Batch Studies of Alginate Nanoparticles for Efficient Removal of Fluoride Ions from Drinking Water

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ABSTRACT

The objectives of the present work include synthesis of nanoparticles of alginate crosslinked with ferric ions, their characterization by techniques such as FTIR, TEM and XRD followed by their batch and column sorption studies for defluoridation of water. In order to study the effect of various factors like adsorbent dose, initial concentration, pH and temperature on defluoridation of water using nanoparticles of alginate a series of batch sorption experiments were conducted. The obtained results were analyzed by Langmuir and Freundlich isotherms and it was found that defluoridation closely follows Freundlich adsorption isotherm. The results were also analyzed through various kinetic models like Lagergreen pseudo-first order kinetics, the pseudo-second order kinetics, and intraparticle diffusion model. Adsorption of F ions from aqueous solutions is best described by pseudo second order Lagergreen equation. It was also found that intra particle transport is not the rate limiting step.

Keywords: Fluorosis, fluoride, defluoridation, alginate, nanoparticles, adsorption, batch, column, breakthrough

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1   Introduction

Fluoride in drinking water may be beneficial or harmful to health, depending on its concentration. The optimum fluoride level in drinking water for general good health set by WHO, is considered to be between 0.5 and 1.0 mg/l. A concentration higher than this can lead to fluorosis which is a serious health problem caused by an excess ingestion of fluoride. It affects the teeth and the bones and its accumulation for a long period of time can alter the DNA structure[1].Excess fluoride in drinking water is reported from more than 35 countries around the globe with India and China, being the worst affected. In countries like India, the severe contamination of drinking water with excess fluoride, acquired the dimensions of a socio-economic rather than a public health problem triggering defluoridation research[2]. Removal of fluoride from groundwater is the only remedy since source substitution is not possible due to non-availability of alternate sources.

Various defluoridation techniques have been used to reduce the excess fluoride below the safe limits [3].These include membrane processes, adsorption[4,5], coagulation and precipitation[6], ion-exchange[7], reverse osmosis[8], nano-filtration[9],electrodialysis[10] and Donnan dialysis[11].The Nalgonda technique based on chemical precipitation using alum and lime is the most commonly used technique for defluoridation, however, generation of aluminium and fluoride rich sludge and aluminium carryover in treated water are major disadvantages of precipitation-based techniques. To overcome the limitation of conventional techniques adsorption-based fluoride removal systems are emerging as the feasible options[3].These processes are effective and can remove fluoride to a suitable level but they are expensive and require frequent regeneration of beads or membrane and cleaning of the scaling and fouling. Among them adsorption is still widely accepted pollution removal technique because of its ease of operation and cost-effectiveness [12]. The efficiency of this technique mainly depends on nature of the adsorbents. Some adsorbents tried for fluoride removal include activated alumina[13], activated carbon [14], ion-exchange resins[15], clay[16], cement paste[17], composite[18], hydrotalcite[19], hydroxyapatite [20], plaster of Paris[21], quick lime[22], chitosan beads[23], etc.

Alginate, a natural polysaccharide extracted from brown seaweeds, is a very promising biosorbent. It was preferred over other materials because of its various advantages such as biodegradability, hydrophilic properties, natural origin, abundance and presence of binding sites due to its carboxylate functions. Alginate consists of linear copolymers composed of β-d-Mannuronate (M) and α-l-Guluronate (G), linked by β 1,4- and α 1,4-glycosidic bounds. M and G units are organised in homopolymeric M and G blocks and heteropolymeric M–G blocks. The proportions of these blocks and the ratio M/G vary with the source of the alginate polymer. The carboxylate groups of the polymer provide the ability to form biodegradable gels in the presence of multivalent cations[24].Alginate is a polysaccharide with a high affinity and binding capacity for metal ions. Several alginate-based sorbents have been evaluated for metal uptake from aqueous solutions for possible application in water treatment processes[25].It has been demonstrated that the alginates are capable of binding metal ions through carboxyl groups and calcium alginate beads are usually prepared for their gel forming properties in the presence of multivalent cations[26]. On cross-linking with trivalent Fe^{3+}ions it forms a three-dimensional bonding structure with sodium alginate and hence forms more stable nanoparticles. Alginate undergoes ionotropic gelation when these divalent/trivalent cations and interacts ionically with blocks of guluronic acid residues, thus resulting in the formation of three-dimensional network which is usually described by the 'egg-box' model [27].The packing and coordination of of cations is aided by the egg box structure. The junction between the chains formed in this way are kinetically stable towards dissociation while the polymannuronate units show the normal polyelectrolyte characteristics of cationic binding[28]. The trivalent Fe^{3+} is accepted to form a three-dimensional network by a trivalent bonding structure with the sodium alginate. This three-dimensional bonding results in extended crosslinking through the whole bead. This is because the crosslinking occurs in two different planes at the same time resulting in compacting the alginate molecules (Figure 1)[29]. Alginates have been used for radiation poisoning, polluted water and toxic site clean-up as a biological adsorbent, and de-metallization of hydrogenated oils. Alginates have demonstrated superior ability to bind heavy metals, such as mercury, lead, copper, cadmium, and zinc[30].

