

## **Preparation and Application of Zeolitic Adsorbents for Removal of Fluoride from Aqueous Solution; Equilibrium, Kinetic and Thermodynamic Studies**

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### **ABSTRACT**

*The presence of fluoride in drinking water has profound effect on teeth and bones strengthening. But at concentrations higher than 1.5 mgL<sup>-1</sup>, fluoride becomes a serious contaminant of water. In this study, removal of fluoride from aqueous solution was studied by adsorbent prepared by modification of Y-zeolite. The parent and modified zeolites were characterized by Fourier Transform Infrared Spectrometry (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). (The effect of different parameters including pH, fluoride concentration, contact time and temperature on the adsorption capacity of the adsorbents was investigated. At the optimized conditions, the adsorption capacity of 200 mgg<sup>-1</sup> was obtained which was higher than the previous reported values. The fluoride adsorption on modified zeolite (Fe-Y) was well described by the Freundlich adsorption isotherm model. The kinetic of adsorption followed pseudo second-order model and the process was endothermic.*

**Keywords:** Fluoride, Y-zeolite, Modified zeolite, Ion exchange, Adsorption

### **INTRODUCTION**

When fluoride concentrations are above the permissible level, it is considered as a health hazardous compound. World Health Organization classified fluoride as one of the contaminants of water for human consumption [1,2]. Pollution of water by fluoride occurs through natural resources and human activities [3]. Various minerals such as fluorite, biotites, topaz, and their corresponding host rocks such as granite, basalt, and syenite, contain fluoride that is gradually released into groundwater [4-6]. Besides the natural geological sources, various industries intensively contribute to fluoride pollution. The industries which discharge wastewater containing high fluoride concentrations include nuclear installments, glass and ceramic production, semiconductor manufacturing, electroplating, coal fired power stations, beryllium extraction plants, brick and iron works, and aluminum smelters [7,8]. Fluoride as a strong electronegative anion is combined with positively charged calcium of teeth and bones resulting dental, skeletal, and non-skeletal forms of fluorosis and associated health complaints [9]. For removal of excessive amount of fluoride from drinking water, and waste streams several methods including adsorption [10,11] and precipitation [12] have been investigated. Among them, adsorption method due to its simplicity, low cost, and environmental friendly is frequently used. Different adsorbents have been examined for fluoride removal, including activated alumina [13], carbon nanotubes [14], calcite [15], red mud [16] and zeolite [17].

Zeolites are three dimensional aluminosilicate materials with porous structure that have valuable properties such as cation exchange, molecular sieving, catalysis and adsorption [18]. The fundamental building structure of zeolites consisted of tetrahedron composed of four oxygen atoms surrounding silicon or aluminum atom. Since aluminum has lower positive charge than silicon, the framework usually has a net negative charge which is balanced by exchangeable cation such as K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> [19]. Modification of zeolite can be conducted by different methods including ion exchange in which the exchangeable cation of the parent zeolite is replaced by appropriate ingoing cations. Modified zeolites have been used for removal of some anions from aqueous solutions and showed high adsorption capacity and selectivity [20,21].

In this research, the Fe-exchanged form of Y-zeolite was prepared by ion exchange process. The modified zeolite (Fe-Y) was used for removal of fluoride from aqueous solutions under different experimental conditions.

## MATERIALS AND METHODS

NaF (99.9%), ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium chloride (NaCl) were supplied from Merck company (Germany) and Y-zeolite we purchased from Johnson Matthey Company (Germany).

### Modification of Y-zeolite

The Fe-exchanged zeolite was prepared through ion exchange process. 5.0 g the synthesized Na-Y zeolite was shaken with 100 mL of 0.15M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution for 48 h at 45°C. The zeolite exchanged form was separated and washed thoroughly with deionized water. The modified zeolite (Fe-Y) was dried at 110°C and stored in a desiccator containing saturated sodium chloride solution.

### Adsorption studies

Stock solution ( $1000 \text{ mgL}^{-1}$ ) of fluoride was prepared by dissolving 0.221 g of anhydrous sodium fluoride into 1000 mL of deionized water. The standards and fluoride solutions were prepared by the stock solution by dilution. The adsorption performance of the Na-Y and Fe-Y adsorbents was studied by contacting accurately weighed amount of the adsorbent with 25 mL of fluoride solution in a plastic bottle. The mixture was continuously shaken until the equilibrium was established. The sample was separated by filtration and the fluoride concentration in the remaining solution was measured by fluoride ion selective electrode (Sartorius PY-I01). Before measurement, the sample and the standard solutions were diluted with TISAB adjusting buffer (TISAB) solution (1:1V/V) in order to eliminate the interfering effect of ions and to maintain the ionic strength and the pH of the solution constant. To realize the influence of the surface charge of the adsorbent on removal of fluoride, the pH (pzc) of the adsorbents was measured as follows:

A series of solutions was prepared by transferring 25 mL of 0.01 M NaCl solution into polyethylene vessels. The pH of the solutions was accurately adjusted between 1 and 9 by addition of HCl or NaOH (0.1M solutions).  $\text{N}_2$  was continuously bubbled into the solution to prevent the dissolving of  $\text{CO}_2$ . 0.1 g of the adsorbent was then added to the solution and after 3 hours, the final pH was measured. The measured pH was plotted versus the initial pH of the solution. The straight line of "pH initial=pH final" was also drawn. The pH at which the curve crossed the straight line was taken as the point of zero charge (pHpzc).

