



ADSORPTIVE FLUORIDE REMOVAL FROM AQUEOUS SOLUTION BY USING SAPONIFIED ORANGE PEEL RESIDUE IMMOBILIZED SORBENT

EVANGELINE CHRISTINA AND PRAGASAM VISWANATHAN*

*Renal Research Laboratory, School of Bio Sciences and Technology, VIT University,
Vellore-632014, Tamil Nadu, India*

ABSTRACT

Fluoride is a widespread element, which contaminates majority of the water resources in India. Fluoride, beyond its maximum permissible limit (1.5 mg/L) causes various physiological problems of which dental and skeletal fluorosis are noteworthy. This study aims to develop a sorbent, by successfully immobilizing saponified orange peel residue (SOPR) in alginate matrix and applying a 3-step modification procedure to enable F^- sorption from water. Batch equilibrium studies indicate that Langmuir model of isotherm and Pseudo second order rate kinetics were followed with a maximum sorption capacity of 7 mg/g. FTIR studies confirm the involvement of $-OH$ and carbonyl groups in F^- uptake. The morphological changes are evident in SEM micrographs. Hence electrostatic interaction and ion exchange could be the possible mechanisms by which F^- ions are removed from water. Thus the developed sorbent could be used effectively for defluoridation in areas where the F^- concentration exceeds the recommended limit.

KEYWORDS: Alginate, Fluoride, SOPR, Sorption, Surface modification



* Corresponding author

PRAGASAM VISWANATHAN

Renal Research Laboratory, School of Bio Sciences and Technology, VIT University,
Vellore-632014, Tamil Nadu, India

INTRODUCTION

Fluoride in drinking water can unquestionably be referred to a “double edged sword”, since inadequate amounts cause detrimental effects on tooth and bone development, whereas in excess (>1.5 mg/L) leads to dental and skeletal fluorosis^{1,2}. Prolonged exposure to fluoride affects most organs in the body resulting in altered metabolism very harmful to the developing children and the elderly³. Literature reveals that, India is among the 25 nations, where health problems occur due to consumption of fluoride-contaminated water. In India, approximately 62 million people, including 6 million children suffer from fluorosis⁴. Fluoride rich groundwater occurs in many parts of the world, including China, Africa, the Middle East, Turkey, Iraq, Iran, northern Thailand, Afghanistan, southern Asia including India and Sri Lanka⁵. Fluoride either occurs “naturally” in water or as a “toxic waste”. It occurs in rocks, namely sellaite, calcite, fluorapatite, fluorspar, cryolite etc. and is leached by rain to find its way to the underground water sources^{6,7}. The industrial effluents also contaminate the drinking water sources with fluoride⁸. There are a number of conventional methods of defluoridation, which includes adsorption, electro dialysis, reverse osmosis, ion exchange, ultrafiltration, etc. of which adsorption is the most efficient⁹⁻¹². In spite of successful defluoridation, many of these methods have limitations such as leaching, lesser efficiency, high operational costs etc. Here, we attempt to develop, a surface modified-saponified orange peel residue (SOPR) immobilized alginic acid sorbent to defluoridate water which is the first of this kind. Orange peel is mainly composed of cellulose, hemicellulose, chlorophyll, pectin and other low molecular weight compounds. Saponification with lime water converts the methyl ester of pectin to carboxyl group¹³. Saponification is an inevitable step in sorbent preparation, since carboxyl groups provided by the process plays a major role in sorption of fluoride ions. Alginate comprises of repeating blocks of Mannuronic and Guluronic acid residues which contains hydroxyl and carboxylic groups which participate in sorption

process^{14,15}. With all these aforementioned advantages, this study aims to develop a SOPR immobilized alginate matrix for successful defluoridation of water. This is a green technique in which waste orange peels were used to prepare a bio-degradable sorbent and is eco-friendly with literally no side effects.

MATERIALS AND METHODS

(i) Preparation of SOPR

Fresh oranges were collected from a local market in Vellore and specimens were authenticated. The peels were removed and surface sterilized with 1% sodium chloride solution. 100 g of the peel was crushed with 8 g of calcium hydroxide and after adding a substantial quantity of water; the contents were transferred to conical flasks and shaken well for 24 hr at 150 r/min in an orbital shaker to ensure complete saponification¹³. Alkaline pH of 12 was maintained and the mixture was washed repeatedly with deionized water to reduce the pH to neutrality. The mixture was stirred well and filtered using a muslin cloth. The wet residue was dried in a hot air oven at 50°C and then powdered and sieved.

(ii) Preparation and modification of the sorbent matrix

100 ml of water was added to 1.5 g of sodium alginate and heated in a water bath until alginate was completely dissolved and a clear solution was obtained. 0.5% of finely powdered SOPR was added to the alginate solution and stirred well. The SOPR-alginate suspension was added drop-wise to a 2% CaCl₂ solution using a 0.45 mm gauge syringe. The sorbent matrix was allowed to polymerize overnight and then washed well¹⁶. As the sorbent surface is anionic it requires modification for efficient fluoride ion sorption from water. The surface modification involves 3 steps; cross linking with 0.01M Glutaraldehyde, followed by Carboxylation with 0.5 M Chloroacetic acid at pH 8.0 using NaOH and finally the sorbent matrix was loaded with 5% FeCl₃.6H₂O. The un-reacted groups were washed thoroughly

after each step with double distilled water and the sorbent was dried at 50°C in a hot air oven and stored until usage¹⁷. Henceforth, the surface modified sorbent is referred to as FSOPR.

(iii) Batch sorption studies

Batch sorption studies were carried out in 250 ml Erlenmeyer flasks with 50 ml of F⁻ solution. Working solutions were diluted from the fluoride stock of 1000 (mg/L) ppm. The flasks were kept in a shaking incubator (150 r/min) at 30°C to enable sorption of fluoride ions by the modified sorbent. The amount of fluoride adsorbed, was determined at an interval of every 10 min. Reaction parameters like time, pH, sorbent dosage, temperature and initial fluoride concentration (IFC) were studied. This reaction system was further evaluated to predict the equilibrium isotherm and rate kinetic models.