Thus realizing the need for large scale defluoridation of drinking water by cost effective and easily available biosorbents, the objectives of the present work include:

1) Synthesis of nanoparticles of alginate crosslinked with ferric ions

2) Characterization of these nanoparticles by techniques such as FTIR and TEM

3) Batch sorption studies of these nanoparticles to study their defluoridation capacity

4) Batch sorption kinetic study of the data obtained by the sorption experiments

1.1 Experimental

1.1.1 Materials

Sodium alginate and ferric chloride were obtained from Central Drug House, Pune (India). All the other reagents were of Analytical Grade. Double Distilled water was used throughout the experiments.

1.1.2 Methods

1.1.2.1 Preparation of Alginate Nanoparticles

1.0 g Sodium alginate was dissolved in 50ml hot water with constant stirring using magnetic propeller stirrer (Remi Equipments, Mumbai, India) followed by addition of 15ml of paraffin oil. The mixture of polymer and oil was stirred still a homogenous suspension was obtained. 20ml of 5M solution of ferric chloride crosslinker was added drop by drop and stirring was continued for nearly 4 hours to obtain nanoparticles which were separated by filtration under vacuum. The nanoparticles were washed first with toluene and then with acetone. The dried nanoparticles were stored in airtight polythene bags.

1.1.3 Batch Studies

In order to explore the effect of influencing factors such as pH, temperature, contact time, quantity of adsorbent and initial fluoride concentration, a series of batch adsorption experiments were conducted. Batch adsorption experiments were performed by agitating specified amount of adsorbent in a definite amount of fluoride solution. The reaction mixture was agitated at 200 rpm for an optimum period of time at room temperature on a mechanical shaker (Remi Equipments, Mumbai India). After equilibrium the aqueous phase

concentration of fluoride was analyzed with fluoride sensitive electrode ((510, Eutech Instruments, Mumbai, India).. Percentage removal of fluoride was obtained using equation.

$$\% \text{ Removal} = C_i\text{-}C_e / C_i \times 100$$

The amount of fluoride adsorbed per unit mass of adsorbent q_e (ppm/g) was obtained using the equation

$$q_e = (C_i - C_e) / m \times v$$

Where C_i and C_e denoted the initial and equilibrium fluoride ion concentration (mg/L) respectively, m is mass of adsorbents and v being the volume of fluoride solution.

1.1.5 Characterization of Alginate Nanoparticles

1.1.5.1 FTIR Analysis

The infrared spectra were obtained using FTIR Spectrophotometer (Shimadzu 8400 S, Japan). The FTIR spectra of alginate nanoparticles before and after fluoride adsorption were recorded.

1.1.5.2 Transmission Electron Microscopy (TEM) Analysis

Transmission Electron Microscopy (Hitachi Hu-11 B,) was done to observe the size of alginate particles

1.1.6 Analysis of Batch Data

1.1.6.1 Adsorption Isotherm Model

Both Langmuir's and Freundlich adsorption isotherm equilibrium models were used for the analysis of the Alginate–fluoride sorption system.

i) Freundlich Isotherm

Freundlich adsorption isotherm model used to study the non-ideal adsorption involving heterogeneous adsorption phenomena was evaluated by the equation (3) where K_f and $1/n$ are empirical constants.