The uptake of fluoride was calculated by the following equation:

$$q = ((C_i - C_f) \cdot V) / m \quad (1)$$

Where (q), expressed as the amount of ions removed per unit mass of the adsorbent,  $C_i$  and  $C_f$  are initial and final concentrations ( $\text{mgL}^{-1}$ ) respectively, m is the mass of the adsorbent (g) and V is the volume of the solution (L).

## RESULTS AND DISCUSSION

### Characterization of the adsorbents

FTIR spectra of the Na-Y and Fe-Y samples were taken by Perkin Elmer Spectrum 65 Model infrared spectrophotometer (**Figure 1**). For Na-Y sample, the absorption bands appeared at 464, 576, 690, 1006, 1655, and  $3477 \text{ cm}^{-1}$  agreed well with the infrared spectral data reported by Flanigen et al. (**Figure 1a**) [22]. The similarity in the FTIR spectra of Na-Y and Fe-Y zeolites implied that the original zeolite structure was retained after replacement of Fe with Na (**Figure 1b**). The adsorption bands appeared at  $1480 \text{ cm}^{-1}$  indicated the presence of the Fe on the structure of the modified zeolite. Moreover the band at  $464 \text{ cm}^{-1}$  was enhanced by the presence of iron.

The XRD pattern of the adsorbents was taken by use of Xpertpro diffractometer instrument (Netherlands).  $\text{CuK}_\alpha$  was used as radiation source and Ni as filter. The range of scanning angle ( $2\theta$ ) was between  $0-80^\circ$  (**Figure 2**). Comparison of the Na-Y(a) and Fe-Y(b) XRD patterns indicated that the diffraction lines basically remained intact after replacement of Na by Fe indicating that the no crystalline transformation occurred during treatment of the sample.

The SEM images of the adsorbents were prepared by scanning electron microscope, MIRA3LMU model, TESCAN Company. The surface morphology of Na-Y sample was changed after ion exchange with Fe (**Figure 3**). In the SEM image of Na-Y sample well defined separated crystals with average diameter of  $1 \mu\text{m}$  were observed while in Fe-Y sample the particles became powder in form with smaller particle size.

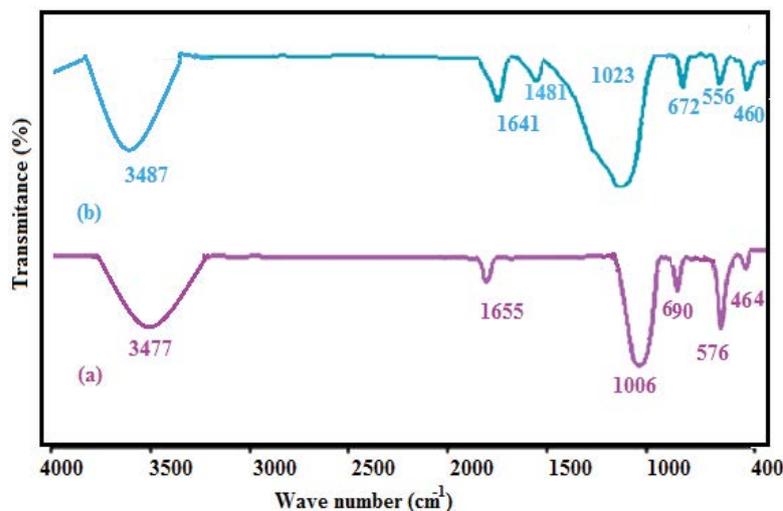


Figure 1: FTIR spectrum of (a) Na-Y and (b) Fe-Y.