(iv) Sorption isotherm

The interaction of fluoride with FSOPR at equilibrium conditions can be explained well by using adsorption isotherm models. The linearized Freundlich isotherm can be represented as¹⁸:

$$\log_{10}(q_e) = \log_{10}(K_f) + \log_{10}C_e/n \quad (1)$$

where q_e is the amount of F⁻ adsorbed at equilibrium conditions, K_f is the Freundlich constant, C_e is the residual F⁻ concentration, and n is the adsorption intensity. K_f and n values are obtained by plotting $\log_{10}(q_e)$ versus $\log_{10}(C_e)$. The linear form of Langmuir model is expressed by the equation¹³:

$$C_e/q_e = (1/q_0b) + C_e/q_0 \quad (2)$$

where C_e is the equilibrium residual F⁻ concentration, q_e is the F⁻ concentration adsorbed on the sorbent at equilibrium, q_0 is the maximum F⁻ concentration and b is the Langmuir constant. The sorption capacity of FSOPR can be theoretically explained by a plot of C_e/q_e versus C_e .

(v) Sorption kinetics

Adsorption kinetics describes the rate at which F⁻ is being adsorbed to the FSOPR sorbent surface. Lagergren's pseudo first order reaction can be given by the following equation¹⁹:

$$\log(q_e - q_t) = \log_{10} q_e - (k_1/2.303)t \quad (3)$$

where q_e and q_t are the amount of F⁻ adsorbed at equilibrium and at time t and k_1 is the pseudo first order rate constant. If pseudo first order is applicable, the plot of $\log(q_e - q_t)$ vs t gives the linear relationship with which the constant k_1 is determined. A simplified Lagergren's pseudo second order reaction can be written as^{20,21}:

$$1/(q_e - q_t) = (1/q_e) + k_2t \quad (4)$$

where q_e and q_t are the amount of F⁻ adsorbed at equilibrium and at time t , and k_2 is the pseudo second order rate constant. If pseudo second order is applicable, the plot of (t/q_t) vs t gives a linear relationship with which the constant k_2 is determined.

(vi) Characterization of the FSOPR

The elements present in the matrix, the morphological changes, the position and role of functional groups in F⁻ sorption were analyzed by characterization using XRD (BRUKER, Germany), SEM with EDX (FEI Quanta 200F, Netherland), and FTIR (AVATAR 330). The sorbent was analyzed before and after interaction with F⁻ ions.

(vii) Statistical Analysis

The Statistical analysis was done using Tukey's multiple comparison test of One way Anova by using Graph Pad Prism 5.0 software. The results were considered statistically significant, if $P < 0.05$.

RESULTS AND DISCUSSION

(i) Batch adsorption studies

(a) Effect of Time

The minimum time required for maximum sorption of F⁻ ions from water by FSOPR was determined by studying the effect of contact time on the fluoride sorption capacity of the sorbent. An IFC of 20 mg/L was used and the sorption capacity was determined at a 10 min interval until 80 min. The sorption capacity increased from 1.64 mg/g at 10 min to 5 mg/g at 50 min and remained stable thereafter. No significant increase ($P < 0.05$) was observed after 50 min. The effect of time on fluoride sorption capacity using FSOPR at equilibrium is represented in Figure 1a. The increase in sorption capacity up to 50 min and the

saturation observed thereafter could be attributed to the availability and non-availability of free active sites for F^- ions on the sorbent surface respectively. Similar results were recorded while investigating the fluoride sorption capacity of magnesia/chitosan composite²².

(b) Effect of pH

With other constant parameters namely time, sorbent dosage, IFC and temperature, the effect of pH on F^- sorption was carried out in a wide range from 3 to 9. The sorption capacity increased from 0.29 mg/g at pH 3 to 5.02 mg/g

at neutral pH and decreased when pH was increased any further. Effect of pH on equilibrium sorption of fluoride ions by FSOPR is presented in Figure 1b. This could be explained by the fact that beyond neutral pH more $-OH$ groups compete for F^- ions in solution and thereby decreased the sorption capacity. Hence pH 7.0 was fixed as optimum for any further investigations. The results obtained are in complete agreement with the investigations on the fluoride sorption by neodymium-modified chitosan²³

