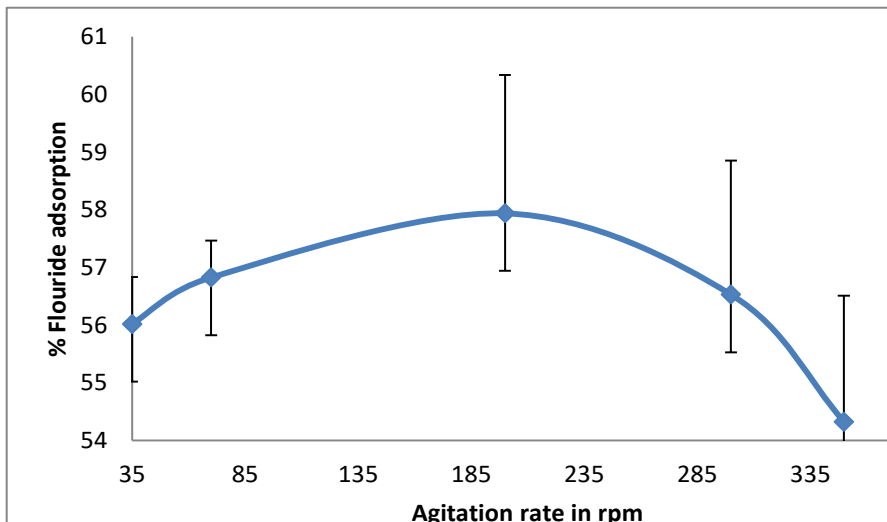

Figure 5: Effect of agitation rate using 50 mL of the adsorbate solution containing 10 ppm of F⁻ 6 g mass, 30 minutes at 298 K.

Effect of change in fluoride solution pH

The percentage of fluoride adsorption was plotted as a function of initial solution pH and the results presented in Figure 6. From the figure, % adsorption of flouride by SPS increased steadily from 74% to 87% with a pH range of 1-7, there after the adsoption % decreased sharply when the pH was between 9-11. This shows that highest fluoride uptake by SPS occured at pH 7. It has been found that removal efficiency of adsorbent increases with increased pH values (Keerthi, 2015). Because the protonated surface is responsible for adsorption of anions, the highest adsorption of fluoride in many adsorbents occurs at acidic pH (Goswami & Purkait, 2012) and decreases at higher pH values.
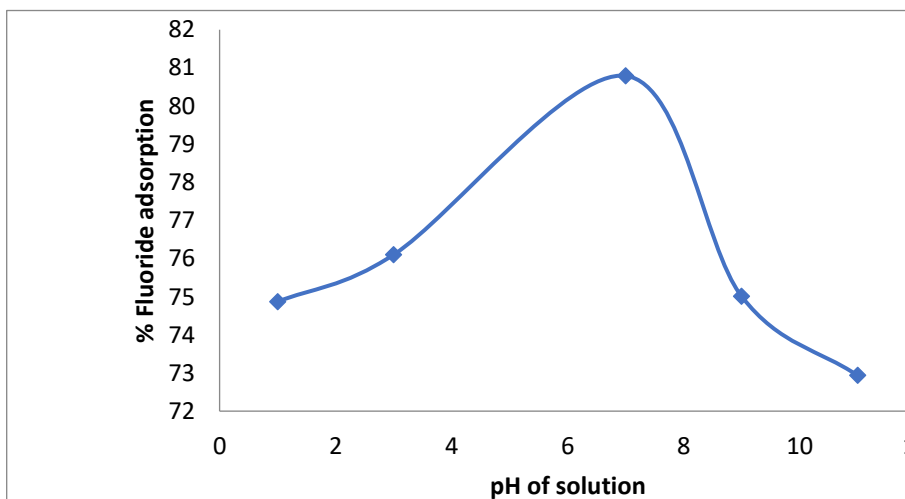

Figure 6: Effect of solution pH using 50 mL of the adsorbate solution containing 10 ppm of F⁻ 6 g mass, 30 minutes, 300 rpm at 298 K