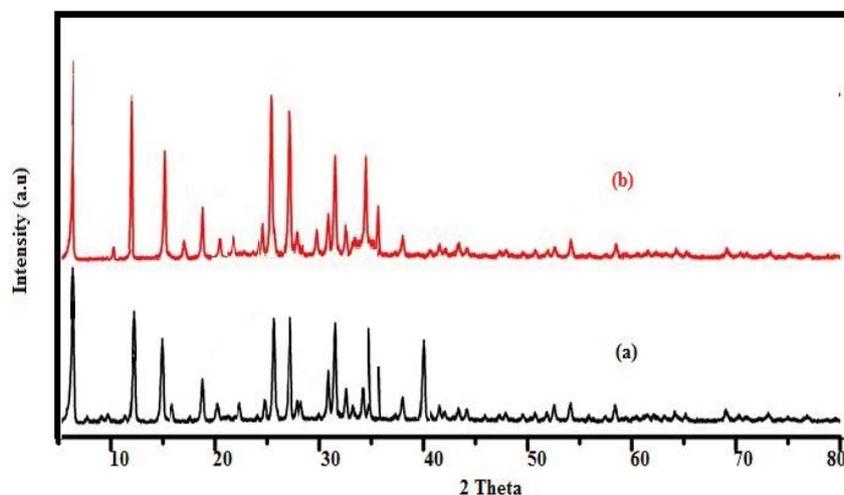


Figure 2: XRD patterns of the (a) Na-Y and (b). Fe-Y.

### Optimized adsorption capacity

The primary experiments showed that the adsorption capacity of Fe-Y was significantly higher than Na-Y zeolite indicating the enhancing effect of Fe on the adsorption of fluoride. However to optimize the adsorption capacity of the modified adsorbent, the effect of different parameters on the adsorption capacity was investigated. The effect of initial concentrations of fluoride on the adsorption capacity was examined in concentration range of 500-5000 mgL<sup>-1</sup> (Figure 4). The maximal adsorption capacity of 100 and 180 mgg<sup>-1</sup> was obtained at initial fluoride concentration of 2500 and 3500 mgL<sup>-1</sup> respectively for Na-Y and Fe-Y samples. This indicated that replacement of Na by Fe significantly increased the adsorption capacity of the adsorbent. The adsorption capacity obtained for the modified zeolite was higher than the previous reported values; in fly ash [23], polypyrrole/Fe<sub>3</sub>O<sub>4</sub> magnetic nano-composite [24], and hydrous ferric oxide [25]. The higher adsorption capacity obtained for Fe-Y adsorbent can be justified by the following reactions [26,27]:



The fluoride ions (F<sup>-</sup>) subsequently adsorbed through ion exchange process according to Equations (4) and (5).





Or undergo non-specific columbic interaction through reaction (6):

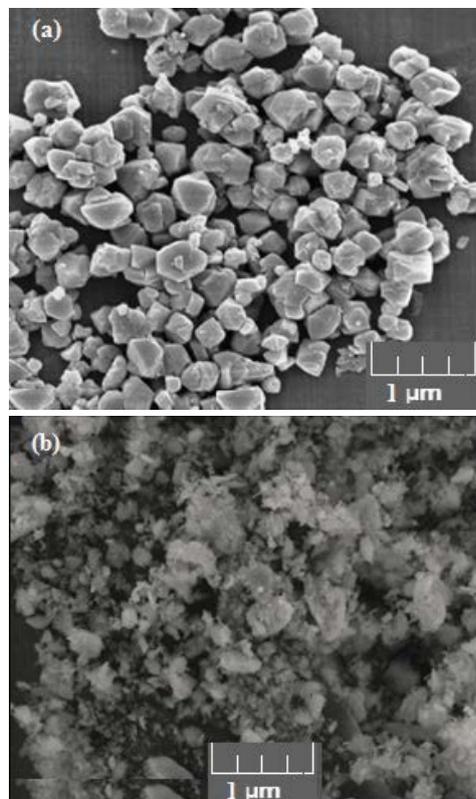


Figure 3: SEM image of (a) Na-Y and (b) Fe-Y.

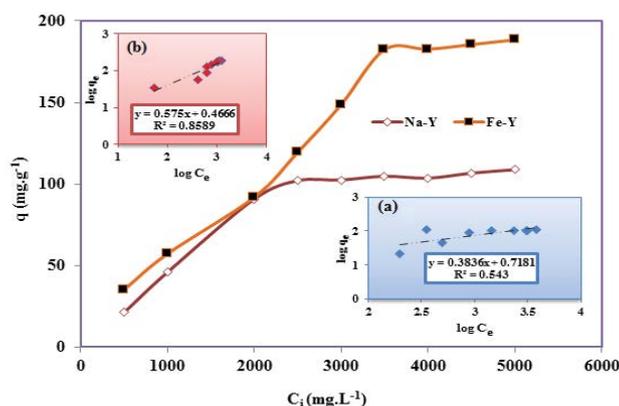
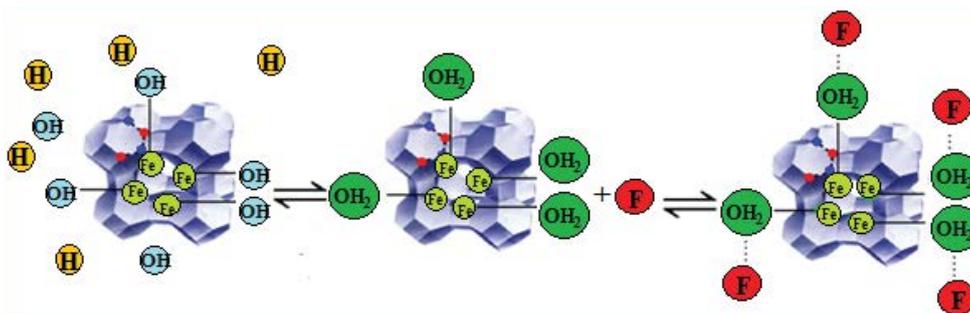