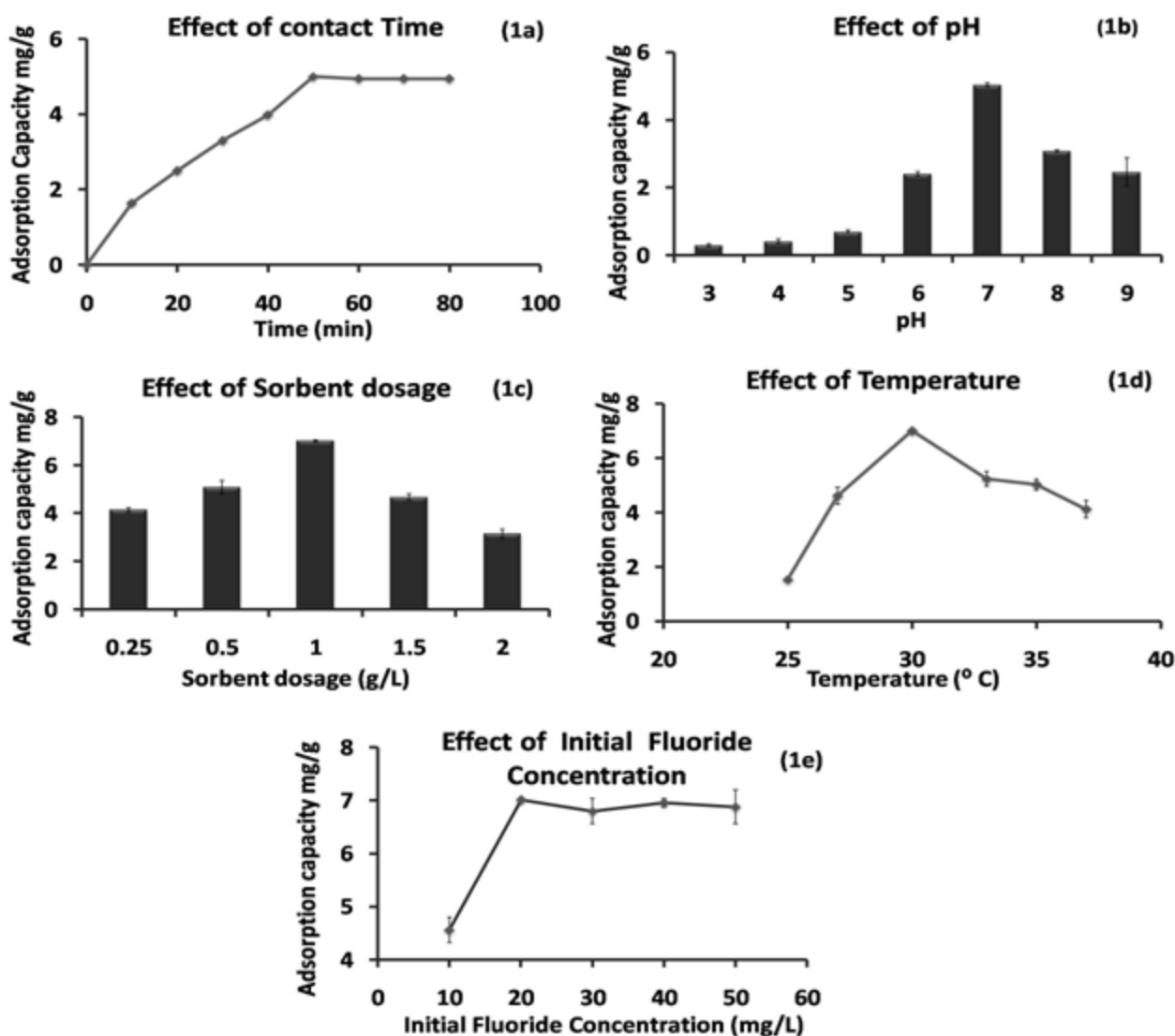


Figure 1

represents the plot of sorption capacities of FSOPR at various parameters (1a) Time, (1b) pH, (1c) Sorbent dosage, (1d) Initial fluoride concentration, (1e) Temperature

(c) Effect of sorbent dosage

To study the effect of sorbent dosage on fluoride sorption, batch studies were carried out at fixed time 50 min, and neutral pH and IFC of 20 mg/L. When the amount of FSOPR sorbent added to the fluoride solution was increased from 0.25 to 1 g/L, the fluoride sorption capacity increased from 4.13 mg/g and reached a maximum of 7 mg/g. It also presents a decreasing pattern with a gradual increase in sorbent dosage beyond 1 g/L. The effect of sorbent dosage on F⁻ sorption is represented in Figure 1c. This phenomenon can be attributed to the availability of active binding sites for F⁻ on the sorbent surface. High sorption capacity indicated the availability of free active sites, and decreased sorption capacity beyond 1 g/L indicates that the free active sites are being occupied by the F⁻ ions in solution. Hence this dosage was fixed as optimum to carry out further equilibrium studies. Supportive findings while studying the kinetics and equilibrium for treating water with high fluoride concentration by Mg-Al-CO₃ layered double hydroxides have been reported²⁴.

(d) Effect of temperature

The effect of temperature on fluoride sorption onto FSOPR was investigated at various temperatures ranging from 25 to 37°C. An increasing trend in sorption capacity (1.53 mg/g at 25°C to 7 mg/g at 30°C) with increasing temperature was observed. The sorption

capacity decreased from 7 mg/g to 4.12 mg/g when the temperature was increased to 37°C. The effect of temperature on fluoride sorption is depicted in Figure. 1d. The temperature dependency of the reaction can be explained as the tendency of the F⁻ ions to escape from the sorbent surface with an increase in temperature. A similar phenomenon has been described while investigating the fluoride sorption from aqueous solution by geomaterials²⁵.

(e) Effect of Initial fluoride concentration

The minimum fluoride concentration required for maximum fluoride sorption was determined by varying the fluoride concentration from 10 to 50 mg/L keeping other parameters constant. The sorption capacity increased from 4.56 mg/g with 10 mg/L fluoride concentration, to 7 mg/g with 20 mg/L, and there is no significant change in sorption capacity with any further increase in IFC. The effect of IFC on fluoride sorption capacity is shown in Figure 1e. This phenomenon can be inferred as the unavailability of active binding sites for the excess F⁻ ions in solution. Similar phenomenon was reported while investigating the sorption of Cd (II) and Pb (II) by exopolymeric substances (EPS) extracted from activated sludge and pure bacterial strains²⁶. A comparison of SOPR with other reported sorbents for fluoride removal is represented in Table 1.

Table 1
A comparative tabulation of sorbents used in fluoride removal from aqueous solution with the developed sorbent FSOPR

Adsorbent	Time	pH	Temperature	IFC (mg/L)	Adsorption Capacity	Reference
Aluminum impregnated chitosan	60 min	6.5	25±2°C	10	1.73 mg/g	27
Chitosan supported zirconium(IV) tungstophosphate composite	30 min	7.0	303K	10	2025-2142 mg/kg	28
Hydrotalcite/chitosan composite	30 min	Acidic	30°C	9-15	1255 mg/kg	29
Al loaded saponified orange juice residue	4h	6	30°C	1.05 mmol/dm ³	1.03 mol/kg	13
Sm(III)	~3h	5	30°C	~15	1.22 mmol/g	30
Zr(VI) loaded dried orange juice residue	4h	4	30°C	~15	1.43 mmol/g	31
FSOPR	50 min	7	30°C	20	7 mg/g	Current study