Effect of change in solution temperature

Temperature can impact the physical binding processes of fluoride to a sorbant and can also have direct impact on the physical properties of a sorbant, 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 sorbant 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 effect of change in solution temperature on flouride adsorption onto SPS was carried out at different temperatures between 288 K - 353 K and the results are shown in Figure 7.
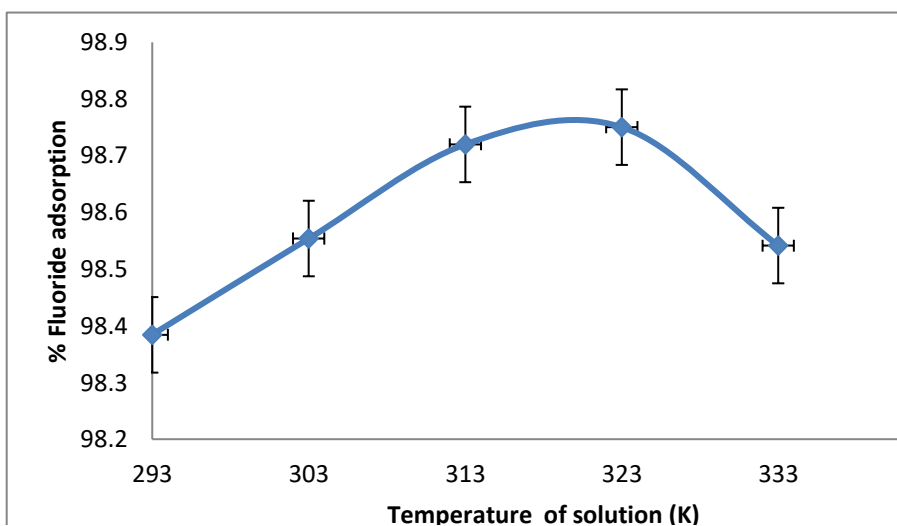
Figure 7: Effect of temperature using 50 mL of the adsorbate solution containing 10 ppm of F⁻ 6 g mass, 30 minutes, 300 rpm, pH 7

The adsorption of flouride onto SPS at different temperatures from Figure 7, illustrates that the optimum temperature was 323 K with 98.75% adsorption, in addition the % adsorption across the different temperatures did not have a wide range since the adsorption was 98%.

Effect of adsorbate concentration

The effect of change in fluoride concentration on its removal from water using the adsorbent was studied and the results presented in Figures 8.
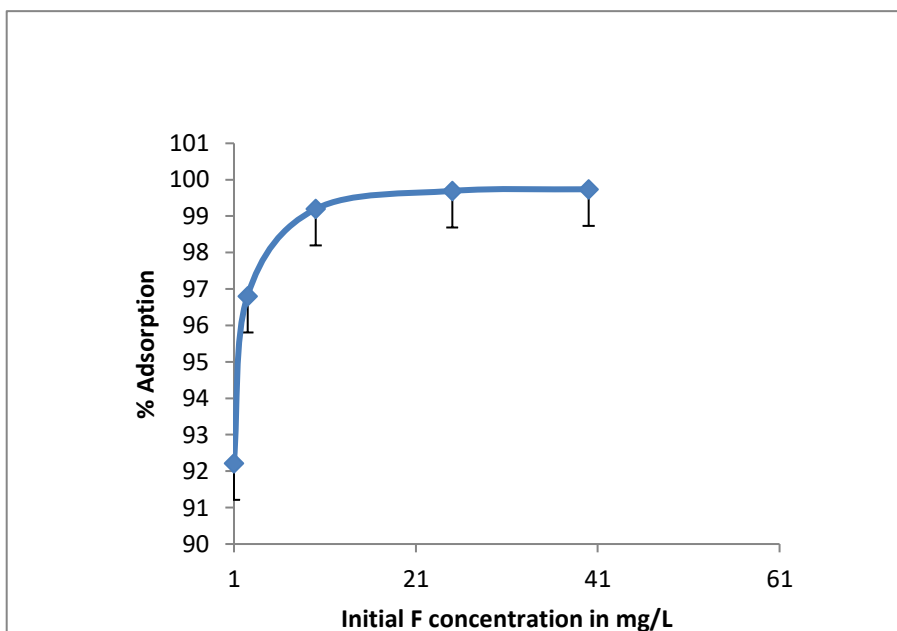

Figure 8: Effect of change in initial adsorbate levels on fluoride adsorption onto SPS.

The results from Figure 8 indicate that the percentage adsorption for SPS increased between 1-10 mg/L initial fluoride concentration where the adsortion percentage ranged from 92-99 %, there after the adsorption remained constant.

The efficiency of fluoride adsorption decreases with increasing initial fluoride concentration for a constant adsorbent dose and contact time. The decrease in efficiency at higher initial fluoride concentrations is due to the exhaustion of the active sites of the adsorbent. However, the total capacity of the adsorbents increases when the initial fluoride concentration is 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 contain 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).