Figure 4: Effect of initial concentration on fluoride adsorption. The inset shows the Freundlich isotherm Plot for fluoride adsorption on (a) Na-Y and (b) Fe-Y.

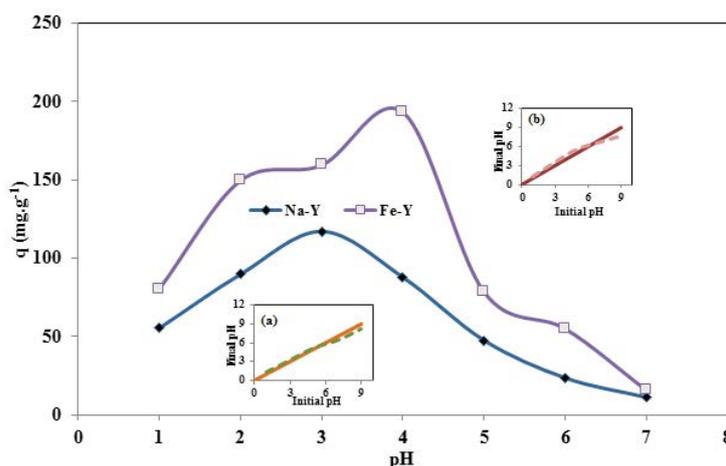
The schematic representation of fluoride adsorption by iron atoms is illustrated in **Figure 5**. The influence of pH on the adsorption of fluoride was studied in pH range of 1.0-7.0 (**Figure 6**). The adsorption performance of zeolite towards F<sup>-</sup> strongly was governed by the pH of the solution. As the solution pH increased, the adsorption capacity increased and the maximum adsorption capacity of 193.2 and 117.1 mgg<sup>-1</sup> was obtained respectively for Fe-Y and Na-Y at pH=4 and at pH=3.

The pH(pzc) of the adsorbent was close to 5.0 and 6.0 respectively for Na-Y and Fe-Y adsorbents. Basically when the pH of the solution is below the pH(pzc), the adsorbent surface is positively charged and the fluoride anions are attracted to the surface of the adsorbents. In the meantime, at very low pHs, the adsorption was not favored because

fluoride was converted to weakly ionized hydrofluoric acid. Thus fluoride adsorption was maximized at pHs lower than pH (pzc) and when the F<sup>-</sup> concentration was high. This was occurred at pH =3 and pH=4 respectively for Na-Y and Fe-Y zeolites. At high pHs, fluoride adsorption was sharply decreased because of competition of hydroxide ions for the adsorption sites. However the adsorption capacity obtained in this work was significantly higher than the results reported by other workers. Sun et al. modified natural zeolite stilbite with Fe<sup>3+</sup> for removal of fluoride and obtained the maximal adsorption capacity of 2.31 mgg<sup>-1</sup> at pH=6.94. Karthikeyan et al. used polyaniline/alumina adsorbent for removal of fluoride from aqueous solutions and reported the maximal adsorption value of 6.6 mgg<sup>-1</sup> at pH value ranging from 3 to 9 [28].



**Figure 5:** Schematic illustration of fluoride adsorption by modified adsorbent via complex formation.



**Figure 6:** Effect of pH on fluoride adsorption. The inset shows the pH (pzc) of (a) Na-Y and (b) Fe-Y.

The effect of contact time on the adsorption of fluoride indicated that the uptake was at equilibrium after 60 minutes (**Figure 7**) and the equilibrium adsorption capacity of 201.6 mgg<sup>-1</sup> and 115.6 mgg<sup>-1</sup> was obtained respectively for Fe-Y and Na-Y adsorbents. The required time for equilibration in this work was significantly shorter than the reported value for adsorbents such as activated alumina [29], nano-hydroxyapatite [30], and carbon nanotubes [31]. The fast kinetic of this work encourages the application of the prepared adsorbent for removal of fluoride from aqueous solutions by column operation.

The influence of temperature on the fluoride adsorption was studied at 298K to 328K (**Figure 8**). At higher temperature the mobility of highly electronegative fluoride ions was increased, diffusion of fluoride ions into the adsorption sites was accelerated and consequently the formation of fluoride complex was enhanced. The effect of temperature on the adsorption capacity of the adsorbent of this work was not as significant as in the previous studied adsorbents such as aluminium complexed amino phosphonic type resins [32]. This was attributed to the wider opening Y-zeolite channels.

