



Matrix supported tailored polymer for solid phase extraction of fluoride from variety of aqueous streams

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ABSTRACT

Fluoride related health hazards (fluorosis) are a major environmental problem in many regions of the world. It affects teeth; skeleton and its accumulation over a long period can lead to changes in the DNA structure. It is thus absolutely essential to bring down the fluoride levels to acceptable limits. Here, we present a new inorganic–organic hybrid polymer sorbent having tailored fixed-sites for fluoride sorption. The matrix supported poly (bis[2-(methacryloyloxy)-ethyl]phosphate) was prepared by photo-initiator induced graft-polymerization in fibrous and microporous (sheet) host poly(propylene) substrates. These substrates were conditioned for selective fluoride sorption by forming thorium complex with phosphate groups on bis[2-(methacryloyloxy)-ethyl] phosphate (MEP). These tailored sorbents were studied for their selectivity towards fluoride in aqueous media having different chemical conditions. The fibrous sorbent was found to take up fluoride with a faster rate (15 min for $\approx 76\%$ sorption) than the sheet sorbent. But, the fluoride loading capacity of sheet sorbent (4320 mg kg^{-1}), was higher than fibrous and any other sorbent reported in the literature so far. The sorbent developed in the present work was found to be reusable after desorption of fluoride using NaOH solution. It was tested for solid phase extraction of fluoride from natural water samples.

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1. Introduction

Fluoride in drinking water has a profound effect on teeth and bones. According to World Health Organization (WHO) guidelines, the fluoride concentration in drinking water should not exceed 1.5 mg L^{-1} [1]. Up to a small level ($1\text{--}1.5 \text{ mg L}^{-1}$) this strengthens the enamel. Concentrations in the range of $1.5\text{--}4 \text{ mg L}^{-1}$ result in dental fluorosis. In the case of prolonged exposure at still higher fluoride concentrations ($4\text{--}10 \text{ mg L}^{-1}$), the dental fluorosis progresses to skeletal fluorosis [2,6]. The fluoride occurs in nature mainly as sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). These fluoride minerals are nearly insoluble in water. Hence fluoride will be present in groundwater only when conditions favor their dissolution or high fluoride containing effluents are discharged to the water bodies from the industries. High fluoride concentrations in groundwater, up to more than 30 mg L^{-1} , have been observed widely in many parts of the world [3–6].

Different methods are being used for the removal of fluoride from water [2]. These methods are based on the principle of adsorption [7], ion-exchange [8], precipitation–coagulation [9,10], and

membrane separation process [2,11–26]. Ion-exchange methods are usually non-selective. The most commonly adopted method in India is Nalgonda technique of community defluoridation, which is based on the precipitation process [7]. The major limitations of Nalgonda technique are daily addition of chemicals, large amount of sludge production and it is least effective with water having high total dissolved solids and hardness. Moreover, it converts a large portion of ionic fluoride into soluble aluminum complex and practically removes only a small portion of it (18–33%) [7]. Residual aluminum from 2.01 to 6.86 mg L^{-1} was also reported which is dangerous to human health as aluminum is a neurotoxin, concentration as low as 0.08 mg L^{-1} in drinking water has been reported to cause Alzheimer's disease. The membrane and adsorbent based separation methods are most popular because of their simplicity, cost effectiveness and amenability to process large volume of the water streams.

Membrane based processes suggested for defluoridation are reverse osmosis [11,12], nanofiltration [13–16], membrane distillation [17], Donnan dialysis [18–21] and electrodialysis [22–26]. Although membrane based methods have successfully reduced fluoride concentration to acceptable levels, the surface adsorption retains a major place in defluoridation research and practice because of its greater accessibility and lower cost. The development of low-cost and effective adsorbents and to improve efficiency of all

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the adsorbents has been a major area of research for defluoridation of aqueous streams [27–34]. Alumina and alumina coated materials are used as adsorbents for fluoride and heavy metal removal [2]. Alumina immobilized in chitosan has been found to be superior to other inorganic sorbents and inorganic particles immobilized in polymer matrix [35].

In the present work, we have developed a new inorganic–organic hybrid polymer sorbent having tailored fixed-sites for fluoride sorption. In order to achieve chemically and mechanically a uniform material all the components have been incorporated in the membrane by chemical bonds. The sorbents have been developed by photo-initiator induced graft-polymerization of a precursor monomer bis[2-methacryloyloxy)-ethyl] phosphate (MEP) on poly(propylene) chains. The selection of precursor monomer has been based on its ability for highly stable complex formation with Th(IV) ions. The thorium has high chemical affinity towards fluoride [36] and un-neutralized positive charge on Th(IV) in the sorbent provided fixed positive charges for fluoride sorption. The host poly(propylene) provides mechanical integrity for using these as the flat sheet sorbent or membrane. Two types of poly(propylene) host substrates used are microporous and thermally bonded fibrous sheets. These sorbents have been characterized in terms of parameters that influence the defluoridation of aqueous streams like pH, loading capacity, contact time, effects of competing ions, reusability and chemical stability of Th complex in the host matrix. Finally, the optimized sorbent was examined for its efficacy for fluoride removal from real water samples.

2. Experimental

2.1. Reagents and apparatus

Bis[2-methacryloyloxy)-ethyl] phosphate (MEP), N-methylene-bis-acrylamide (MBA), and α,α' -dimethoxy- α' -phenyl acetophenone (DMPA) were obtained from Sigma–Aldrich (Steinheim, Switzerland). Tetrahydrofuran (THF), methanol, and N,N-dimethylformamide (DMF) were obtained from Merck (Mumbai, India). Thermally bonded non-woven poly(propylene) macroporous fibrous sheet (NK Filter Fabric, Mumbai, India) was used as a substrate for grafting MEP. This fibrous substrate was having thickness ≈ 2 mm and density ≈ 0.26 g cm⁻³. Another substrate used for grafting was microporous poly(propylene) flat sheet membrane (Accurel® 1E R/P from Membrana) having nominal pore size of 0.1 μ m and thickness of 92.5 μ m. The scanning electron microscopic images of these substrates are given in Fig. 1.