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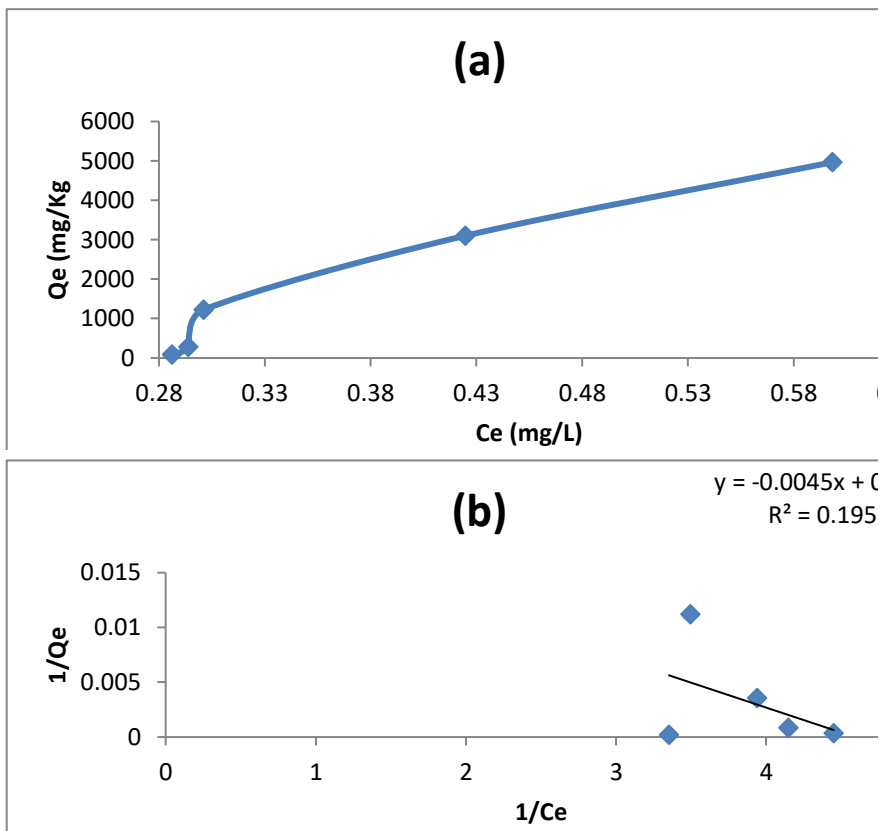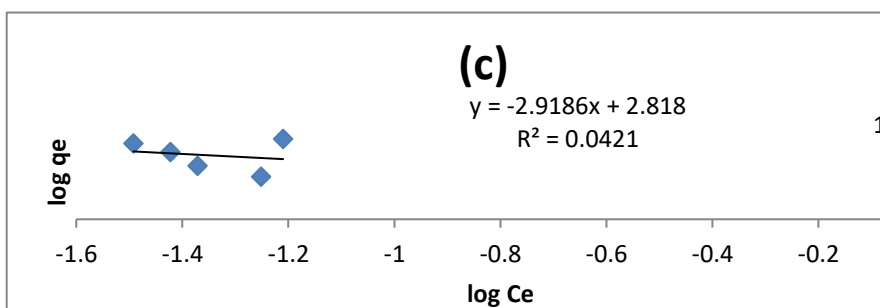
Figure 9: equilibrium isotherm plots onto the SPS (a) Giles, (b) Langmuir and (c) Freundlich

According to Figure 9, the adsorbent 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 (Hinz, 2001). The equilibrium data for fluoride adsorption onto the adsorbent was fitted by the Langmuir and Freundlich isotherms with R^2 values of 0.1965 and 0.0421, respectively.

Table 1: Langmuir isotherm constants for the adsorption of fluoride onto the adsorbents

Adsorbent	pH	Temperature(K)	k_l (mg/Kg)	b	R
SPS	7	323	22.22222	0.000936	0.1965

Table 2: Freundlich isotherm constants for the adsorption of fluoride onto the adsorbents

Adsorbent	pH	Temperarure(K)	k_f	n	R
SPS	7	323	22.22222	0.000936	0.0421

The values of the Langmuir constants, k_l and b, indicated less efficient fluoride binding onto the adsorbent, while for Freudlich the value of the constant n (adsorption intensity) was less than unity, indicating favourable adsorption.

Adsorption kinetics

Fluoride adsorption onto surfaces consists 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 psueudo-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.