$$\text{Log } q_e = \log K_f + 1 / n \log C_e$$

ii) Langmuir Isotherm

The rearranged Langmuir's adsorption isotherm model for evaluating the monolayer sorption phenomena as depicted in equation (4) where q_e (mg/g) is the amount of metal ion sorbed by the adsorbent at the equilibrium, Q_o (mg/g) the maximum metal sorption, C_e (mg/L) the concentration of metal in solution at

the equilibrium and b (L/mg) is the Langmuir adsorption equilibrium constant[30].

$$C_e / q_e = 1 / Q_o b + C_e / Q_o$$

iii) R$_L$ Factor
-----(1)

In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter   ------(2)

$$R_L = [a / 1 + bC_o]$$

where b is the Langmuir isotherm constant and C_o is the initial concentration of fluoride (mg L^{-1}). The R_L values lying between 0 and 1 indicate favorable sorption for all the temperatures studied (Table 1)[31].

1.1.6.2 Sorption Kinetics

For a solid liquid adsorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. The adsorption dynamics can be described by the following three consecutive steps:

• Transport of solute from bulk solution through liquid film to adsorbent exterior surface;

• Solute diffusion into pore of adsorbent except for a small quantity of sorption on external surface; parallel to this is intraparticle transport mechanism of surface diffusion; and

• Adsorption of solute on interior surfaces of the pores and capillary spaces of adsorbent.

The last step is an equilibrium reaction. Of these three steps, the third step is rapid and negligible. The overall rate of adsorption will be controlled by the slowest step that would be either film diffusion or pore diffusion controlled.

Various kinetic models have been suggested for adsorption, including the Lagergren pseudo-first order kinetics, the (3) pseudo-second order kinetics, and intraparticle diffusion model, which are expressed by equations (6), (7) and (8)[32].

$$\ln (q_e - q_t) = \ln q_e - K_1 / t$$

$$t/q_t = 1/K_2 q^2_e + 1/q_e t$$

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

1.2   Results and Discussion

1.2.1   Characterization of Particles

1.2.1.1   FTIR Analysis

The FTIR spectra of alginate nanoparticles crosslinked with ferric chloride is shown in **Figure 2**. FT-IR analysis was performed to examine the functional groups present in the alginate nanoparticles. The FT-IR spectrum of alginate nanoparticles (Figure 2 (a)) displays a number of absorption peaks. The broad peak around 3453 cm^{-1} is an indicative of existence of bonded hydroxyl group. The peak near 3000 cm^{-1} was caused by C--H stretching. The absorption peak at 1740 cm^{-1} represents the stretching band of the free carbonyl double bond from the carboxyl functional group[34].The bands around 1046 cm^{-1} (C—O--C stretching) and 800 cm^{-1} (C--O stretching) present in the IR spectrum are attributed to its saccharide structure. In addition, the bands at 1594 and 1442 cm^{-1} are assigned to asymmetric and symmetric stretching peaks of carboxylate salt groups[35]. These results indicate that the carboxylic groups of alginate are dissociated into –COO– groups that can associate with trivalent cations through electrostatic interactions to form the egg box structure. Thus, in the IR spectrum of fluoride adsorbed nanoparticles (Figure 2 (b)) we can observe that the broad peak at 3453 is shifted to 3443cm^{-1} which is due to attachment of fluoride ions at the OH group and thus causing intermolecular hydrogen bonding.

1.2.1.2   Transmission Electron Microscopy (TEM) Analysis

In order to examine the size of alginate particles at nanoscale, TEM studies were performed. The TEM image (**Figure 3**) indicates that average size of novel alginate particles falls in the range of 18-38 nm and shape of particle is uniform. The nanoscale and uniform size of these particles facilitates greater defluoridation capacity of these novel alginate particles.

1.2.2   Batch Studies

1.2.2.1 Effect of Initial Concentration

Effect of initial concentration on the percentage removal of fluoride was studied at different initial fluoride concentrations by keeping other parameters constant. The effect of initial concentration on removal of fluoride and the equilibrium concentration values q_e for the different fluoride concentrations is shown in **Figure 4 (a) and (b).**It was observed that with the increase in fluoride initial concentration, the percentage removal of fluoride decreases. This may be because at higher adsorbate concentration, the binding capacity of the adsorbent approaches saturation, resulting in decrease of overall percent removal.

