



An excellent fluoride sorption behavior of modified amberlite resin

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ABSTRACT

The article describes a convenient method for the modification of Amberlite XAD-4TM resin by introducing thio-urea binding sites onto the aromatic rings. The modified (ATU) resin has been employed for the quantitative sorption of fluoride ions in batch as well as column experiments. The parameters (i.e. pH, contact time, etc.) were optimized and desorption of fluoride ions was fulfilled by using 0.01 M HCl solution. The equation isotherms such as Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin were also successfully applied to model the experimental data. The sorption capacity of the ATU resin was found as 3.286 mmol g⁻¹. From the D–R isotherm parameters, it has been calculated that the uptake of fluoride ion by ATU resin occurs through ion exchange sorption mechanism. The study will contribute toward the remediation of fluoride polluted areas as well as in the various fields of materials science.

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1. Introduction

The toxic ions contamination in drinking water is hazardous to human health as well as to the aquatic life. Among the most hazardous contaminants, the fluoride ion has major effects in terms of dental and skeletal fluorosis. The fluoride ion demonstrates versatile nature, as its concentration in optimum dose (0.5–1.0 mg L⁻¹) in drinking water is beneficial to health and excess concentration (>1.0 mg L⁻¹) causes serious health effects on human being. Normally, the fluoride exposure in the environment and human body has been observed through water, food, industrial effluents, drugs, cosmetics, etc. However, drinking water is the major source of daily intake of fluoride [1,2]. The long-term intake of excess of fluoride through food and beverages may be one of the causes of dental and skeletal fluorosis. Ground water is the major source of drinking water in rural areas of Pakistan and in some parts of the country, it is contaminated with excess of fluoride ion (>1.5 mg L⁻¹), which is a great concern to the public health [2]. Moreover, some serious effects were also observed in different countries, such as China [3,4], India [5–7], Mexico [8] and Africa [9]. Due to its detrimental effects, it is essential to remove the excessive amount of fluoride ions from drinking water. Various methods have been reported for the removal of fluoride from water [10–21]. Consequently, different sorbent materials such as natural, synthetic, and biomass have been investigated for the removal of fluoride from the aqueous solutions.

Among them chitosan beads [22–26], bed laterite [27], waste fungus [28], granular red mud [29], hydrated cement [30], Attapulgitte [31], geomaterials and acid treated spent bleaching earth are well reported [32,33].

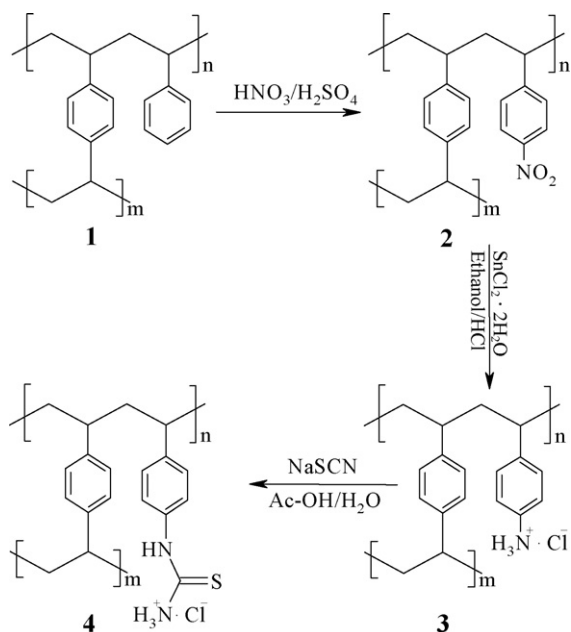
Recently, impregnated resins have also been used to investigate the sorption efficiency of anions [34–37]. However, for the impregnation of chelating reagents, macroporous organic-polymer beads of Amberlite XADs are regarded as an excellent support material because of their high surface area and good mechanical stability [38–43]. The Amberlite XAD-4TM resin is commercially cheap material and could be modified conveniently to seek an efficient ion exchange resin as reported previously [44]. However, the present work is an extension of previous studies [44] concerning the removal of fluoride ion from aqueous environment by modified Amberlite XAD-4TM resin. Herein, we report the thio-urea modified ATU resin for the same purpose in order to overcome insignificant effects of the previously reported resin.

2. Materials

The Ion-Chromatography (ΩMetrohm, Switzerland) instrument model 861 Advance Compact with 833 IC liquid handling unit equipped with self regenerating suppressor, which consists a double gradient peristaltic pump along with conductivity detector has been used. The I.C. anion column (4.0 mm × 250 mm) METROSEP A SUPP 4–250 (6.1006.430) was used to quantitate the anions in the aqueous media. The pH measurements were made on 781-pH/Ion meter, Metrohm with glass electrode and internal reference electrode. Janke & Kunikel automatic shaker model KS 501 D, Singapore, was used for the batch experiments at ambient temperature (*ca.*

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Scheme 1. Structural representation of modified Amberlite XAD-4.

25 °C). IR spectra were recorded on a Thermo Nicolet 5700 FT-IR spectrometer as KBr pellets. The scanning electron microscope (SEM) images were taken by using JSM-6490 model instrument. For the clarification of surface analysis, the SEM images were taken by applying 15 kV voltage with 40 and/or 500 times magnification. All chemicals used were of analytical or equivalent grade. Stock standard solutions of fluoride (1000 mg L⁻¹) have been prepared. The pH (1–10) of the solution was adjusted by mixing appropriate amount of 0.1 M HCl/NaOH.