(ii) Equilibrium sorption isotherm

Equilibrium sorption analysis was performed for FSOPR under optimal conditions of, time - 50 min, pH - 7, sorbent dosage - 1g/L, temperature -30°C and IFC - 20mg/L. The reacting system was subjected to modelling using Langmuir and Freundlich isotherms. The Langmuir and Freundlich constants and correlation coefficients for fluoride sorption onto FSOPR at equilibrium conditions are represented in Table 2. FSOPR exhibited a maximum sorption capacity of 7.0 mg/g and fitted best with Langmuir model of isotherm (R^2

= 0.995). The plot of C_e/q_e versus C_e is shown in Figure 2a. Langmuir model corresponds to surface homogeneity of FSOPR matrix, and explains a single and uniform monolayer of F^- ion sorption onto the sorbent surface. F^- sorption was further enhanced by surface modification which increased the availability of active binding sites specific to F^- ions. Studies carried out on chitosan based mesoporous Ti-Al binary metal oxide supported beads for defluoridation of water is in complete agreement with the data presented in this study³².

Table 2
Isotherm constants and correlation coefficients for fluoride sorption on FSOPR at optimized conditions

System	Langmuir			Freundlich		
	q_e (mg/g)	b (L/mg)	r^2	K_f (mg/g)	n (L/mg)	r^2
FSOPR	7.008	0.524	0.995	3.706	5.464	0.671

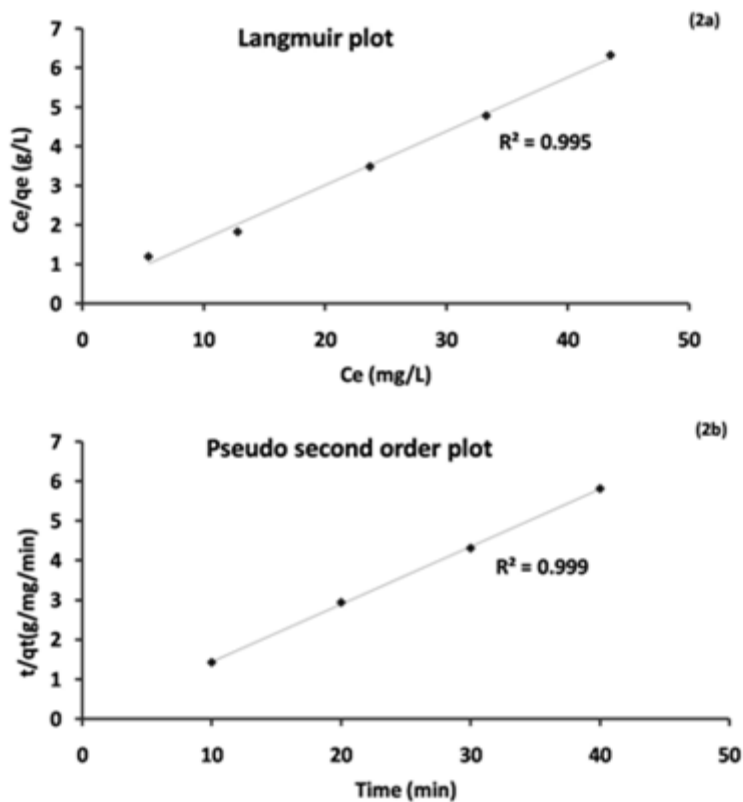


Figure 2
represents Langmuir plot (2a) and pseudo second order kinetic plot (2b) of FSOPR at equilibrium conditions

(iii) Equilibrium rate kinetics

The sorption kinetic study was carried out for FSOPR sorbent matrix at equilibrium conditions. An R^2 value of 0.999 showed that the reaction kinetics best fitted to the pseudo second order model. A plot of (t/q_t) vs t is presented as Figure 2b. Pseudo first order (k_1) and pseudo second order (k_2) rate constants are tabulated in Table

3. The pseudo second order model explains sorbent capacity as the rate limiting step, which depends on the availability of active binding sites for F^- or ion-exchange on the sorbent surface in the presence of excess F^- ions in solution. Similar results were reported by the investigations on defluoridation of drinking water using chitosan based mesoporous alumina³³

Table 3
Comparison of pseudo first order and pseudo second order rate constants for FSOPR at optimized conditions

System	Pseudo first order model			Pseudo second order model		
	k_1 (min)	q_e (mg/g)	r^2	k_2 (g/mg/min)	q_e (mg/g)	r^2
FSOPR	0.078	1.288	0.590	2.33	6.89	0.999

(iv) Characterization of the sorbent**(a) X – Ray Diffraction**

The X-ray diffraction technique was applied to the fabricated sorbent FSOPR and sodium alginate as control. The samples were dried, crushed into fine particles and subjected to XRD analysis³⁴. Figure 3a shows two peaks of Fe which is due to Fe^{3+} loading and Figure 3b shows the XRD pattern of sodium alginate which acts as control. Fe^{3+} is attributed to the fluoride sorption to the sorbent surface by electrostatic sorption mechanism¹⁷.