1.2.2.2   Effect of Adsorbent Dose

The effect of adsorbent dose on fluoride removal at fixed initial fluoride concentration is shown in **Figure 5 (a) and (b).** It was observed that percentage removal of fluoride increased with the increase in adsorbent dose. This can be explained by the fact that greater the mass of the biosorbents, larger would be the contact surface offered for the adsorption.

1.2.2.3   Effect of Temperature

The temperature effect was carried out at 5°C, 25o C and 50°C to study the influence of temperature on the defluoridation capacity of alginate nanoparticles **(Figure 6 (a) and (b))** Studies show that adsorption and removal increases at lower temperature. Increase in temperature lowers adsorption. This may be due weakening of adsorptive forces between alginate particles and fluoride ions. These results show that increase in temperature is unfavorable and decrease in temperature is a favorable factor for defluoridation by alginate particles [36].

1.2.2.4   Effect of pH

Figure 7 shows the effect of pH on fluoride removal by alginate nanoparticles. The studies were carried in the pH range of 4-12. It was observed that defluoridation was maximum at pH 4 and then steeply decreases as pH increases from the acidic range to alkaline range. In alkaline pH range there is a sharp drop in adsorption which may be attributed to the competition of hydroxyl ions with fluoride for adsorption. In the acidic range the adsorption was slightly decreased and it may be due to the formation of weak hydrofluoric acid[37].

1.2.3   Sorption Kinetics

1.2.3.1 Adsorption isotherm

Figure 8 (a) shows the linear plots of log q_e vs log C_e indicating that adsorption follows the Freundlich adsorption model and the linear plots of C_e Vs q_e in **Figure 8 (b)** shows the Langmuir adsorption isotherm. The values of Freundlich constants K_f and $1/n$ are calculated from slope and intercept of Freundlich plot and they are summarized in Table 2 . The value of

regression coefficient for Freundlich isotherm is 0.9191. The values of Q_o and b were calculated from the slopes and intercepts of the Langmuir plots respectively (Table 2) .The value of regression coefficient was found to be 0.697 for Langmuir isotherm. The two values of regression coefficient show that defluoridation by alginate particles follows the Freundlich isotherm. The R_L value obtained is 0.8849 falling in the range of favorable adsorption.

1.2.3.2 Adsorption Kinetics

The values of K_1, K_2 and q_e are given in Table 4. **Figure 9 (a) and (b)** shows the pseudo first and second order plots. The values of regression coefficient for pseudo first and second order rate equations are 0.9192 and 0.9939, respectively. From the R^2 values it can be seen that the adsorption of F^- ions from aqueous solutions is best described by pseudo second order Lagergreen equation. This model is based on the assumption that fluoride sorption process follows second order chemisorptions.

1.2.3.3 Intra Particle Diffusion

Values of K, q_t and $\sqrt{t}$ values are summarized in Table 4. Kinetic results could be used to determine that if particle diffusion is the rate limiting step for adsorption of fluoride onto the nanoparticles of alginate. In the plot (**Figure 9 (c)**) the curve deviates from the origin indicating that intra particle transport is not the rate limiting step and other mechanisms may be involved. Such a deviation from the origin may be due to the difference in the rate of transfer at the earlier stage of adsorption [38]

1.3 Conclusions

Removal of fluoride ions from aqueous solution by alginate nanoparticles was investigated through batch studies and the following conclusions were obtained.

1. The nanoparticles of sodium alginate crosslinked with ferric chloride were synthesized and used for the removal of fluoride.

2. Batch sorption studies were carried and different effects like initial concentration, adsorbent dose, pH and temperature on defluoridation capacity were studied.

3. Adsorption follows the Freundlich isotherm and it proves to be a better fit for the adsorption process. The process

of adsorption follows the pseudo second order equation and intra particle diffusion plots show that intra particle diffusion is not the rate limiting step.

4. Results obtained suggest that the adsorbent has potentials as a low-cost adsorbent for the removal and recovery of ions from wastewater.