The thickness of the membrane samples was measured using a digital micrometer (Mitutoyo, Japan) with a precision of ± 0.001 mm. Multilamp photoreactor from Heber Scientific (model No. HML-SW-MW-LW-888) having six UV lamps (8 W) arranged in a circle was used for photo-initiator induced grafting. EDXRF measurements were carried out using an EX 3600-M spectrometer, Jordon valley AR Ltd. (Migdal Haemek, Israel). Determination of thorium in the aqueous solutions treated with the membrane sample was carried out using a VG PQ Ex Cell (Thermo Elemental) inductively coupled mass spectrometry ICP-MS. Fluoride concentrations in aqueous samples were determined by Metrohm Ion Chromatograph.

2.2. Preparation of sorbents

The steps involved in the preparation of membrane are given in Scheme 1. Briefly, the polymerizing solution was prepared by dissolving monomer MEP and cross-linker MBA (5 mol% of monomer) in 1:1 mixture of DMF and methanol. The UV-initiator DMPA was

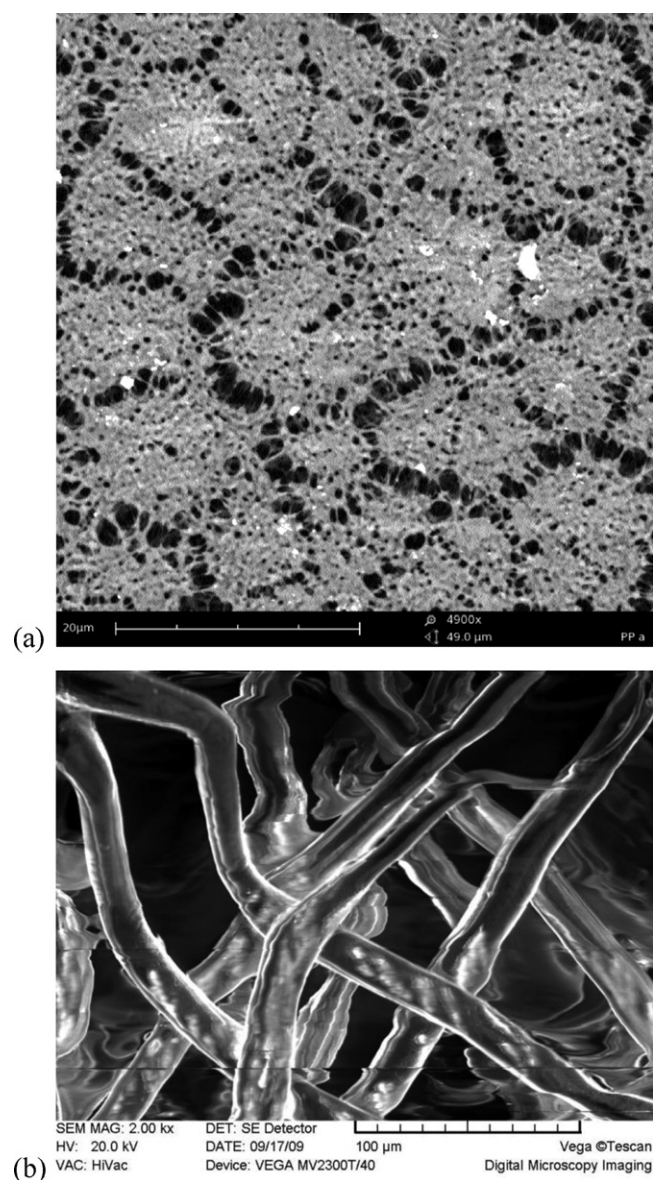
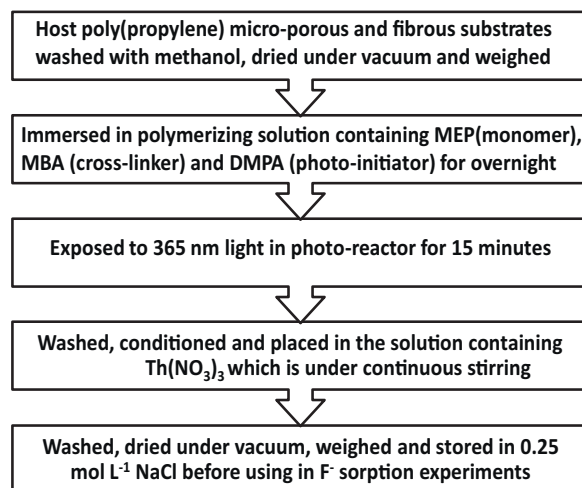


Fig. 1. SEM images of host poly(propylene) microporous (a) and fibrous (b) substrates used for preparing grafted sorbents.