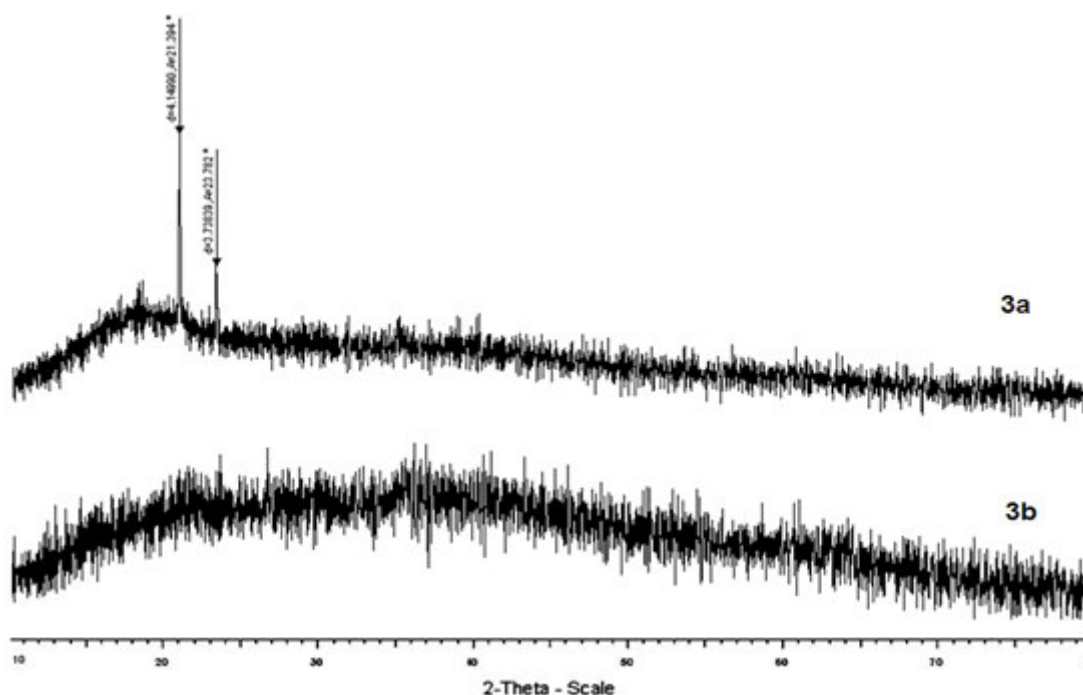


Figure 3
shows the XRD pattern of two Fe peaks which is due to Fe^{3+} loading (3a) and sodium alginate control (3b)

(b) High Resolution Scanning Electron Microscopy - Energy Dispersive X-ray spectroscopy

The FSOPR sorbent matrix is subjected to gold sputtering before SEM analysis to prevent any damage to the sorbent surface due to electrical conductivity and vacuum environment. The effect of F^- interaction on the surface morphology of FSOPR was analyzed. SEM micrographs were taken before and after interaction with F^- ions. The porous nature of the sorbent was very evident and the change in

the sorbent morphology due to F^- adsorption could be well observed. The smooth surface of the sorbent before interaction with F^- ions was found to be roughened after sorption. Energy Dispersive X-ray (EDX) analysis shows the elements present on the sorbent surface and the emergence of an extra fluoride peak shows its sorption onto the sorbent surface³⁵. The SEM micrographs of FSOPR before and after fluoride interaction are presented in Figure 4a and 4b, and their respective EDX patterns are presented in Figure 4c and 4d.

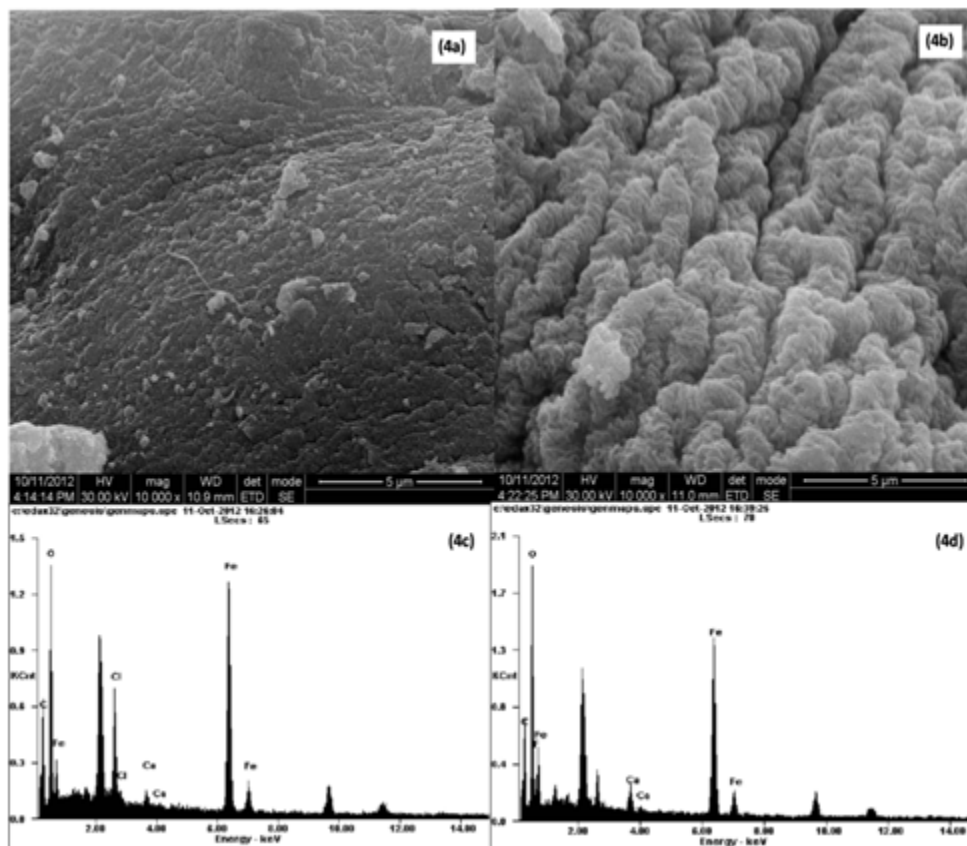


Figure 4
represents SEM micrograph of FSOPR sorbent before (4a) and after interaction (4b) with fluoride ions and their respective EDAX (4c) and (4d) pattern

(c) Fourier Transform-Infra Red Spectrometer

The chemical characteristics of FSOPR before and after interaction with F^- ions were analyzed using FTIR spectroscopy. The dried sorbent was crushed and pressed with KBr to form tiny pellets and then subjected to analysis. The peak broadening at frequencies 3421 from 3446 cm^{-1} , a slight shift from 2926 to 2931 cm^{-1} and 2854 cm^{-1} , represent $-OH$ groups which confirm

electrostatic interaction with F^- ions in solution. The presence of a peak at 1641 cm^{-1} indicates the presence and interaction of carbonyl group with F^- ion that was confirmed by the characteristic stretching³⁶. The hydroxyl ion dominates the reacting system and is available in excess; this favors F^- ion sorption by FSOPR^{13,37}. The FTIR spectrum of FSOPR before and after interaction with fluoride ions is shown in Figure 5.