Amberlite XAD-4TM (surface area of 825 m² g⁻¹, pore diameter 14.4 nm and bead size 20.50 mesh) was procured from Fluka, Germany. The surface area, pore diameter and mesh size were quoted by the supplier.

2.1. Synthesis

Amberlite XAD-4TM has been modified to **2** and **3** according to the previously reported methods [44] as illustrated in Scheme 1. Further derivatization of **3** was carried out as follows:

10 g of Amberlite XAD-4TM amine derivative (**3**) has been taken in 20 mL glacial acetic acid in 100 mL flask and stirred for 30 min. Then, 15 mL of 0.1 M NaSCN were added with continuous stirring followed by 1 h stirring at room temperature. Finally, the contents were cooled in ice bath for 30 min, then filtered and washed with deionized water till neutralization. The resulting resin beds were dried in oven at 100 °C and characterized by FT-IR spectroscopy and elemental analysis. IR (KBr) 2059 cm⁻¹ (–C=S). Found: C, 62.31; H, 7.21; N, 7.78; S, 8.79%. Calculated for C₁₉H₂₂N₂SCl·2H₂O: C, 62.36; H, 7.16; N 7.66; S, 8.76%.

2.2. Sorption procedures

2.2.1. Static method for the sorption of fluoride ion

Batch-wise sorption study was carried out for fluoride at room temperature, i.e. 25 ± 1 °C. The sample solution (10 mL) containing fluoride ion (16 mg L⁻¹) was taken in a 50 mL erlenmeyer flask. The modified resin (100 mg) was added and the mixture was equilibrated for 40 min. The resin was filtered and the adsorbed fluoride ion was determined by IC. The % sorption of fluoride ion was calcu-

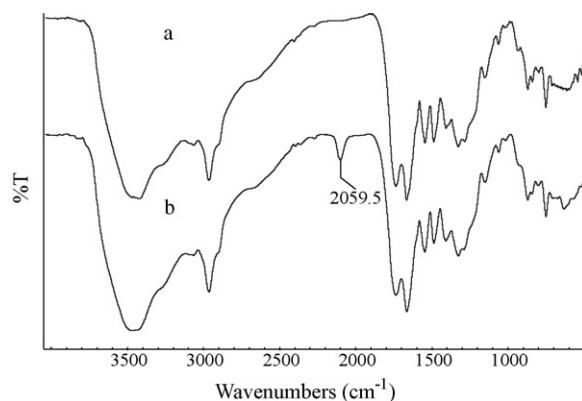


Fig. 1. FT-IR spectra (a) XAD-4TM amino derivative **3** and (b) XAD-4TM thio-urea derivative **4**.

lated as follows:

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

where C_i (mol L⁻¹) is initial concentration of solution before the sorption and C_f (mol L⁻¹) is the final concentration after the sorption of the fluoride ion.

2.2.2. Dynamic method for sorption of fluoride ion

The modified resin (2 g) was poured into a Pyrex glass column (0.8 mm Ø × 50 mm). A small amount of glass wool was placed at the bottom and top of resin in order to prevent any loss of the resin beads during the sample loading. A solution of fluoride was passed through the column at flow rate of 1 mL min⁻¹. The concentration of fluoride in the column effluents was determined by IC.

3. Results and discussion

3.1. FT-IR spectra

The FT-IR spectrum of Amberlite XAD-4TM and its nitro and amino derivatives are previously interpreted [44,45]. The Amberlite XAD-4TM thio-urea derivative (ATU resin) was characterized by FT-IR as in Fig. 1. At the end of reactions the new band was observed at 2059 cm⁻¹ for C=S, which conforms the conversion of amino to thio-urea derivative of Amberlite XAD-4TM.

3.2. Evaluation of different parameters

3.2.1. pH effect on the sorption of fluoride ions

The influence of pH plays a significant role on sorption phenomenon, to recognize the effect of pH, sorption studies were carried out at different pHs (1–10). In this study the sorption of fluoride ions onto ATU resin was explored at fixed concentration of

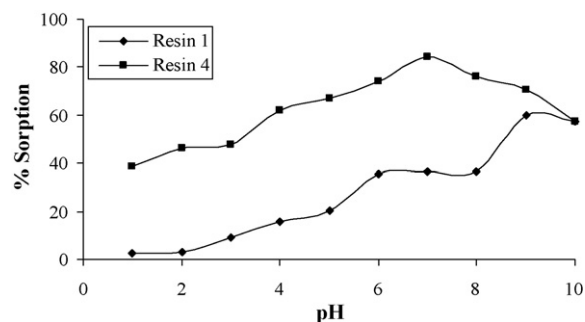


Fig. 2. Sorption of fluoride ions onto resin **1** (♦) and **4** (■) at pH 1–10.

Table 1
Reagents used for the elution of fluoride ion: reagent^a, concentration (M), % recovery.

Reagents ^a	Concentration (M)	% Recovery
HCl	0.001	75.7
HCl	0.01	99.9
H ₂ SO ₄	0.001	42.4
H ₂ SO ₄	0.01	77.6
HNO ₃	0.001	13.2
HNO ₃	0.01	32.2
NaOH	0.001	19.5
NaOH	0.01	60.8

^a Volume of each reagent used = 5 mL.

fluoride ions (Fig. 2). The % sorption of fluoride increases by increasing pH of the solution and attains maximum value at pH 7; may be due to the absence of interfering competitive ions (i.e. Cl⁻ or OH⁻) at this neutral pH. However, the effectiveness of ATU resin is in the range of 6–8 pH (i.e. ideal range for the ground waters); it means that the smaller quantity of interfering ions does not affect the sorption capacity of ATU resin. It has also been noticed in the interference study of other ions in Section 3.4. Obviously, if the quantity of other anions increases, it may cause the disturbance among the hydrogen bond formation between the sites of ATU resin and fluoride that ultimately results in low sorption. The higher affinity toward fluoride as compared to other ions is may be due to the high electronegativity of fluoride as well as the best fit of ionic radii of fluoride with the cavity size of the resin.