Scheme 1. Steps involved in the preparation of tailored sorbents for fluoride uptake.

added to this solution. The amount of UV-initiator was taken as 1 wt.% as this was found to be minimum quantity required to initiate the bulk polymerization. The host poly(propylene) microporous and fibrous host substrates (5×5 cm area) were immersed in the polymerizing solution for overnight. The excess of polymerizing solution adhering on the surface was removed. This solution filled substrate was sandwiched between two transparent polyester sheets to prevent any possible loss of solution filled in the pores. Care was taken to remove excess grafting solution and air bubbles trapped between the membrane and polyester sheets covering the membrane surface. Finally, the sandwiched substrates were exposed to 365 nm UV light in a multilamps photoreactor for a period of 15 min. After exposure in the photoreactor, the membranes were washed thoroughly with hot DMF, methanol and distilled water to remove the un-polymerized components. The substrate was washed till a constant weight of the membrane sample was obtained. Conditioning of the grafted samples was carried out by immersing them in aqueous solution having 0.25 M NaCl for 24 h. Finally, these substrates were equilibrated with 25 mL of $\text{Th}(\text{NO}_3)_4$ having 100 g L^{-1} concentration in 1 M HNO_3 for overnight with constant stirring. After equilibration, samples were washed thoroughly with 1 M HNO_3 and water, and used for the experiments.

2.3. Characterization of sorbents

The extent of cross-linked polymer anchored in the host substrate was determined gravimetrically using the following equation:

$$\% \text{degree of anchoring} = \frac{(W_f - W_i)}{W_i} \times 100 \quad (1)$$

where W_i and W_f are the dry weights of nascent and grafted Th-loaded sorbents, respectively. The presence of thorium in the sorbents was confirmed from EDXRF measurements. $\text{Th } L_\alpha$ at 12.96 keV and $\text{Th } L_\beta$ at 16.199 keV were used for Th determination. Sorbent samples were equilibrated with aqueous solutions containing varying acidities for one week to examine the extent of leaching out of Th from the sorbent. The amounts of Th leached out in the equilibrated solutions were measured by ICP-MS.

2.4. Fluoride sorption–desorption experiments

The fluoride sorption experiments were carried out using thorium loaded sorbents having $1 \times 1 \text{ cm}^2$ area. The experiments were carried out using well-stirred standard solutions (25 mL) containing 1 mg L^{-1} , 5 mg L^{-1} and 10 mg L^{-1} fluoride. To test the selectivity of the sorbent towards fluoride, these experiments were repeated in the presence of known concentration of certain competing ions like chloride, nitrate, sulphate, bicarbonate and phosphate along with fluoride. After continuous equilibration with stirring using a magnetic stirrer for a predetermined time interval, the sorbent samples were taken out and fluoride concentrations left in aqueous samples were determined by Metrohm Ion Chromatograph. In the case of interference studies, the samples were diluted prior to determination for preventing the column overloading in Ion Chromatograph. All the experiments were carried out at ambient temperature ($25 \pm 2^\circ \text{C}$). The desorption experiments were carried out by equilibrating fluoride loaded sample in solutions containing NaOH ($\text{pH} \geq 10$). For this study, the fluoride loaded membranes were placed in 20 mL NaOH solutions and kept for a period of 24 h. The solutions were analyzed for fluoride concentrations before and after removing the sorbents.

3. Results and discussion

3.1. Preparation and characterizations of sorbents

The extent of grafting of monomer MEP along with cross-linker MBA in the microporous poly(propylene) host substrates was found to be $130 \pm 10 \text{ wt.}\%$. The scanning electron microscopic (SEM) images showed that the pores of host substrate (Fig. 1a) were completely blocked. The grafting yields in fibrous substrate were $100 \pm 10 \text{ wt.}\%$. In fibrous substrates void spaces between the fibers were not affected. However, the size of fibers in grafted fibrous substrate was ranged from 20 to $30 \mu\text{m}$. Thus, physical structures of these two grafted substrate were quite different. The exchange sites were more accessible in fibrous substrate than the densely blocked cross-linked poly-MEP sheet host substrate. All grafted membranes prepared in the present work were found to sorb water up to 40–45 wt.%.