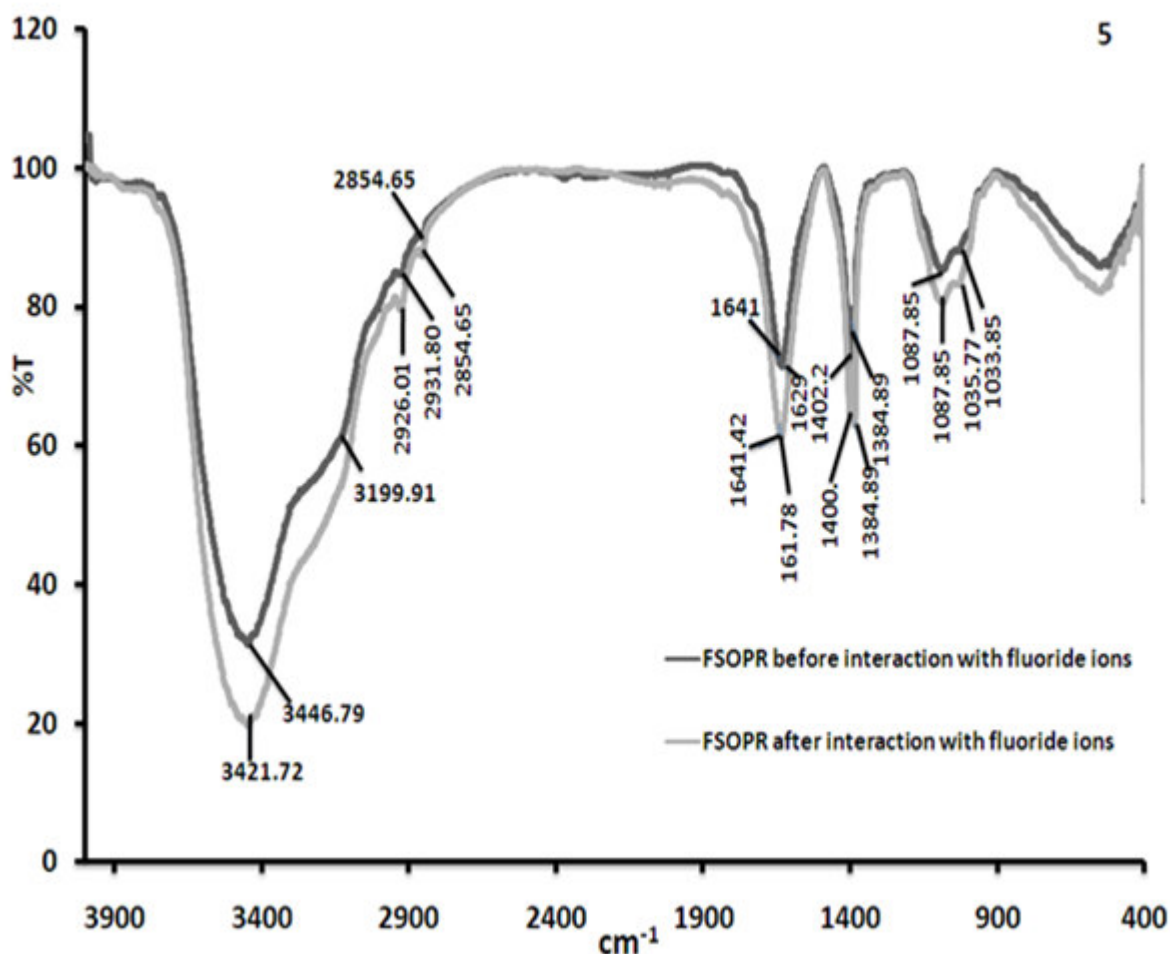


Figure 5
FTIR pattern of FSOPR before and after interaction with fluoride ions

(d) Mechanism of fluoride adsorption

The surface modifications render additional functional groups on the sorbent surface, which enable sorption of more F^- ions. Glutaraldehyde cross-linking introduces additional hydroxyl groups on the sorbent surface which are converted to carboxyl groups on subsequent carboxylation with chloroacetic acid. Following $FeCl_3$ loading, an exchange of Fe^{3+} ion for the H^+ ion of the carboxyl group can also be anticipated. The carboxyl group contains oxygen atom that might act as an electron donor to the Lewis acid and the fluoride ions

were removed by electrostatic and strong Lewis acid-base interaction³⁸. Simultaneously the oxygen atom of the pyranose ring of pectic acid and the carboxyl group of the SOPR forms a stable five membered chelate complex with the Fe^{3+} ion which adsorbs fluoride ion by electrostatic interaction. Thus electrostatic interaction and ion-exchange could be the possible mechanism of F^- removal³⁹. A schematic representation of a possible mechanism of fluoride sorption onto FSOPR matrix is presented in Figure 6a and 6b.