3.2.2. Optimum shaking time

The effect of shaking time on sorption of fluoride ion onto **4** was studied over a range of 0–40 min, at pH 7, using 10 mL of 16 mg L⁻¹ fluoride ion solution and 100 mg of sorbent. For the equilibrium study, the pH of the fluoride ion solution was maintained during the sorption experiment. Sorption increases with the increase of shaking time, the equilibrium was established within 30 min and there was only a slight increase in percent sorption up to 40 min. Thus, further experimental work was carried out at 40 min shaking time in order to avoid sorption error.

3.2.3. Recovery of fluoride ion

Desorption of fluoride ion from ATU resin (**4**) was evaluated by using 5 mL of different concentrations of HNO₃, H₂SO₄, HCl and NaOH. For this purpose, 100 mg of used ATU resin (on which fluoride ions have been adsorbed) was agitated for 40 min with 5 mL of each reagent (discussed above) of desired concentration. The percent recoveries of fluoride ions are given in Table 1. The maximum % desorption of fluoride ion was found to be quantitative (99.9%) with 5 mL of 1 × 10⁻² M HCl.

3.2.4. Comparison of F⁻ sorption with other sorbents

The maximum fluoride sorption capacity of ATU resin at pH 7 and 25 °C has been calculated as 3.286 mmol g⁻¹ of resin. A

comparison of maximum fluoride sorption capacity Q_m of newly synthesized ATU resin with other sorbents reported in the literature [22–24,27–30,32,33] is given in Table 2. The data show that the sorption capacity of ATU resin is relatively high when compared with other sorbent materials. It may be explained by the fact that the ATU resin has more efficient binding sites present on the surface for the coordination of fluoride ions.

3.2.5. Sorption mechanism

The mechanism of fluoride removal by ATU resin is shown in Scheme 2. The ATU resin framework possesses thio-urea groups onto its surface and has been confirmed as ion exchange resin according to the Temkin isotherm. Since, the resin possesses two amide groups in thio-urea moiety having ability to accept proton and enhance the probability of hydrogen bond formation with halide ions. The environment is feasible for hard acid and hard base interaction as demonstrated by Pearson [46]. Herein, in this case the interaction between hydrogen bond forming sites and the chloride/fluoride may result in overall sorption phenomenon as shown in Scheme 2.

3.2.6. Sorption isotherms

The experimental data was validated by using Freundlich, Langmuir, Dubinin and Radushkevich (D–R), and Temkin isotherm models.

The linear forms of Freundlich, Langmuir, D–R and Temkin isotherm equations are as;

$$\log C_{\text{ads}} = \log A + \left(\frac{1}{n}\right) \log C_e \quad (2)$$

$$\left(\frac{C_e}{C_{\text{ads}}}\right) = \left(\frac{1}{Qb}\right) + \left(\frac{C_e}{Q}\right) \quad (3)$$

$$\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2 \quad (4)$$

$$C_{\text{ads}} = B_1 \ln K_T + B_1 \ln C_e \quad (5)$$

where, C_{ads} is the amount of fluoride ion sorbed per unit mass of the sorbent and C_e is the amount of fluoride ion in liquid phase at equilibrium. A , n , Q , b , X_m , β , B_1 and K_T are Freundlich, Langmuir, D–R and Temkin constants respectively. These equation are applied to correlate the amount of the fluoride sorbed per unit amount of the sorbent and can be calculated from slope and intercept, the initial concentration of sorbate is in the range of 6.95×10^{-4} to 1.73×10^{-3} mol dm⁻³ using 100 mg sorbent per 10 mL of sorbate and 40 min shaking time at 25 °C.

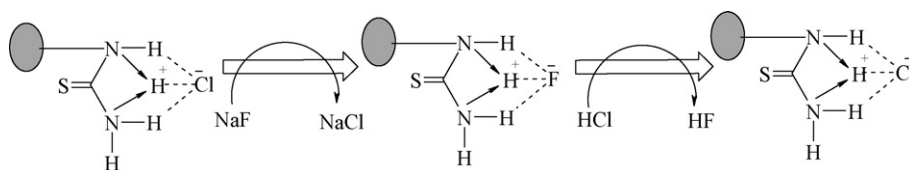
In Fig. 3 plot of C_e/C_{ads} (mol g⁻¹) versus C_e (mol dm⁻³) shows straight line which demonstrates that sorption data followed by Langmuir sorption equation very well. The value of Q is 3.21 mmol g⁻¹ and the Langmuir constant b is 1.04×10^4 mol dm⁻³.

The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium

Table 2
Comparison of fluoride sorption capacity of ATU resin with other sorbents.

Name of sorbent	pH	Temperature (K)	Q_m^* (mmol g ⁻¹)	Reference
Protonated chitosan beads	7	303	0.385	[22]
Carboxylated cross-linked chitosan beads	7	303	0.585	[23]
Fe(III) loaded carboxylated chitosan beads	7	303	0.810	[24]
Laterite bed	≥9.8	313	0.032	[27]
Waste fungus (Pleurotus ostreatus 1804)	2	303	0.067	[28]
Granular red mud	4.7		0.470	[29]
Hydrated cement	3–10		0.141	[30]
Orissa Mining Corporation (OMC)	5–6	303	0.798	[32]
Spent bleaching earth	3.5		0.408	[33]
ATU resin	7	303	3.210	In current study

* Q_m stands for Langmuir sorption capacity of sorbent.