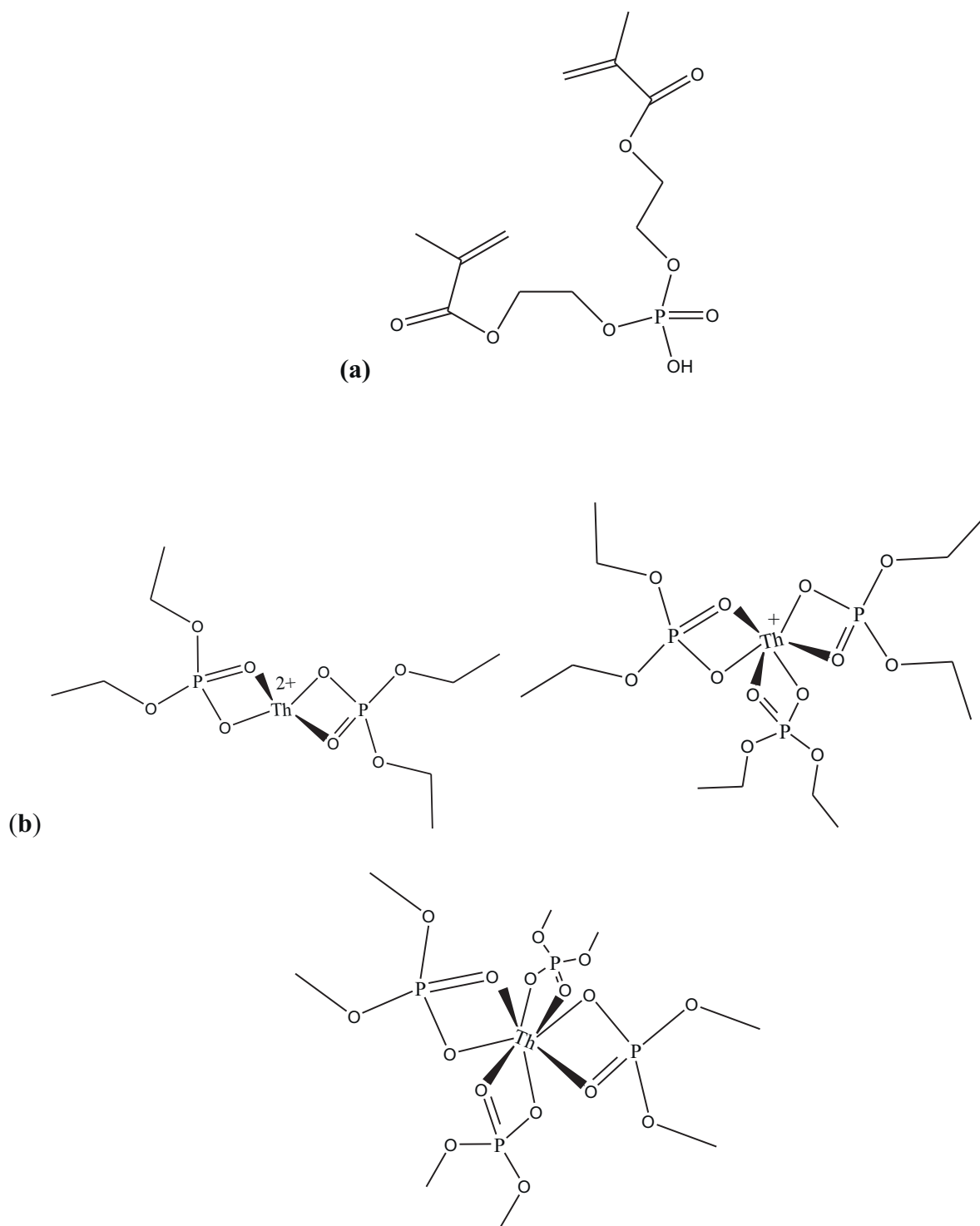
It is clear from the chemical structure of MEP, given in Scheme 2a, that the sorbents have fixed mono-acidic phosphate groups. It is well known that phosphate groups have high affinity towards Th(IV) ions. Thus, Th(IV) ions can be strongly bound in the MEP-grafted poly(propylene) sorbents. However, it is difficult to neutralize all the four positive charges on Th ions in the sorbents due to geometrical constraint of cross-linking. This may result in one or two positive charges due to non neutralization of charge on the complex of Th-phosphate in the sorbent as shown in Scheme 2b. Since Th(IV) has affinity towards fluoride, the fixed positive charges on complexed Th(IV) ions provide binding sites for fluoride. Thus, the fluoride removal by the thorium loaded membrane appears to be controlled by electrostatic and complexation as shown in Scheme 2c.

Th(IV) ions in the sorbent samples were loaded from 1 mol L^{-1} HNO_3 containing excess of Th(IV) ions as described in Section 2. The presence of Th(IV) in the sorbents was confirmed by EDXRF analysis and a typical spectrum is shown in Fig. 2. In order to test stability of the Th-complex in the sorbent, thorium leaching from the sorbents was studied in ground water and aqueous solutions with varying pH. ICP-MS analyses confirmed that there was no leaching of thorium from the sorbent in the treated aqueous samples.

3.2. Sorption and desorption of fluoride

The small samples ($1 \times 1 \text{ cm}^2$) of sheet Th-MEP-sorbent were equilibrated for overnight with 25 mL of solutions containing known concentration of fluoride. Fluoride uptake at each concentration of fluoride was calculated from the difference of fluoride concentration before and after equilibration and the results thus obtained are plotted as a function of concentration in Fig. 3. It is seen from this figure that fluoride is quantitatively sorbed (>80%) in the sorbent up to a concentration of 6–7 mg L^{-1} , and thereafter decrease due to saturation of binding sites in the sorbent. Similar observation was obtained by using fibrous sorbent. In order to determine the loading capacity of fluoride in sheet and fibrous sorbents, the samples of known weights were equilibrated with solutions containing excess of fluoride. The fluoride uptake capacities in the sheet and fibrous sorbents were found to be 0.24 meq g^{-1} and 0.09 meq g^{-1} , respectively.

The comparison of fluoride loading capacities of different sorbents developed in the present work with those reported in literature is given in Table 1. It is evident from this comparison that sheet sorbent developed in the present work has maximum fluoride loading capacity (4320 mg kg^{-1}) among the sorbents reported in literature [35,37–45] and fibrous sorbent has lower fluoride loading capacity (1620 mg kg^{-1}). This is because of the fact that MEP grafted on fibrous substrate may have close proximity of the phosphate groups that may neutralize +ve charges on Th(IV) ions compared to



Scheme 2. Chemical structures of MEP grafted (a) and different possible complexes of Th(IV)-phosphate sites (b) in the poly(propylene) sorbents. (c) Mechanism of fluoride uptake by thorium loaded membrane.

that in the pores of sheet sorbent. The higher fluoride loading capacity of the sorbent developed in the present work can be attributed to high +ve charge density obtained by high degree of grafting of MEP that have phosphate groups for complexation with Th(IV) ions. Also, the high degree of cross-linking prevents neutralization of +ve charge on thorium ions in the complex as shown in Scheme 2b. The higher fluoride loading capacity of the sorbent developed in the present work would lead to lower inventory of the sorbent for defluoridation of aqueous streams. It is also important to note that

the sorbents developed in the present work is in the form of sheets and therefore they have better mechanical integrity and are more amenable to use for defluoridation. Using bulk polymerization, the Th-poly(MEP) can be made in the bead forms for using it in the ion-exchange column.