1.4 References

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**Table 1: Characteristics of Langmuir adsorption isotherms**

Separation Factor (R_L)	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 > R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 2 Langmuir and Freundlich constants and their R^2 values

Langmuir constants				Freundlich constants		
b	Q_o	R_L	R^2	1/ n	K_f	R^2
.0013 0.697	86.956		0.8849	1.0184	8.8291	0.9191

Table 3: Intra particle diffusion, Lagergren first order and pseudo second order constants for adsorption of fluoride ions on alginate nanoparticles

Intra particle diffusion		Lagergreen first order		Pseudo second order		
K_i	R^2	K_1	R^2	K_2	q_e	R^2
0.5406	0.8491	0.057	0.9192	0.0319 0.9939	9.35	
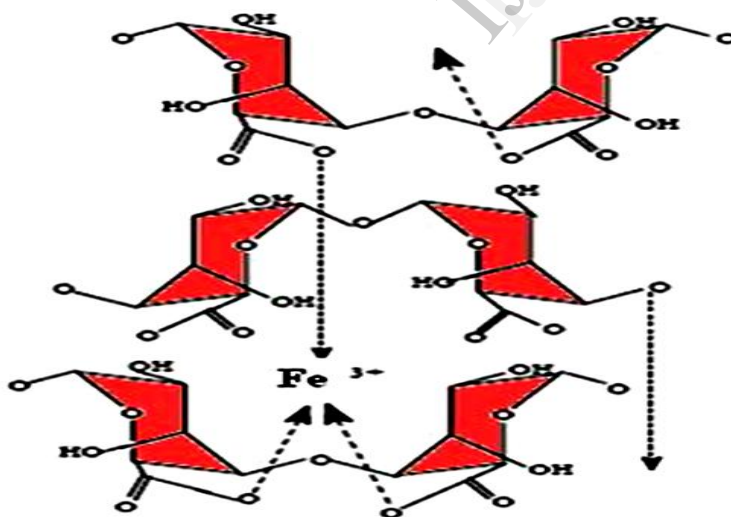
Figure 1 Schematic presentation of experimental set-up of column studies
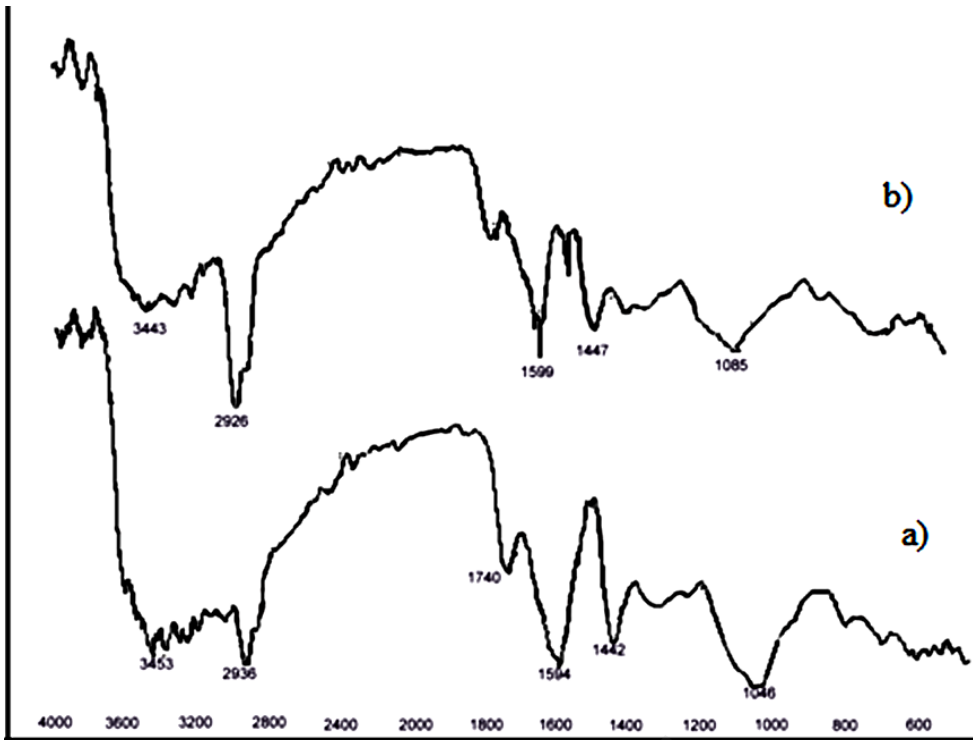
Figure 2   FTIR spectra of nanoparticles of alginate crosslinked with ferric ions (a) before adsorption of fluoride ions, and (b) after adsorption of fluoride ions
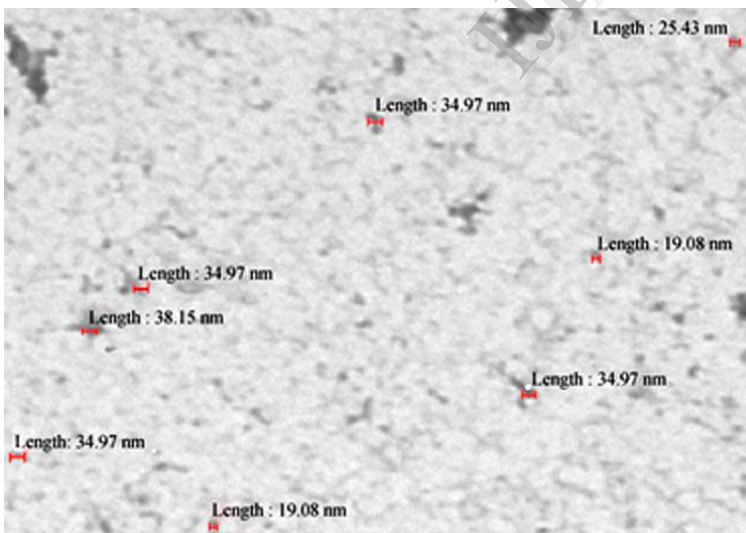
Figure 3   TEM image of nanoparticles of alginate formed by crosslinking with ferric ion
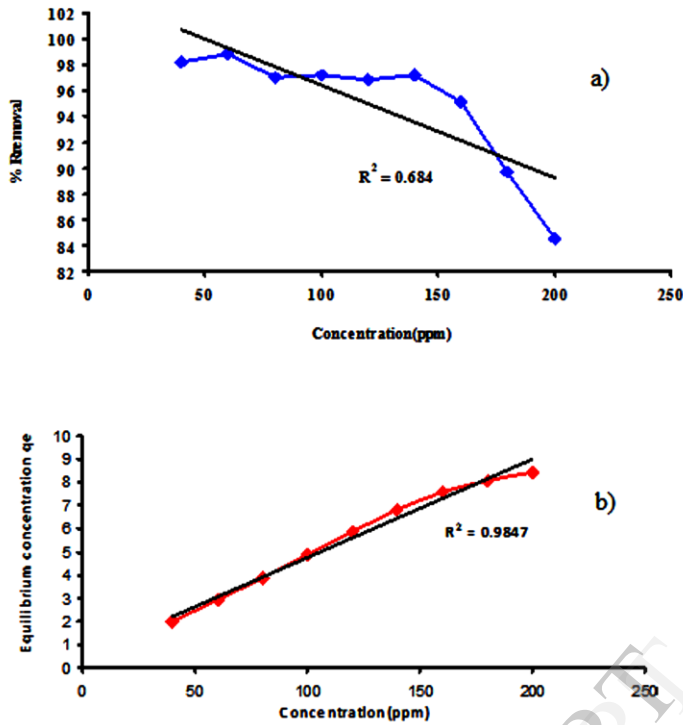
Figure 4 Effect of concentration ranging from 40-200 ppm on the % removal of fluoride and equilibrium concentration.
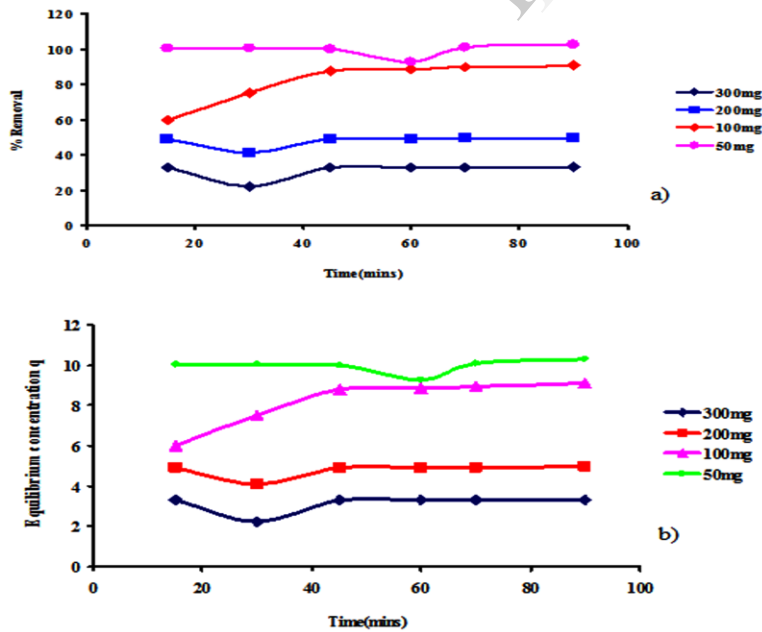