Scheme 2. Mechanism of fluoride sorption phenomenon on ATU resin.

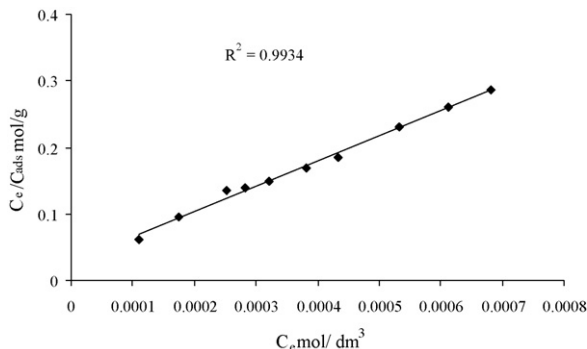


Fig. 3. Langmuir plot for the sorption of fluoride.

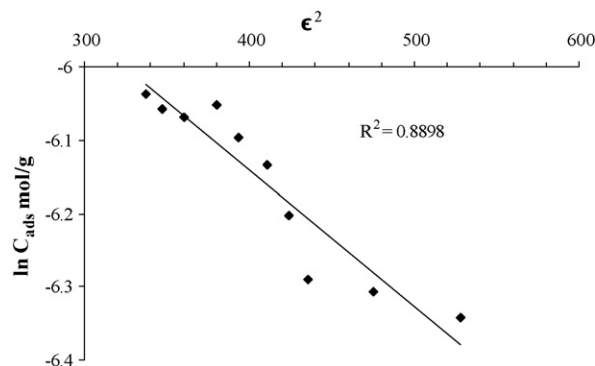


Fig. 5. D-R plot for the sorption of fluoride.

parameter, R_L , calculated as;

$$R_L = \left(\frac{1}{1 + bC_i} \right) \quad (6)$$

where b is the Langmuir constant and C_i is the initial concentration of sorbate (mol dm^{-3}), the R_L values indicate the type of isotherm [44,47].

- $R_L = 0$: irreversible isotherm
- $0 < R_L < 1$: favorable isotherm
- $R_L = 1$: linear isotherm
- $R_L > 1$: unfavorable isotherm

In Fig. 4 plot of $\log C_{\text{ads}}$ (mol g^{-1}) versus $\log C_e$ (mol dm^{-3}) shows straight line which demonstrates the applicability sorption data which follows the Freundlich sorption equation. In Table 2 the constant values $1/n$ and A (i.e. 0.194 and $9.981 \text{ mmol g}^{-1}$) were calculated. From the linear graph the correlation coefficient R^2 value and sorption capacity were found 0.89 and $9.981 \text{ mmol g}^{-1}$ respectively. The experimental data observed is well to fit the Freundlich isotherm model. The condition for the validity of a Freundlich type sorption model is sorption on heterogeneous surfaces [34].

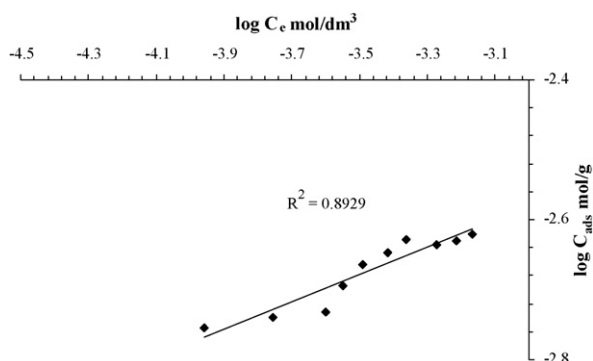


Fig. 4. Freundlich plot for the sorption of fluoride.

The characteristic of another equation used in the analysis of D-R isotherms is ε , i.e. the Polanyi potential which is described as;

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where R is the gas constant and T is the temperature in Kelvin. The mean sorption energy, E (kJ/mol) can be calculated by Eq. (8) [48–50];

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

Fig. 5 plotted ε^2 versus $\ln C_{\text{ads}}$ (mol g^{-1}) which shows the linear graph with correlation coefficients R^2 0.88 for the sorption of fluoride and the corresponding constants are calculated from slope and intercept respectively and presented in Table 3. The R^2 for the D-R isotherm is the lowest in comparison to the values obtained for the Freundlich, Langmuir and Temkin isotherms. Therefore, the D-R isotherm is the lowest-fit isotherm for the sorption of fluoride onto this sorbent under the experimental conditions used in this study. The monolayer sorption capacity (X_m) was evaluated as 4.53 mmol g^{-1} . The mean sorption energy (E) was found to be 16.22 kJ/mol for the sorption of fluoride on the sorbent. The E value ranges from 1.0 to 8.0 kJ/mol for physical sorption and from 9.0 to 16.0 kJ/mol for chemical sorption [49,51]. The value of E , which is nearly 16.22 kJ/mol , may suggest that, the mechanism

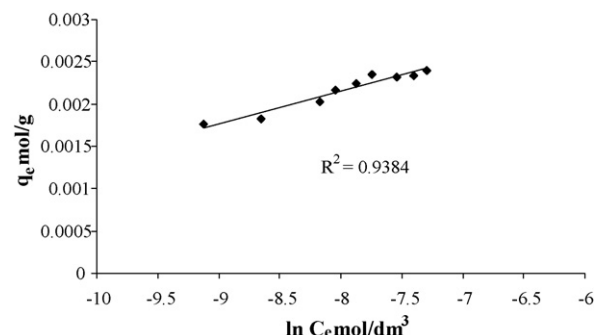


Fig. 6. Temkin isotherm plot for the sorption of fluoride.