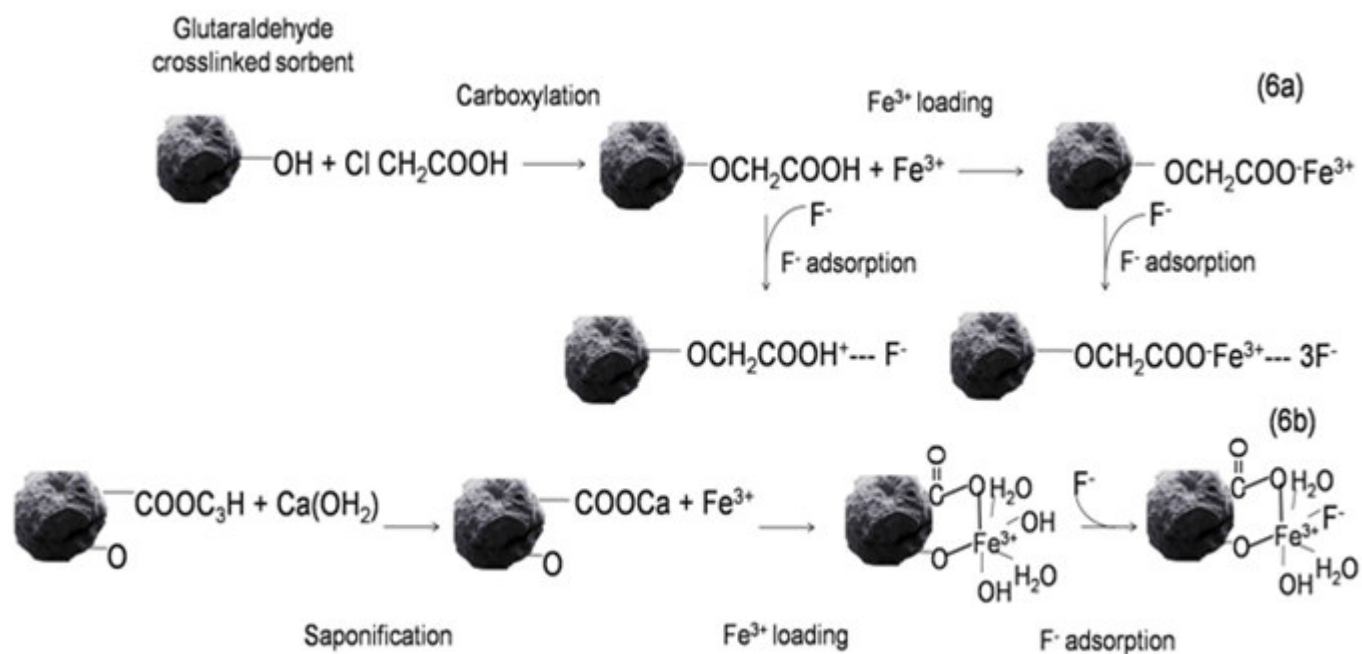


Figure 6a

and 6b schematic representation of a possible mechanism of fluoride sorption by FSOPR

CONCLUSION

The maximum sorption capacity obtained with the surface modified FSOPR sorbent was 7 mg/g, which was higher than many reported sorbents. The reaction followed Langmuir isotherm and Pseudo second order rate kinetics. The HR-SEM-EDX analysis corroborates the sorption of F^- ions onto the sorbent surface. Moreover, FTIR analysis confirms electrostatic interaction and ion exchange as the possible mechanism of F^-

removal from water. The authors have attempted for a green technique where waste orange peels were used to prepare an efficient, bio-degradable sorbent for defluoridation which is eco-friendly with literally no side effects. Hence, this FSOPR sorbent matrix could be used effectively for defluoridation in areas where the fluoride concentration exceeds the maximum permissible limit.

ACKNOWLEDGEMENT

Ms. Evangeline Christina is thankful to the VIT University, Vellore, for the resources and the Research associateship. The authors are thankful to Prof. Angeline, Department of Botany, Voorhees college, Vellore for the plant specimen authentication and SAIF, IITM for SEM micrographs.

REFERENCES

- McDonagh M.S., Whiting P.F., Wilson P.M., Sutton A.J., Chestnutt I., Cooper J., Misso K., Bradley M., Treasure E., Kleijnen J. Systematic review of water fluoridation. *BMJ*, 321 (7265): 855-859, (2000).

2. Mohapatra M., Anand S., Mishra B.K, Gileb D.E, Singh P., Review of fluoride removal from drinking water. *J Environ Manage*, 91(1): 67–77, (2009).
3. Lia Y.H., Wang S., Zhang X., Wei J., Xu C., Luan Z., Wu D. Adsorption of fluoride from water by aligned carbon nanotubes. *Mater. Res. Bull*, 38 (3): 469–476, (2003).
4. Misra K., Mishra A. Study of quaternary aquifers in Ganga Plain, India: Focus on groundwater salinity, fluoride and fluorosis. *J Hazard Mater*, 144 (1–2): 438-448, (2007).
5. NRC (National Research Council). Fluoride in Drinking Water: A Scientific Review of EPA's Standards. The National Academies Pres: Washington, DC (2006).
6. Dissanayake B. The fluoride problem in the groundwater of Sri Lanka – environmental management and health, *Int J Environ Stud*, 38 (2-3): 137-155, (1991).
7. Murthy S.S., Murthy D.V.R. A study of high fluoride bearing waters around Nalgonda town, Nalgonda district in A.P. Indian academy of geological science, proceedings, symposium on Fluorosis, Hyderabad, 1974, pp. 311–315.
8. Brougham K.M., Roberts S.R., Davison A.W., Port G.R. The impact of aluminium smelter shut-down on the concentration of fluoride in vegetation and soils. *Environ Pollut*, 178: 89-96, (2013).
9. Amor Z., Bariou B., Mameric N., Taky M., Nicolas S., Elmidaoui A., Fluoride removal from brackish water by electrodialysis. *Desalination*, 133 (3): 215–223, (2001).
10. Anand B.C., Sujish D., Murugappa M.S., Mohanakrishnan G., Kalyanasundaram P., Baldev R. A comprehensive treatment method for defluoridation of drinking water. *Indian J Chem Technol*, 18 (4): 314-318, (2011).
11. Essadki H., Gourich B., Vial Ch., Delmas H., Bennajah M. Defluoridation of drinking water by electrocoagulation/ electroflotation in a stirred tank reactor with a comparative performance to an external-loop airlift reactor. *J Hazard Mater*, 168 (2–3): 1325–1333, (2009).
12. Parthasarathy N., Uffle J.Y.B., Haerdi W. Study of interaction of polymeric aluminium hydroxide with fluoride. *Can J Chem*, 64 (1): 24-29, (1986).
13. Paudyal H., Pangen B., Inoue K., Kawakit H., Ohto K., Harada H., Alam S. Adsorptive removal of fluoride from aqueous solution using orange waste loaded with multi-valent metal ions. *J Hazard Mater*, 192 (2): 676–682, (2011)
14. Haug A., Larsen B., Smidsrod O. Uronic acid sequence in alginate from different sources. *Carbohydr Res*, 32 (2): 217-225, (1974).
15. Rodrigues J.R., Lagoa R. Copper Ions Binding in Cu-Alginate Gelation. *J Carbohydr Chem*, 25 (2-3): 219-232, (2006).
16. Wu D., Zhao J., Zhang L., Wu Q., Yang Y., Lanthanum adsorption using iron oxide loaded calcium alginate beads. *Hydrometallurgy*, 101 (1-2): 76–83, (2010).
17. Viswanathan N., Meenakshi S. Selective sorption of fluoride using Fe (III) loaded carboxylated chitosan beads. *J Fluorine Chem*, 129 (6): 503–509, (2008).
18. Cai P., Zheng H., Wang C., Ma H., Hu J., Pu Y., Liang P. Competitive adsorption characteristics of fluoride and phosphate on calcined Mg–Al–CO₃ layered double hydroxides. *J Hazard Mater*, 213–214: 100–108, (2012).
19. Lagergren S. Zur theorie der sogenannten adsorption geloester stoffe, *K Sven Vetenskapsakad Handl*, 24: 1–39, (1898).
20. Kamga E.T., Ngameni A., Darchen A. Evaluation of removal efficiency of fluoride from aqueous solution using new charcoals that contain calcium compounds. *J Colloid Interface Sci*, 346 (2): 494–499 (2010).
21. Nie Y., Hu C., Ko C., Enhanced fluoride adsorption using Al (III) modified calcium Hydroxyapatite. *J Hazard Mater*, 233–234: 194–199, (2012).
22. Sundaram C.S., Viswanathan N., Meenakshi S. Defluoridation of water using magnesia/chitosan composite. *J Hazard Mater*, 163 (2-3): 618–624, (2009).
23. Yao R., Meng F., Zhang L., Ma D., Wang M. Defluoridation of water using neodymium-modified chitosan, *J Hazard Mater*, 165 (1-3): 454–460, (2009).