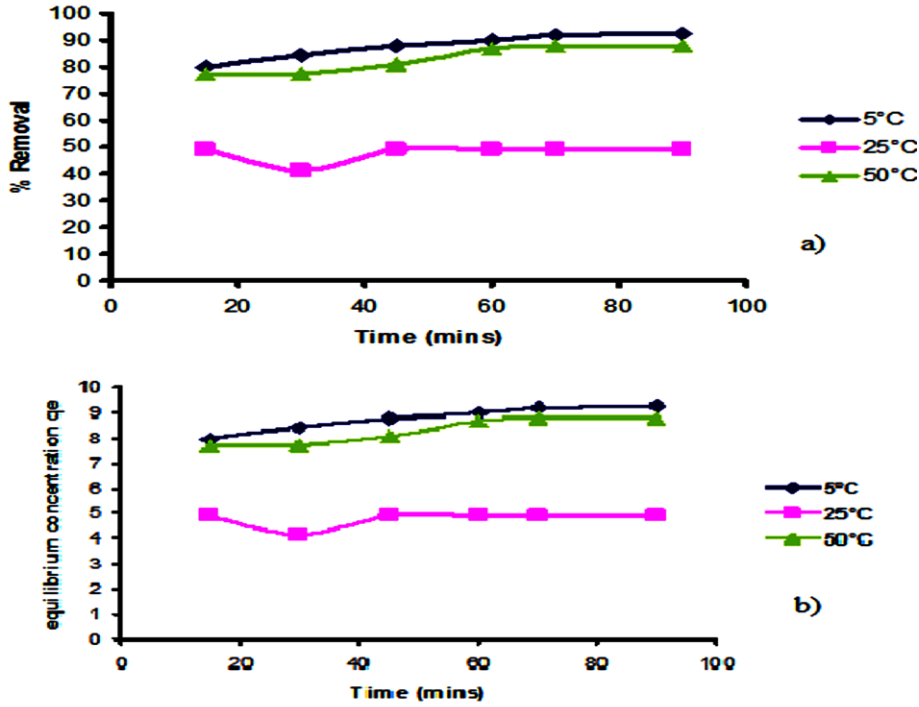**Figure 5 Effect of adsorbent doses 50-300mg on the % removal of fluoride and equilibrium concentration**

Figure 6 Effect of temperature 5°C, 25°C and 50°C on the % removal of fluoride and equilibrium concentration
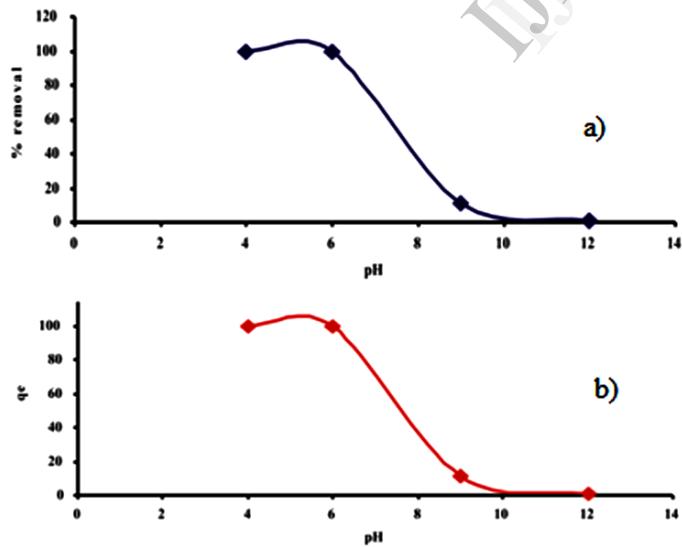