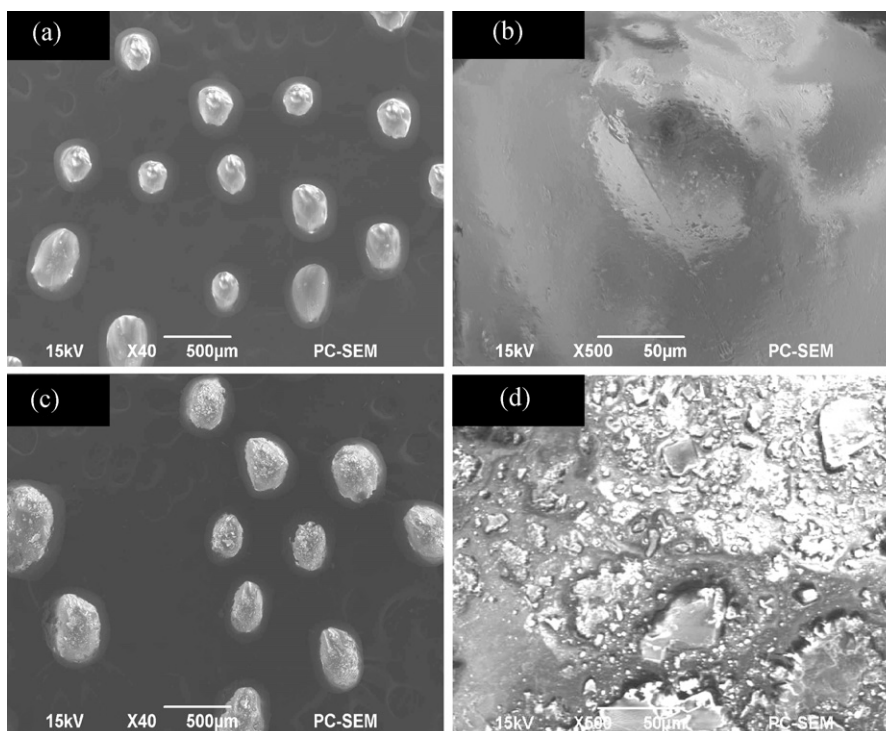


Fig. 7. SEM images of ATU resin: (a and b) before the sorption of fluoride; (c and d) after the sorption of fluoride.

for the sorption of fluoride on the sorbent is of purely chemical in nature.

Fig. 6 shows the Temkin isotherm plotted. A linear relationship between q_e and $\ln C_e$ indicates the applicability of this model. The Temkin isotherm constant can be calculated by Eq. (9) given as;

$$B_1 = \frac{RT}{b} \quad (9)$$

Temkin isotherm contains a factor that clearly takes into the account sorbing species and sorbent interactions. The heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate–sorbate interactions [50]. This isotherm assumes that (i) the heat of sorption of all the molecules in the layer decreases linearly with coverage due to sorbent and sorbate interactions, and that (ii) the sorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [52].

From the results it is apparently clear that the precursor Amberlite XAD-4TM resin (**1**) is poor extractant for fluoride at different pH (Fig. 1). It is in agreement with the literature results [53,54] that the pure XADs are non-ionic in nature and are good sorbents only for

neutral molecules, while modifications on **1** may convert them as a good sorbent for ionic species [44]. In this study, Amberlite XAD-4TM amino derivative **3** was further modified to thio-urea derivative **4** having thio-urea binding sites directly attached onto the aromatic core of copolymer backbone. The amide groups of these binding sites are capable of forming hydrogen bonds with fluoride. Thus, the strategy adopted in this Scheme 1 fits well in this process based on ion exchange mechanism and it has been proved that the ATU resin is a good sorbent particularly for the removal of fluoride from the ground water of Thar Desert at an acceptable range of pH (i.e. 6–8).

3.2.7. SEM

The scanning electron microscope (SEM) images were used for the evaluation of surface analysis of fluoride treated and untreated ATU resin as shown in Fig. 7(a–d). The SEM images shown in Fig. 7a and c were taken by applying 15 kV voltage with 40 times magnification; while the SEM micrographs of Fig. 7b and d were taken at 500 times magnification for the clarification of surface. The Fig. 7a demonstrates that the beads of modified resin are spherical with

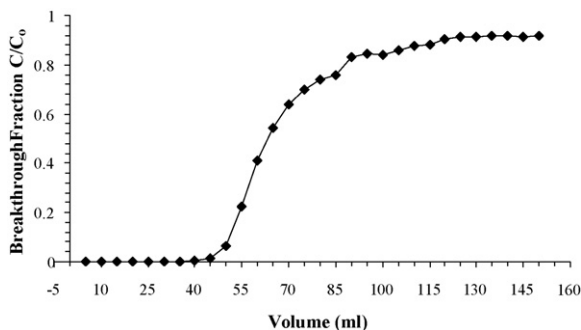


Fig. 8. Breakthrough curve with respect to volume (mL).