24. Lv L., He J., Wei M., Evans D.G., Zhou Z. Treatment of high fluoride concentration water by Mg-Al-CO₃ layered double hydroxides: kinetic and equilibrium studies. *Water Res*, 41 (7): 1534–1542, (2007).
25. Sujana M.G., Pradhan H.K., Anand S., Studies on sorption of some geomaterials for fluoride removal from aqueous solutions, *J Hazard Mater*, 161 (1): 120–125, (2009).
26. Guibaud G., Hullebusch E., Bordas F., d'Abzac P., Joussein E. Sorption of Cd(II) and Pb(II) by exopolymeric substances (EPS) extracted from activated sludges and pure bacterial strains: Modeling of the metal/ligand ratio effect and role of the mineral fraction, *Bioresour Technol*, 100 (12): 2959–2968, (2009).
27. Swain S., Dey R.K., Islam M., Patel R.K., Jha U., Patnaik T., Airoldi C. Removal of Fluoride from Aqueous Solution Using Aluminum-Impregnated Chitosan Biopolymer. *Sep Sci Technol*, 44 (9): 2096–2116, (2009).
28. Viswanathan N., Meenakshi S. Development of chitosan supported zirconium (IV) tungstophosphate composite for fluoride removal. *J Hazard Mater*, 176 (1-3): 459–465, (2010a).
29. Viswanathan N., Meenakshi S. Selective fluoride adsorption by a hydrotalcite/chitosan composite. *Appl Clay Sci*, 48 (4): 607–611 (2010b).
30. Paudyal H., Pangen B., Ghimire K.N., Inoue K., Ohto K., Kawakita H., Alam S. Adsorption behavior of orange waste gel for some rare earth ions and its application to the removal of fluoride from water. *Chem Eng J*, 195–196: 289–296, (2012).
31. Paudyal H., Pangen B., Inoue K., Kawakita H., Ohto K., Ghimire K.N., Harada H., Alam S. Adsorptive removal of trace concentration of fluoride ion from water by using dried orange juice residue. *Chem Eng J*, 223: 844–853, (2013).
32. Thakre D., Jagtap S., Sakhare N., Labhsetwar N., Meshram S., Rayalu S. Chitosan based mesoporous Ti–Al binary metal oxide supported beads for defluoridation of water. *Chem Eng J*, 158 (2): 315–324, (2010).
33. Jagtap S., Yenkie M.K.N., Labhsetwar N., Rayalu S. Defluoridation of drinking water using chitosan based mesoporous alumina. *Microporous Mesoporous Mater*, 142 (2-3): 454–463, (2011).
34. Lim S.F., Zheng Y.M., Zou S.W., Chen J.P. Uptake of arsenate by an alginate-encapsulated magnetic sorbent: Process performance and characterization of adsorption chemistry. *Colloid Interface Sci*, 333 (1): 33–39, (2009).
35. Yakun H., Wenming D., Xia H., Jingnian X., Menghua Z. Fluoride Removal by Lanthanum Alginate Bead: Adsorbent Characterization and Adsorption Mechanism. *Chin J Chem Eng*, 19 (3): 365–370, (2011).
36. Viswanathan N., Sundaram C.S., Meenakshi S. Development of multifunctional chitosan beads for fluoride removal. *J Hazard Mater*, 167: 325–331, (2009).
37. Vijaya Y., Popuri S.R., Reddy A.S., Krishnaiah A. Synthesis and characterization of glutaraldehyde-crosslinked calcium alginate for fluoride removal from aqueous solutions. *J Appl Polym Sci*, 120 (6): 3443–3452, (2011).
38. Dąbrowski A., Hubicki Z., Podkościelny P., Robens E. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere*, 56 (2): 91–106, (2004).
39. Biswas K., Inoue K., Ghimire K., Ohta S., Harada H., Ohto K., Kawakita H. The adsorption of phosphate from an aquatic environment using metal-loaded orange waste. *J Colloid Interface Sci*, 312 (2): 214–223, (2007).