The chemical conditions of aqueous media may also influence the uptake of fluoride. One of the important parameters is pH of aqueous streams. The uptake of fluoride in Th-MEP sorbent ($1 \times 1 \text{ cm}^2$) from 25 mL solution having fluoride concentration of

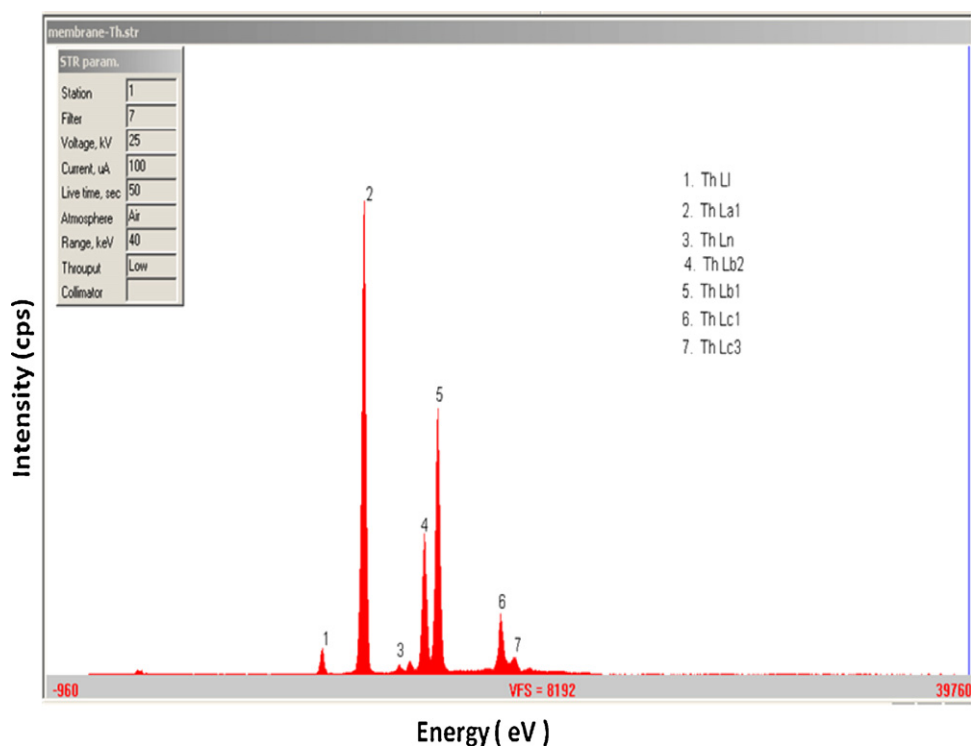


Fig. 2. EDXRF spectrum of thorium-loaded MEP-sorbent.

5 mg L⁻¹ was studied as a function of pH of equilibrating solution. The results thus obtained are shown in Fig. 4. It is seen that uptake in the sorbent remained fairly constant and the values are 86 ± 2% from pH 1 to 3 and 77 ± 2% from pH 4 to 7. The free anions concentration in aqueous solution is governed by the dissociation constant of the acid. HF is a weak acid having pK_a values of 3.14. Thus, the change in degree of dissociation of HF is expected on increasing pH from 3 to 4. Thus, it appears from the variation of fluoride removal efficiency of the Th-MEP sorbent as a function of pH of equilibrating solution that fluoride exchange equilibrium shift to membrane side at lower pH. This is due to complexation of HF with neutral Th-MEP binding sites as it does not require electrostatic charge neutralization. Thus, the Th-MEP sites that did not have +ve charge as shown in Scheme 2b could act as the binding sites for un-dissociated

fluoride. However, the Th-MEP sites without residual positive charge in the sorbent should be small in number due geometrical constraint of the cross-linked polymer chains. This explains why there is fixed 10% decrease in fluoride removal efficiency of Th-MEP sorbent from pH ranging from 4 to 7. It is also reported in the literature that the high degree of association (low dissociation) of the acid favors its transfer in the membrane phase [49]. The uptake of fluoride in the sorbent sample was found to decrease with increase

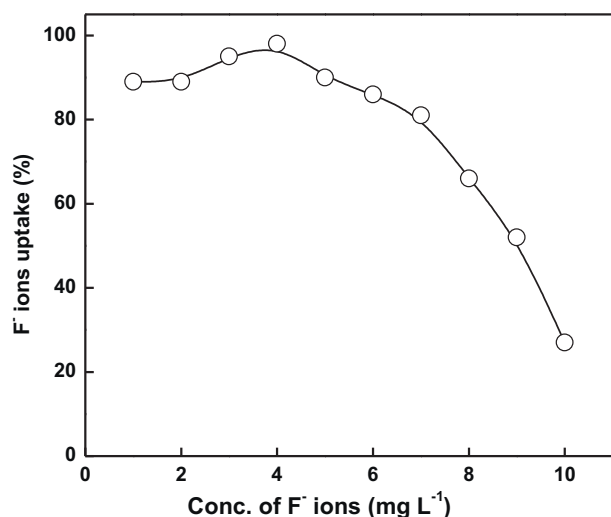


Fig. 3. Uptake of fluoride in fixed size (1 × 1 cm²) Th-MEP sheet sorbent.

Table 1
Comparison of fluoride loading capacities in different sorbents.