(a)

(b)

y = 0.0081x - 9E-05
R² = 1

(c)
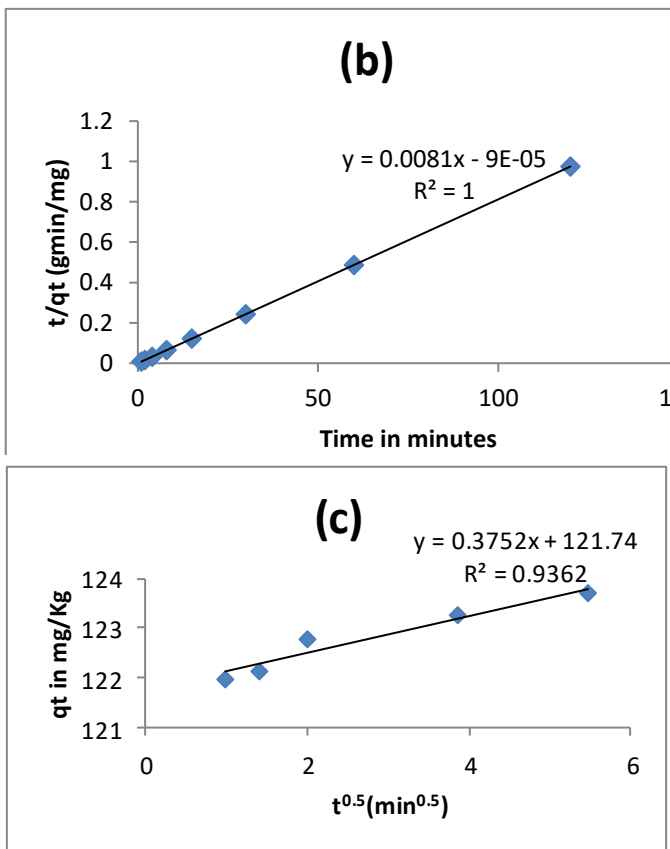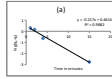
y = 0.3752x + 121.74
R² = 0.9362

Figure 10: Time profile for fluoride adsorption onto adsorbent showing (a) Pseudo-first order, (b) Pseudo-second order and (c) Weber- Morris intraparticle diffusion plot

According to Figure 10 (a), the plot was found linear with good correlation coefficient (0.9882) indicating the applicability of pseudo first-order model in this study. The correlation coefficient (R^2) values had a higher value, 1, implying adsorption kinetics of fluoride onto SPS can be better described by pseudo second-order adsorption model. A similar phenomenon has been recorded in literature (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 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 was 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 fluoride adsorption onto the adsorbents T (K): 303; Co (mg/L): 1000; pH: 7; M (g/l00 mL): 293-40]

Adsorbent	$K_{1\,ads}(min^{-1})$	q_e (mg/Kg)	R^2
SPS	0.499751	2.893343	0.9882

Table 4: Kinetics constants for Pseudo-second order fluoride adsorption onto the adsorbents T (K): 303; C_o (mg/L): 1000; pH: 7; M (g/l00 mL): 293-40].

Adsorbent	$h_0=k_{2,ads}\,q_e^2$ (mg/g/min)	$k_{2,ads}$ (g/mg/min)	q_e (mg/g)	R^2
SPS	11111.11	89.971	123.4568	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/l00 mL): 293-40].

Adsorbent	k_p(mg/Kg/min^2)	C	R^2
SPS	0.3752	121.74	0.9362

CONCLUSION

The adsorbent was successfully synthesized and this was confirmed by FTIR analysis which indicated the presence of the anchored functional groups. Observed changes in peaks and intensities are indications that interactions leading to the adsorption actually occurred between the adsorbents and fluoride ions. FTIR studies on fluoride removal by the adsorbents show the involvement and participation of surface sites and potential functional groups in adsorption. As confirmed by the SEM, images show morphological defects, irregular shape and coarse surfaces. According to the batch simulation tests, the adsorbent showed maximum fluoride adsorption capacity of 53.3 mg/g, which was quite high. The fluoride adsorption capacities of the adsorbents were, however, strongly controlled by solution parameters including the pH, temperature, adsorbent mass, contact time and agitation time. Optimum fluoride adsorption by the adsorbent would best be conducted in neutral pH of 7 at temperatures between 303K -323 K. The SPS showed a similarity with the C isotherm classification by Giles. However, the adsorbent did not fit on both the Langmuir and Freundlich isotherms giving R^2 of 0.1965 and 0.0421, respectively. Additionally, the fluoride adsorption data for the adsorbents were correlated to pseudo-first order, pseudo second order and Weber-Moris intraparticle diffusion kinetic models and the adsorbent proved the applicability of all the models.

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