### Adsorption isotherms

The adsorption data were analyzed by Langmuir and Freundlich isotherm models. The Langmuir isotherm equation assumes monolayer coverage of the adsorbate over a homogeneous adsorbent surface. The linear form of Langmuir isotherm equation is given by Equation (7).

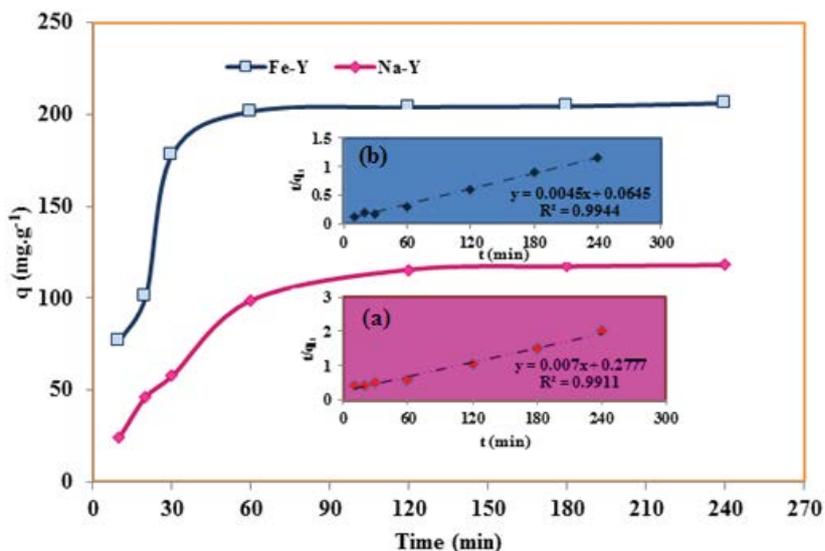


Figure 7: Effect of contact time on fluoride adsorption. . Effect of contact time and adsorption kinetics for fluoride adsorption. The inset shows the Pseudo- second order kinetic of (a) Na-Y and (b) Fe-Y.

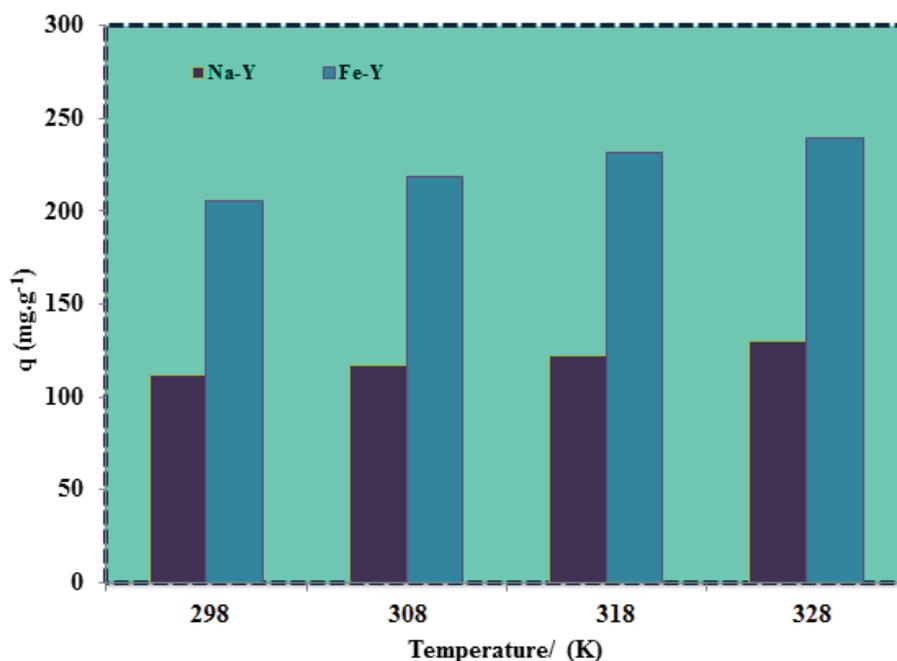


Figure 8: Effect of temperature on fluoride adsorption.