Sorbents	Defluoridation capacity (mg F ⁻ kg ⁻¹)	Ref.
Th-MEP grafted in fibrous poly(propylene)	1620	Present work
Th-MEP grafted in sheet poly(propylene)	4320	Present work
Alumina/chitosan composite	3809	[35]
Nano-hydroxyapatite/chitin composite	2840	[37]
Polyacrylamide Ce(IV) phosphate	2290	[38]
Polyacrylamide Zr(IV) phosphate	2166	[38]
Polyacrylamide Al(III) phosphate	2144	[38]
Activated alumina	2136	[39]
Zirconium (IV) tungstophosphate/chitosan composite	2025	[40]
Nano-hydroxyapatite/chitosan composite	1560	[41]
Nano-hydroxyapatite	1296	[42]
Protonated chitosan beads	1664	[43]
Carboxylated chitosan beads	1385	[44]
Pumice	310	[45]
Modified kaolinite clay	105	[46]
Commercial ion-exchange resin	97	[47]

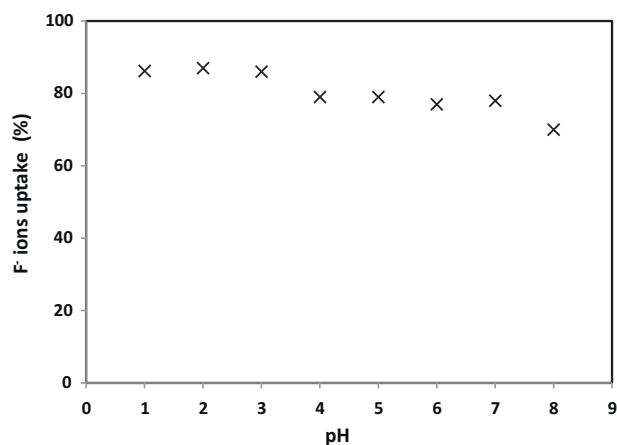


Fig. 4. Uptake of fluoride in Th-MEP sheet sorbent as a function of pH of equilibrating solution.

in the pH above 7. This may be due to the increased OH^- concentration with the increase in pH that competed with the fluoride. However, the wide range of pH (1–7) for fluoride uptake is good enough to make it applicable for a variety of aqueous feed ranging from natural water to industrial acidic waste streams.

As uptake of fluoride is reduced at higher pH, desorption of fluoride from the sorbent were studied by equilibrating fluoride loaded sorbent with NaOH solution of different pH. It is seen from Fig. 5 that desorption of fluoride was not quantitative up to pH 11. However, more than 70% of fluoride was desorbed from the sorbent by onetime equilibration with a solution having pH 13. Three times equilibration with 0.1 M NaOH solution lead to 90% regeneration of the membrane. This indicates that the sorbent developed in the present work is reusable.

The ground water contains several other anions along with fluoride such as chloride, nitrate, phosphate, sulphate and bicarbonate. These anions can compete with fluoride for the binding sites in the sorbents. To study the interference of competing ions, the sorbent samples were equilibrated with solution containing binary mixture of fluoride and one of the competing anions. The initial concentration of fluoride was fixed at 5 mg L^{-1} while for other ions two concentrations i.e. 20 mg L^{-1} and 150 mg L^{-1} were used. The results of this study are presented in Fig. 6. It is seen from this figure that all other competing anions like Cl^- , NO_3^- and SO_4^{2-} have

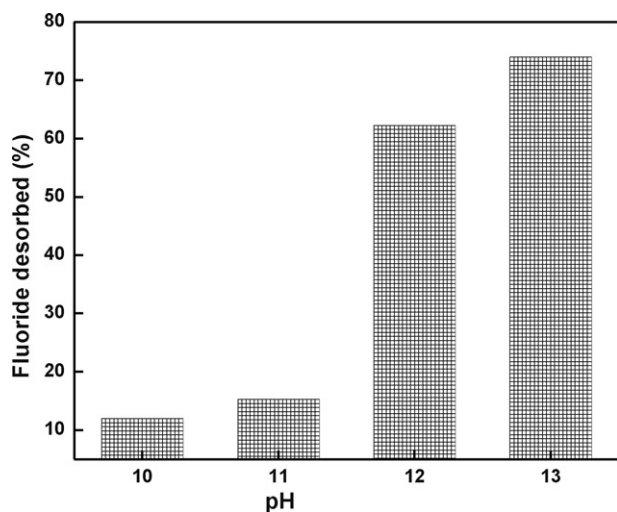


Fig. 5. Desorption of fluoride from the sorbent in aqueous solution having basic range of pH.

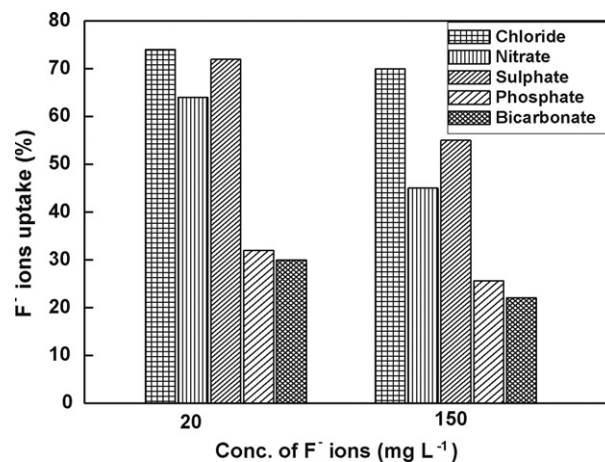


Fig. 6. Effect of different competing anions on fluoride uptake in Th-poly(MEP) sheet sorbent at fixed fluoride concentration (5 mg L^{-1}) in solution.

negligible effect on fluoride sorption at a concentration of 20 mg L^{-1} except PO_4^{3-} and HCO_3^- . Fluoride sorption capacity was reduced by $\sim 30\text{--}35\%$ and by $\sim 40\text{--}45\%$ for an initial concentration of PO_4^{3-} and HCO_3^- of 20 mg L^{-1} and 150 mg L^{-1} , respectively. The anions NO_3^- and SO_4^{2-} also affect fluoride sorption by about $\sim 20\%$ at 150 mg L^{-1} concentration of these ions. It could be seen that phosphate and bicarbonate interfere with fluoride sorption because of their higher affinity with thorium ions complexed with poly(MEP) in the sorbent. It is evident from Fig. 6 that sorbent has high affinity towards fluoride with respect to Cl^- ions.