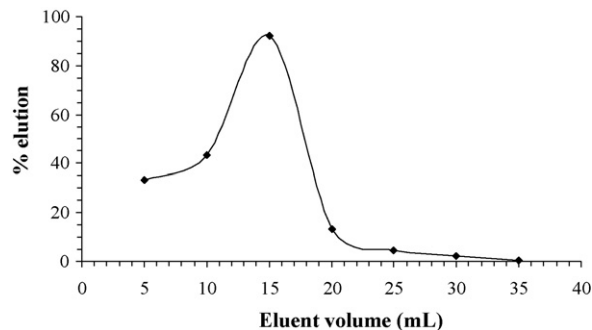


Fig. 9. Elution curve for the desorption of fluoride with 0.01 M HCl.

Table 3
Freunlich, Langmuir, D–R and Temkin characteristic constants for fluoride ions sorption.

Langmuir		Freundlich			D–R			Temkin					
Q (mmol g ⁻¹)	$b \times 10^4$ (mol dm ⁻³)	R_L	R^2	A (mmol g ⁻¹)	n	$1/n$	R^2	X_m (mmol g ⁻¹)	E (kJ mol ⁻¹)	R^2	K_T (mol g ⁻¹)	$B_1 \times 10^{-4}$ (mol dm ⁻³)	R^2
3.21	1.08	0.198–0.042	0.99	9.981	2.44	0.41	0.89	4.53	16.22	0.88	442.41	4	0.93

uniform in shape. It has been noticed from the images (Fig. 7a and b) of untreated ATU resin that all the beads have a smooth surface. Rough and irregular shapes of all the beads of treated resin (Fig. 7c and d) have been observed after the sorption of fluoride onto modified ATU resin, i.e. covered by external material. Thus, these images confirm the fluoride sorption onto the ATU resin.

3.3. Dynamic sorption studies

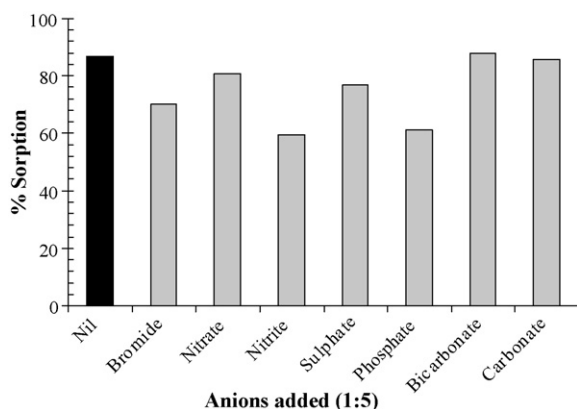
The sorption performance of ATU resin for fluoride was also studied in a column experimental set up (Fig. 8). The sorption efficiency of the sorbent was confirmed as a point on a breakthrough curve of the sorbed fluoride. Thus, a breakthrough curve is a plot of C/C_0 (fraction of initial influent and effluents) versus fluoride content solution (mL) passing through packed beads of resin. In Fig. 8, it was observed that the breakthrough volume starts at 50 mL and the packed ATU resin was completely saturated at 120 mL. The breakthrough sorption capacity of ATU resin is calculated as 2.63 mmol/g. However, the breakthrough curve shows that the ATU resin can be efficiently used for the removal of fluoride from aqueous media.

3.4. Elution experiment

The elution experiment by packed column has also been carried out by using optimized desorption reagent (Table 1). During the desorption process the fluoride was eluted by the constant flow rate of 1 mL/min. The maximum percent recovery of fluoride was observed as 92.3%. The elution curve of fluoride with respective to eluted volume is given in Fig. 9.

3.5. Interference of other ions

The polluted waters as well as industrial effluents contain various other co-existing anions, which may participate with fluoride sorption onto ATU resin. However, the investigation of interference of selected ions (Br⁻, NO₃⁻, NO₂⁻, SO₄²⁻, PO₄³⁻, CO₃²⁻, HCO₃⁻) was conducted. The interference of co-existing ions on the fluoride sorption onto ATU resin was evaluated by IC taking 1:5 (fluoride:other ion) mole ratio at optimized conditions. A little interference of bromide, nitrite and phosphate ions has

**Fig. 10.** Effect of interfering ions onto the sorption behavior of fluoride by ATU resin.

been noticed as shown in Fig. 10, may be due to the competition among them for the sites on the sorbent surface, which is determined by the change in pH, concentration, charge and size of anions. The interference of these ions is insignificant thus; ATU resin can be effectively used for the removal of fluoride ions from water.

4. Conclusion

The current study highlights the convenient modification of Amberlite resin and its application in fluoride removal from the aqueous environment. It has been noticed that the modified resin has high efficiency for the removal of fluoride from water at a wide range of pH mainly at pH 7. The resin can be regenerated several times with 0.01 M HCl and may be used as an ion exchange material in filters for the removal of fluoride from drinking water. The study will be extended to evaluate the efficacy of the resin toward the real samples of drinking water from the Thar Desert of Pakistan with high fluoride content, as well as its applicability for the removal of other ions (cations/anions) from the aqueous media, which will explore its applicability in analytical and environmental sciences.