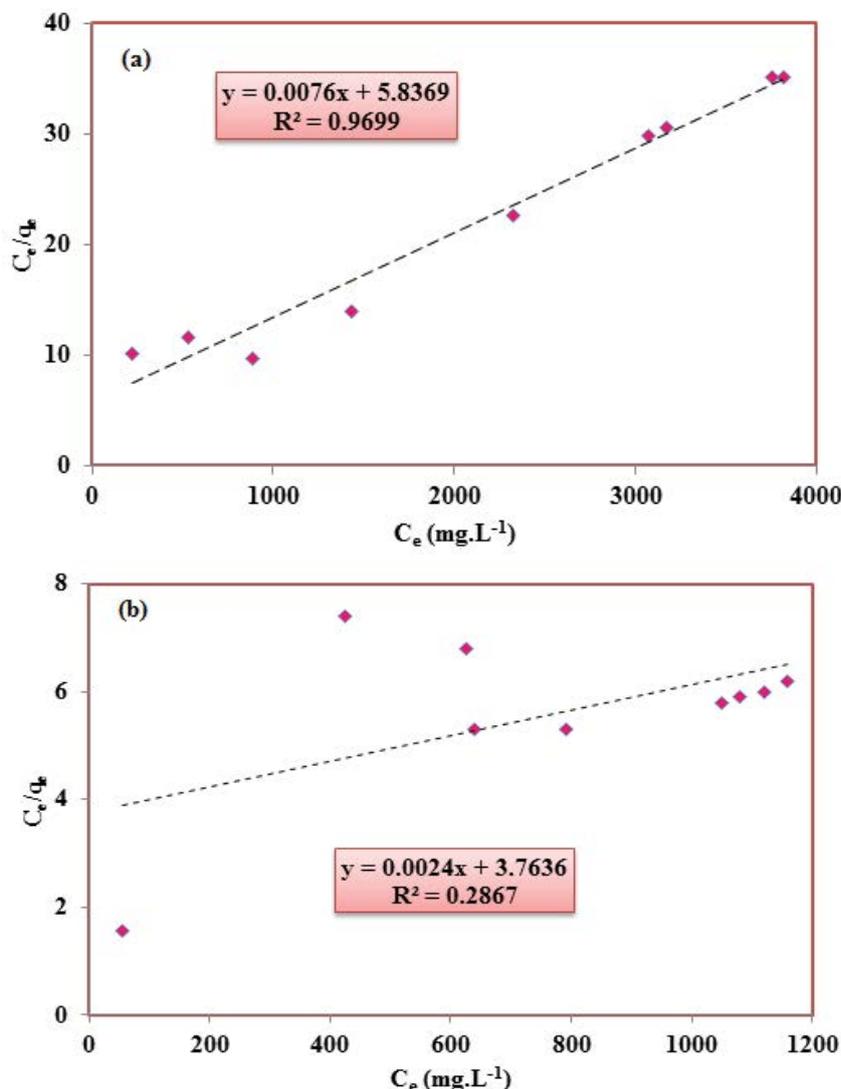
$$C_e/q_e = 1/q_m b + C_e (1/q_m) \tag{7}$$

Where  $C_e$  denotes the equilibrium concentration,  $q_e$  is the adsorption capacity,  $b$  ( $Lmol^{-1}$ ) relates to the heat of adsorption, and  $q_m$  refers to the maximum adsorption capacity, which is the amount of ions at complete monolayer coverage. The Langmuir constants  $q_e$  and  $b$  were determined from the slope and intercept of the plot. This model implies that the adsorption occurs on a homogenous surface and all adsorption sites energetically equal to each other. The plot of specific adsorption ( $C_e/q$ ) versus equilibrium concentration ( $C_e$ ) is shown in **Figure 9** and the related parameters are summarized in **Table 1**. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor  $R_L$  that is given by **Equation (8)**:

$$R_L = 1/1 + bC_0 \tag{8}$$

Where  $C_0$  is the highest initial concentration of the adsorbate ( $mgL^{-1}$ ), and  $b$  ( $Lmg^{-1}$ ) is Langmuir constant. The value

of  $R_L$  indicates the shape of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ).



**Figure 9:** Langmuir isotherm Plot for fluoride adsorption on (a) Na-Y and (b) Fe-Y.

The Freundlich isotherm is an empirical equation, assuming that the adsorption process takes place on heterogeneous surfaces. The linear form of Freundlich isotherm equations is given as:

$$\log q_e = \log k_f + (1/n) \log C_e \quad (9)$$

Where  $k_f$  is the Freundlich constant representing the adsorption capacity,  $q_e$  is the extent of fluoride anion adsorbed per unit mass of adsorbent (mgg<sup>-1</sup>),  $1/n$  is a constant indicative of the adsorption intensity or surface heterogeneity, showing the favorable adsorption if  $1/n > 1$ , and becoming more heterogeneous as its value get closer to zero. The values of Freundlich constants with the correlation coefficients are shown in **Table 1** and **Figure 4**.

$K_f$  and  $n$  are empirical constants, indicating the adsorption capacity and adsorption intensity respectively. The Freundlich model contents  $K_f$  and  $n$  are calculated from the slope and intercept of the plot of  $\log q_e$  versus  $\log C_e$  (**Figure 4**). According to the analysis of the experimental data by Langmuir and Freundlich models, it was found that fluoride adsorption by Fe-Y followed Freundlich adsorption model and by Na-Y follows the Langmuir model. The  $R_L$  values between 0 and 1 indicate favorable adsorption. Although the value of  $R_L$  of the Langmuir isotherm for Na-Y and Fe-Y was respectively 0.24, 0.32 indicating that the adsorption of fluoride by the adsorbents was favored by this model.