3.3. Sorption kinetics

For selecting optimum operating conditions for a full scale batch process kinetics is very important for designing any sorbent system. The uptake of fluoride by these Th(IV) ions loaded sorbents as a function of equilibration time were studied in the well stirred solution having a fixed initial concentration of fluoride as 5 mg L^{-1} . In sheet sorbent it is observed that within 180 min 60% of fluoride was removed and equilibrium uptake ($\sim 90\%$) was obtained after 9 h of equilibration (ca. Fig. 7a). As accessibility of binding sites in densely grafted microporous sorbent is limited at its surface, the initial fluoride uptake might be faster and slowed down as surface binding sites were saturated. To improve the sorption kinetics, the fibrous Th-poly(MEP) sorbent was developed. In fibrous Th-MEP sorbent $\sim 76\%$ of the fluoride sorption took place in first 15 min and reached to $\sim 90\%$ within 50 min of equilibration time (Fig. 7b). Thus, fibrous Th-poly(MEP) sorbent is better sorbent than sheet sorbent in terms of sorption kinetics.

To test whether the removal process followed first order or second order kinetics, the fluoride sorption data were analyzed using two mass transfer models. These models are Lagergren's pseudo first order rate equation and pseudo second order rate equation [48,50,51]. The mathematical representations of these models are as follows:

$$\log(q_e - q_t) = \log q_e - k_1(t/2.303) \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_0^2} + \frac{1}{q_0 t} \quad (3)$$

where q_e and q_t are the amount of fluoride adsorbed at equilibrium and at time 't', respectively, q_0 is the maximum adsorption capacity. The plots for both the above equations for sheet and fibrous Th-poly(MEP) sorbents are shown in Fig. 8. The adsorption rate constant (k_1 and k_2) and correlation coefficient (R^2) were calculated from the plots and are given in Table 2. The plot of t/q_t against

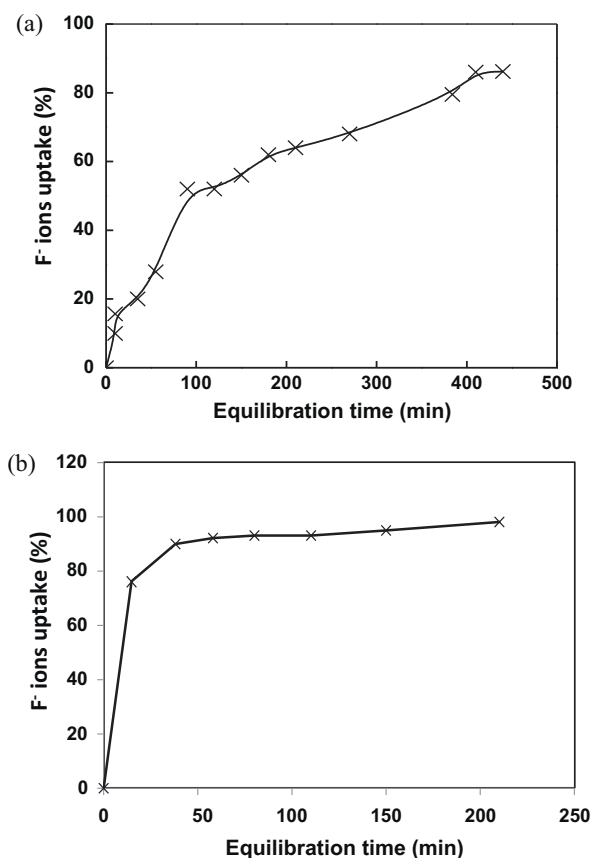


Fig. 7. Fluoride uptake as a function of time in sheet Th-MEP sorbent (a) and fibrous Th-MEP sorbent (b). The concentrations of fluoride in well stirred 25 mL solutions were kept same as 5 mg L^{-1} in both the experiments.

' t ' as a function of time has better linearity than that obtained from pseudo first order rate equation for fibrous sorbent indicating the validity of Lagergren's second order equation for fluoride sorption kinetics in fibrous sorbent. However, it is reversed in the case of sheet sorbent indicating that pseudo first order rate equation better represents the kinetic data. This may be attributed to different physical structures of these sorbents. According to the pseudo-first-order and pseudo-second-order kinetics models, the sorption process obeys pseudo-first-order kinetics at high initial concentration of solute and pseudo-second-order kinetics at lower initial concentration of solute [50]. In present case, the mechanisms of fluoride sorption differed because accessibility of the binding sites in both the sorbents were not same. The fibrous sorbent has large spaces between fibers (Fig. 1b) which provided higher accessibility of binding sites to fluoride. Therefore, the kinetics of fluoride sorption was also governed by the fluoride concentration in aqueous phase adjacent to surface of the fibers in the sorbent leading to fast but pseudo-second-order kinetics. In case of sheet sorbent, only limited binding sites were accessible for fluoride present in the equilibrating solution. As binding sites start saturating at the

Table 2
Rate constants obtained from the graphs for Th-poly(MEP) sheet and fibrous sorbents.