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References

- [1] K. Sarala, P.R. Rao, Endemic fluorosis in the village Ralla, Anantapuram in Andhra Pradesh—an epidemiological study, *Fluoride* 26 (1993) 177–180.
- [2] T. Rafique, S. Naseem, M.I. Bhangar, T.H. Usmani, Fluoride ion concentration in the groundwater of Mithi sub-district, the Thar Desert, Pakistan, *Environ. Geol.* 56 (2008) 317–326.
- [3] Q. Guo, Y. Wang, T. Ma, R. Ma, Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China, *J. Geochem. Explor.* 93 (2007) 1–12.
- [4] Y. Zhao, X. Li, L. Liu, F. Chen, Fluoride removal by Fe(III)-loaded ligand exchange cotton cellulose adsorbent from drinking water, *Carbohydr. Polym.* 72 (2008) 144–150.
- [5] N.S. Rao, D.J. Devadas, Fluoride incidence in groundwater in an area of Peninsular India, *Environ. Geol.* 45 (2003) 243–251.
- [6] S.K. Gupta, R.D. Deshpande, M. Agarwal, B.R. Raval, Origin of high fluoride in groundwater in the North Gujarat–Cambay region, India, *Hydrogeol. J.* 13 (2005) 596–605.
- [7] G. Jaks, P. Bhattacharya, V. Chaudhary, K.P. Singh, Controls on the genesis of some high-fluoride groundwaters in India, *Appl. Geochem.* 20 (2005) 221–228.
- [8] J.J. Carrillo-Rivera, A. Cardona, W.M. Edmunds, Use of abstraction regime and knowledge of hydrogeological conditions to control high-fluoride concentration in abstracted groundwater: San Luis Potosi basin, Mexico, *J. Hydrol.* 261 (2002) 24–47.
- [9] B. Gizaw, The origin of high bicarbonate and fluoride concentrations in waters of the main Ethiopian Rift Valley, *J. Afr. Earth Sci.* 22 (1996) 391–402.
- [10] Y. Cengeloglu, E. Kir, M. Ersoz, Removal of Fluoride from aqueous solution by using red mud, *Sep. Purif. Technol.* 28 (2002) 81–86.
- [11] A. Tor, Removal of fluoride from an aqueous solution by using montmorillonite, *Desalination* 201 (2006) 267–276.
- [12] S. Meenakshi, N. Viswanathan, Identification of selective ion-exchange resin for fluoride sorption, *J. Colloid Interface Sci.* 308 (2007) 438–450.
- [13] M.G. Sujana, R.S. Thakur, S.N. Das, S.B. Rao, Defluorination of wastewaters, *Asian J. Chem.* 9 (1997) 561–570.
- [14] F. Durmaz, H. Kara, Y. Cengeloglu, M. Ersoz, Fluoride removal by Donnan dialysis with anion exchange membrane, *Desalination* 177 (2005) 51–57.
- [15] E. Kir, E. Alkan, Fluoride removal by Donnan dialysis with plasma-modified and unmodified anion-exchange membranes, *Desalination* 197 (2006) 217–224.