**Table 1:** Langmuir and Freundlich adsorption isotherms of the Na-Y and Fe-Y.

Adsorbents	Isotherm models					
	Langmuir Isotherm			Freundlich Isotherm		
	$q_m$	$R_L$	$R^2$	$n$	$K_f$	$R^2$
Na-Y	131.6	0.24	0.9699	2.6	5.2	0.5430
Fe-Y	417	0.32	0.2867	1.7	2.9	0.8589

The fitness of the data related to Na-Y adsorbent to the Freundlich isotherm implied that the adsorbent surface of heterogeneous while Fe-Y adsorbent provides homogeneous adsorption sites. In fact, in Na-Y sample the exchange sites are uniquely occupied by Na cations resulting a homogenous surface and monolayer adsorption of fluoride, but in Fe-Y, sodium cations of the parent zeolite were partially exchanged with Fe resulting a heterogeneous surface at which the adsorption sites were not energetically equivalent. Similar results were reported for removal of fluoride onto polypyrrole/Fe<sub>3</sub>O<sub>4</sub> magnetic nano-composite [24].

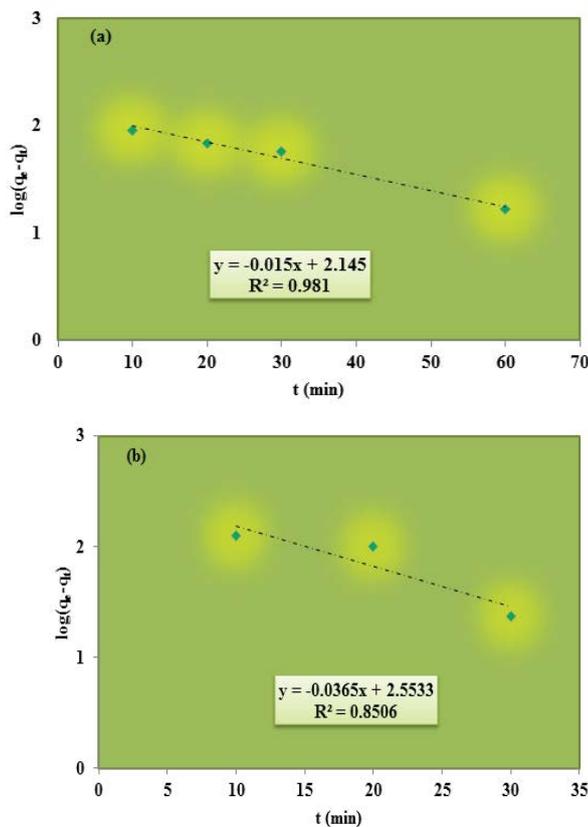
### Kinetic study

Two commonly used kinetic models; pseudo-first order and pseudo-second order kinetic models were employed to analyze the adsorption data. The linearized form of Lagergren pseudo-first-order and the pseudo-second order rate equations are given respectively in the following Equations (10) and (11).

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t \quad (10)$$

$$t/q_t = (1/k_2 q_e^2) + (1/q_e)t \quad (11)$$

Where,  $q_e$  and  $q_t$  are the amount of solute on the surface of the sorbent at equilibrium, and at  $t$  time (mg.g<sup>-1</sup>) respectively.  $k_1$  and  $k_2$  are the rate constant of pseudo-first order and pseudo-second order respectively. **Figure 10** demonstrates the plot of pseudo-first order model;  $\log(q_e - q_t)$  versus time for the adsorption of fluoride by the adsorbents.

**Figure 10:** Plot of the Pseudo-first order kinetic for fluoride adsorption on (a) Na-Y and (b) Fe-Y.

The plot of  $t/q_t$  versus  $t$  for the linear pseudo-second-order model has been depicted in **Figure 7**. The calculated results of the kinetic constants are given in **Table 2**. The higher correlation coefficient ( $R^2$ ) values obtained for pseudo-second-order model indicated the applicability of the pseudo-second-order model for the fluoride sorption onto the

studied adsorbents. The pseudo-second order model is based on chemical adsorption and confirms that the adsorption of fluoride on the adsorbents is chemical in the nature as indicated in Equations 2-6. (Section 3.2). Similar results were reported for the removal of fluoride onto Brushite [33], alumina of alkoxide nature [34] and charcoal contained dispersed aluminum oxide [35].

Table 2: Kinetic parameters for pseudo-first-order and pseudo-second-order.