Sorbent	First order rate parameters		Second order rate parameters	
	k_1	R^2	k_2	R^2
Fibrous	1.4×10^{-1}	0.717	4.36	0.99
Sheet	6.58×10^{-3}	0.99	1.28×10^{-1}	0.98

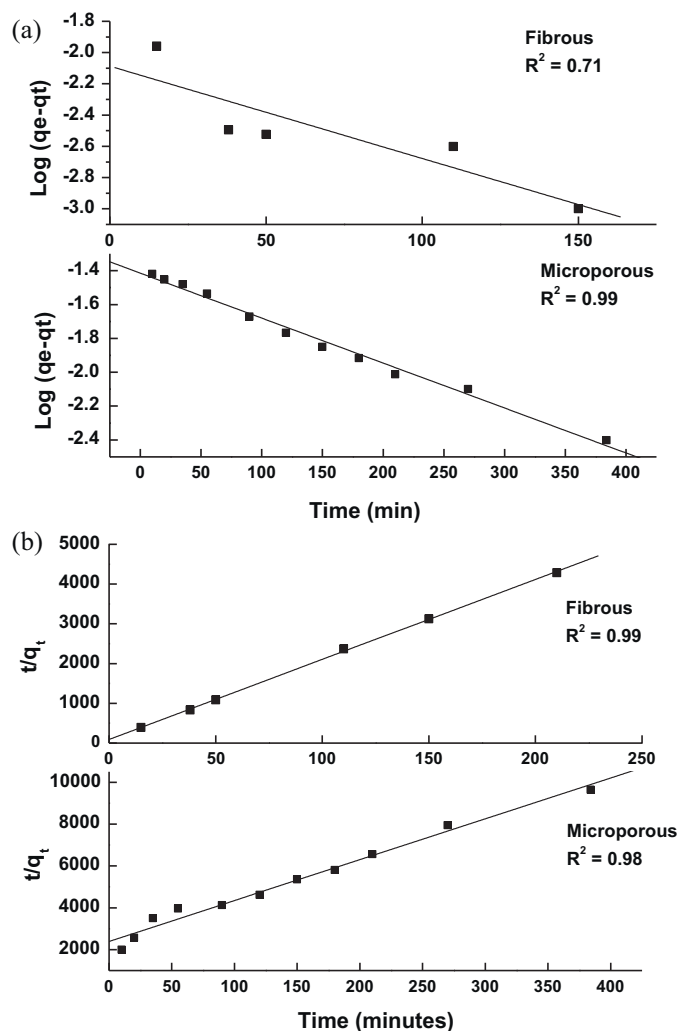


Fig. 8. Comparison of fluoride sorption kinetics data fitted with pseudo first order and pseudo second order rate equations.

surface of the sorbent, further sorption of fluoride would be dependent on its transfer from surface binding sites to interior binding sites. The transfer of fluoride to interior matrix of the sorbent would be the rate determining step in the sheet sorbent as Th-MEP binding sites have strong affinity towards fluoride. The overall result of this was slow and pseudo-first-order kinetics for fluoride sorption in the sheet sorbent. Therefore, change in surface concentration of binding sites may be responsible for switching of fluoride sorption profile from pseudo-first-order in sheet sorbent to pseudo-second-order in fibrous sorbent.

3.4. Applications to real samples

The groundwater sample collected from Punjab, India (channu area) was treated with the thorium (IV) phosphate fibrous membrane. $1 \times 1 \text{ cm}^2$ Th-loaded fibrous membrane was dipped in 10 mL solution. After an equilibration period of 6 h the membrane was taken out and residual fluoride concentration was measured. The initial fluoride concentration of 3 mg L^{-1} was reduced to 0.3 mg L^{-1} (Table 3). Thus, the final concentration left after uptake was well below permissible limit. The pH of aqueous sample was also changed to 3.8 from 6.5 that can be attributed to exchange of H^+ ions from residual un-complexed phosphate groups of MEP with cations in the ground water. The concentration of different cations

Table 3

Removal of fluoride from ground water samples collected from Channu, Punjab, India using Th-poly(MEP) fibrous sorbent.

Water quality parameters	Treatment	
	Before	After
Fluoride (mg L ⁻¹)	3	0.3
pH	6.5	3.8

Table 4

Composition of ground water sample collected from Channu, Punjab, India.

Ions	Concentration (mg L ⁻¹)
Chloride	200.7
Sodium	350.0
Magnesium	33.0
Calcium	18.4
Potassium	14.0

and anions present in the groundwater sample are presented in Table 4.

4. Conclusions

The Th-poly(MEP) sorbents developed in the present work were found to be robust, chemically stable and effective for the removal of fluoride from a wide variety of aqueous matrix having pH ranging from 1 to 7. Most of the common interfering anions have shown insignificant effect on fluoride sorption in the sorbents. This seems to suggest that this sorbent can be used for defluoridation of natural waters as well as industrial aqueous wastes streams. The fluoride sorption capacity and kinetics were found to be dependent on the physical architecture of poly(propylene) host substrate used for anchoring Th-poly(MEP). The sorption capacity of sheet Th-poly(MEP) was found to be 4320 mg fluoride kg⁻¹, which was highest among the sorbents reported in the literature so far. However, Th-poly(MEP) anchored on fibrous substrate was found to have very fast fluoride sorption kinetics. For example, 76% of the fluoride was sorbed in fibrous sorbent within 15 min of equilibration time. However, the fluoride loading capacity of fibrous Th-poly(MEP) sorbent was significantly lower than that of the sheet sorbent. Thus, this sorbent might be preferred when initial concentration of fluoride in aqueous medium is not very high. Both the sorbents developed in the present work were found to be reusable as fluoride could be de-sorbed quantitatively by single equilibration in solution having pH 13. Finally, the sorbent was found to have efficacy for defluoridation of ground water having higher fluoride concentration. The membrane process is preferred because it is user-friendly and cost-effective technique and it does not pose the problems associated with other conventional methods.

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