- [16] M. Hichour, F. Persin, J. Sandeau, C. Gavach, Fluoride removal from waters by Donnan dialysis, *Sep. Purif. Technol.* 18 (2000) 1–11.
- [17] M. Zeni, R. Riveros, K. Melo, R. Primieri, S. Lorenzini, Study on fluoride reduction in artesian well-water from electrodialysis process, *Desalination* 185 (2005) 241–244.
- [18] N.I. Chubar, V.F. Samanidou, V.S. Kouts, G.G. Gallios, V.A. Kanibolotsky, V.V. Strelko, I.Z. Zhuravlev, Adsorption of fluoride, chloride, bromide, and bromate ions on a novel ion exchanger, *J. Colloid Interface Sci.* 291 (2005) 67–74.
- [19] S. Sourirajan, T. Matsurra, Studies on reverse osmosis for water pollution control, *Water Res.* 6 (1972) 1073–1086.
- [20] R. Simons, Trace element removal from ash dam waters by nanofiltration and diffusion dialysis, *Desalination* 89 (1992) 325–341.
- [21] L. Guo, B.J. Hunt, P.H. Santsci, Ultrafiltration behavior of major ions (Na, Ca, Mg, F, Cl, and SO₄) in natural waters, *Water Res.* 35 (2001) 1500–1508.
- [22] N. Viswanathan, C.S. Sundaram, S. Meenakshi, Removal of fluoride from aqueous solution using protonated chitosan beads, *J. Hazard. Mater.* 161 (2009) 423–430.
- [23] N. Viswanathan, C.S. Sundaram, S. Meenakshi, Sorption behaviour of fluoride on carboxylated cross-linked chitosan beads, *Colloids Surf. B* 68 (2009) 48–54.
- [24] N. Viswanathan, S. Meenakshi, Effect of metal ion loaded in a resin toward fluoride retention, *J. Fluorine Chem.* 129 (2008) 645–653.
- [25] N. Viswanathan, S. Meenakshi, Enhanced fluoride sorption using La(III) incorporated carboxylated chitosan beads, *J. Colloid Interface Sci.* 322 (2008) 375–383.
- [26] S. Jagtap, D. Thakre, S. Wanjari, S. Kamble, N. Labhsetwar, S. Rayalu, New modified chitosan-based adsorbent for defluoridation of water, *J. Colloid Interface Sci.* 332 (2009) 280–290.
- [27] M. Sarkar, A. Banerjee, P.P. Pramanick, A.R. Sarkar, Design operation of fixed bed laterite column for the removal of fluoride from water, *Chem. Eng. J.* 131 (2007) 329–335.
- [28] S.V. Ramanaiah, S.V. Mohan, P.N. Sarma, Adsorptive removal of fluoride from aqueous phase using waste algal fungus (*Pleurotus ostreatus* 1804) biosorbent: kinetics evaluation, *Ecol. Eng.* 31 (2007) 47–56.
- [29] A. Tor, N. Danaoglu, G. Arslan, Y. Cengeloglu, Removal of fluoride from water by using granular red mud: batch and column studies, *J. Hazard. Mater.* 164 (2009) 271–278.
- [30] S. Kagne, S. Jagtap, P. Dhawade, S.P. Kamble, S. Devotta, S.S. Rayalu, Hydrated cement: a promising adsorbent for the removal of fluoride from aqueous solution, *J. Hazard. Mater.* 154 (2008) 88–95.
- [31] J. Zhang, S. Xie, Y.-S. Ho, Removal of fluoride ions from aqueous solution using modified attapulgite as adsorbent, *J. Hazard. Mater.* 165 (2009) 218–222.
- [32] M.G. Sujana, H.K. Pradhan, S. Anand, Studies on sorption of some geomaterials for fluoride removal from aqueous, *J. Hazard. Mater.* 161 (2009) 120–125.
- [33] M. Mahramanlioglu, I. Kizilcikli, I.O. Bicer, Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, *J. Fluorine Chem.* 115 (2002) 41–47.
- [34] I. Qureshi, S. Memon, M. Yilmaz, Estimation of chromium(VI) sorption efficiency of novel regenerable *p-tert-butylcalix[8]arene*octamideimpregnated Amberlite resin, *J. Hazard. Mater.* 164 (2009) 675–682.
- [35] F. Luo, K. Inoue, The removal of fluoride ion by using metal (III)-loaded amberlite resins, *Solvent Extr. Ion Exch.* 22 (2004) 305–322.
- [36] M.S. Hosseini, A. Hosseini-Bandegharai, H. Raissi, F. Belador, Sorption of Cr(VI) by Amberlite XAD-7 resin impregnated with brilliant green and its determination by quercetin as a selective spectrophotometric reagent, *J. Hazard. Mater.* 169 (2009) 52–57.
- [37] S.P. Dubey, K. Gopal, Application of natural adsorbent from silver impregnated *Arachis hypogaea* based thereon in the processes of hexavalent chromium for the purification of water, *J. Hazard. Mater.* 164 (2009) 968–975.
- [38] J.A. Marinsky, Y. Marcus (Eds.), *Ion Exchange and Solvent Extraction*, vol. 8, Marcel Dekker, New York, 1981 (Chapter 3).
- [39] A. Warshawsky, Polystyrene impregnated with β -diphenylglyoxime, a selective reagent for palladium, *Talanta* 21 (1974) 624–626.
- [40] J.R. Parrish, Macroporous resins as supports for a chelating liquid ion-exchanger in extraction chromatography, *Anal. Chem.* 49 (1977) 1189–1192.
- [41] L.L. Tavlarides, J.H. Bae, C.K. Lee, Solvent extraction, membrane and ion exchange in hydrometallurgical dilute metals separation, *Sep. Sci. Technol.* 22 (1987) 581–615.
- [42] T.M. Suzuki, H. Matsunaga, The transfer of mofezolac into the inflammatory site and the hypothalamus in rats, *Trends Inorg. Chem.* 19 (1991) 33–40.
- [43] V. Camel, Solid phase extraction of trace elements, *Spectrochim. Acta: B* 58 (2003) 1177–1233.
- [44] I.B. Solangi, S. Memon, M.I. Bhangar, Removal of fluoride from aqueous environment by modified Amberlite resin, *J. Hazard. Mater.* 171 (2009) 815–819.
- [45] K.O.V. Flores, A. Palermo de Aguiar, M.R.M. Palermo de Aguir, L.C. Maria, Microwave assisted Friedel-Crafts acylation reactions of Amberlite XAD-4TM resin, *Mater. Lett.* 61 (2007) 1190–1196.
- [46] R.G. Pearson, Hard and soft acids and bases, *J. Am. Chem. Soc.* 85 (1963) 3533–3539.
- [47] J.R. Memon, S.Q. Memon, M.I. Bhangar, M.Y. Khuhawer, Banana peel: a green and economical sorbent for Cr(III) removal, *Pak. J. Anal. Environ. Chem.* 1 (2008) 20–25.
- [48] R. Donat, A. Akdogan, E. Erdem, H.C. Etis Li, Thermodynamics of Pb²⁺ and Ni²⁺ adsorption onto natural bentonite from aqueous solution, *J. Colloid Interface Sci.* 286 (2005) 43–52.
- [49] S.S. Tahir, R. Nasseem, Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution, *J. Chem. Thermodyn.* 35 (2003) 2003–2209.
- [50] M. Hosseini, S.F.L. Mertens, M. Ghorbani, A. Afshar, Asymmetrical Schiff bases as inhibitors of mild steel corrosion in sulphuric acid media, *J. Mater. Chem. Phys.* 78 (2003) 800–808.
- [51] M. Sarkar, A. Banerjee, P.P. Pramanick, A.R. Sarkar, Use of laterite for the removal of fluoride from contaminated drinking water, *J. Colloid Interface Sci.* 302 (2006) 432–441.
- [52] Y. Kim, C. Kim, I. Choi, S. Rengraj, J. Yi, Arsenic removal using mesoporous alumina prepared via a templating method, *Environ. Sci. Technol.* 38 (2004) 924–931.
- [53] D.W. Lee, C.H. Eurn, I.H. Lee, S.J. Jeon, Adsorption behavior of 8-hydroxyquinoline and its derivatives on amberlite XAD resins, and adsorption of metal ions by using chelating agent-impregnated resins, *Anal. Sci.* 4 (1988) 505–510.
- [54] P.A.M. Freitas, K. Iha, M.C.F.C. Felinto, M.E.V. Suárez-Iha, Adsorption of di-2-pyridyl ketone salicyloylhydrazone on Amberlite XAD-2 and XAD-7 resins: characteristics and isotherms, *J. Colloid Interface Sci.* 323 (2008) 1–5.