Figure 7 Effect of pH (4-12) on the % removal and equilibrium concentration values of fluoride, [m=100mg], [v=10mL], [C_i=200ppm], [agitation time=1.5 hrs], [pH=8.1±1], temp=25°C±2]
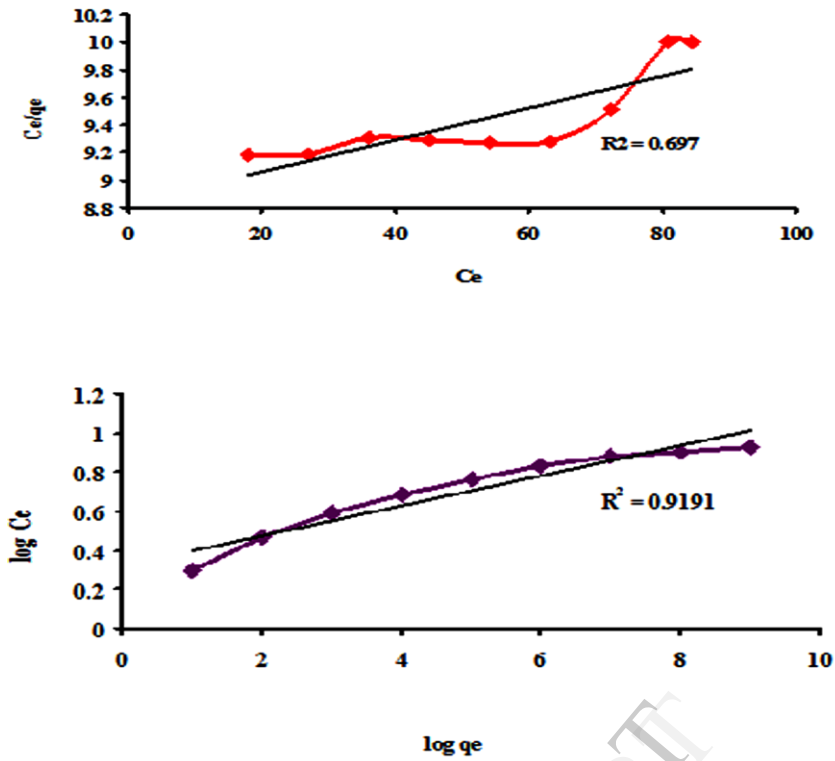
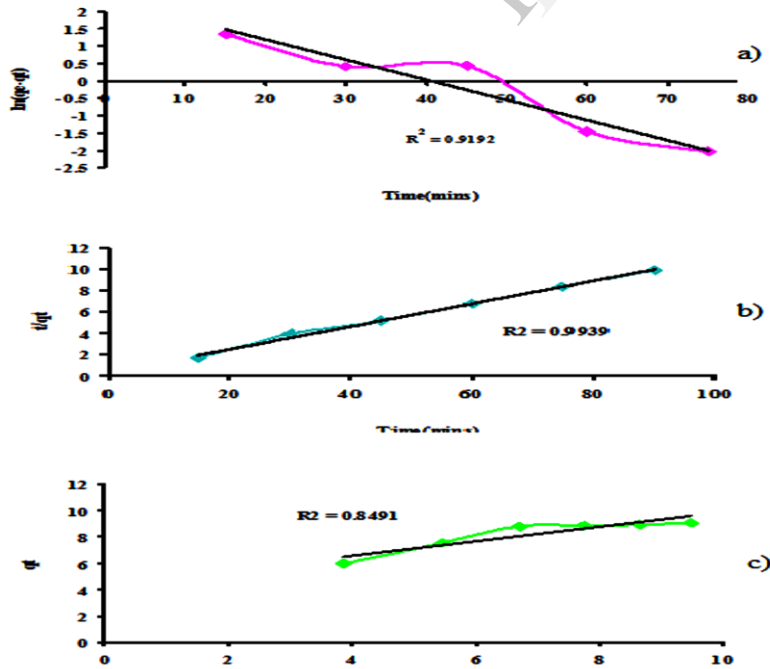**Figure 8 Plot showing the Langmuir and Freundlich adsorption isotherms**

Figure 9 Pseudo first, second order and intra particle diffusion plot