Adsorbents	Kinetic models			
	Pseudo-first-order		Pseudo-second-order	
	K <sup>1</sup>	R <sup>2</sup>	K <sup>2</sup>	R <sup>2</sup>
Na-Y	0.035	0.9810	0.00018	0.9907
Fe-Y	0.084	0.8506	0.00031	0.9944

**Adsorption thermodynamics**

Thermodynamic parameters were evaluated using Equations (12) To (14).

$$K_d = q_e / C_e \tag{12}$$

$$\ln K_d = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \tag{13}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

Where C<sub>e</sub> is the amount of fluoride ion adsorbed per unit mass of the adsorbent and C<sub>e</sub> is the concentration of fluoride in aqueous phase. The distribution coefficient K<sub>d</sub> reflects the binding ability of the surface for the ingoing species. T (K), R is the ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>); ΔG<sup>o</sup> and ΔH<sup>o</sup> are in Jmol<sup>-1</sup> and ΔS<sup>o</sup> is in J mol<sup>-1</sup>K<sup>-1</sup>. According to equation (13), the plot of T<sup>-1</sup>(K<sup>-1</sup>) versus lnK<sub>d</sub> gave a straight line (Figure 11). The value of ΔH<sup>o</sup> and ΔS<sup>o</sup> obtained respectively from the slope and intercept of the plot and given in (Table 3). The positive values of ΔG<sup>o</sup> confirmed that the sorption of fluoride by the adsorbents was unspontaneous indicating the reversible nature of the adsorption under experimental conditions. The positive value of the entropy change (ΔS<sup>o</sup>) reflected that the increase of randomness which occurred with increasing in the number of fluoride species at the solid-liquid interface, because the hydrated fluoride from the aqueous phase before distribution on to the solid surface released their hydrated spheres. The positive values of ΔH<sup>o</sup> confirmed the endothermic nature of sorption process. Similar results were also reported for the removal of fluoride onto conducting polymer/alumina composites.

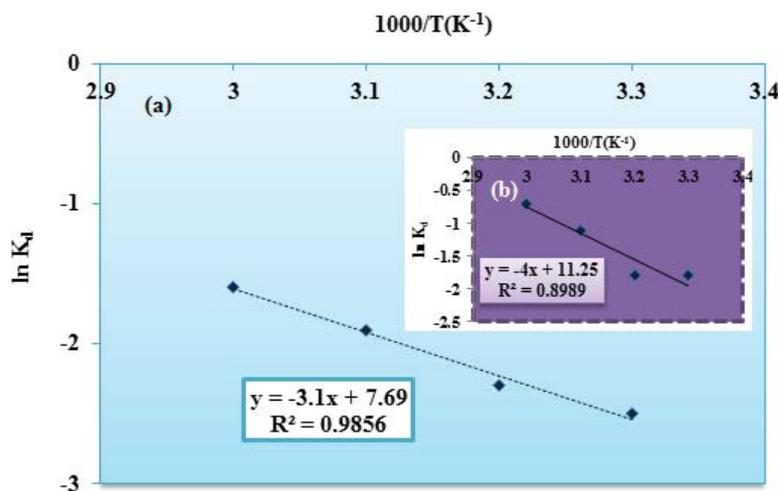


Figure 11: The plot of 1000/T (K<sup>-1</sup>) versus lnK<sub>d</sub> for the estimation- of thermodynamic parameters on the adsorption of fluoride by (a) Na-Y and (b) Fe-Y.

Table 3: Thermodynamic parameters of F-adsorption by Na-Y and Fe-Y adsorbents.

Thermodynamic parameters							
Adsorbents	ΔH <sup>o</sup> (J/mol)	ΔS <sup>o</sup> (J/mol.K)	ΔG <sup>o</sup> (J/mol)				R <sup>2</sup>
			298K	308K	318K	328K	
Na-Y	25.8	64	-19046	-19686	-20326	-20966	0.9856
Fe-Y	33.3	93.5	-27830	-28765	-29700	-30635	0.8989

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## CONCLUSION

The Fe-Y adsorbent prepared by modification of Na-Y zeolite was used for removal of fluoride from aqueous solutions. The performance of the modified zeolite compared to the parent zeolite indicated that Fe-Y adsorbent possesses higher capability for removal of fluoride from aqueous solutions. The methods used for characterization of the modified zeolite including XRD and FTIR indicated that the structure of zeolite remained intact during the exchange process. The adsorption capacity of Fe-Y sample was much higher than the reported values for the previous studied adsorbents. The fluoride uptake was kinetically fast and affected by temperature, contacting time, pH and initial concentration of fluoride. The maximal adsorption capacity was obtained at fluoride initial concentration of 3500 mgL<sup>-1</sup>, pH=4, contact time of 60 min. Fluoride adsorption on Fe-Y followed Freundlich model and on Na-Y followed the Langmuir model. The adsorption process was unspontaneous and endothermic. Evaluation of the adsorption kinetics showed that the adsorption of fluoride on the Na-Y and Fe-Y followed pseudo second-order kinetics.

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