

# Modelling the Effects of Competing Anions on Fluoride Removal by Functionalized Polyacrylonitrile Coated with Iron Oxide Nanoparticles

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## ABSTRACT

Fe<sub>2</sub>O<sub>3</sub> nano particles supported on functionalized poly-acrylonitrile was prepared. PAN-oxime-nano Fe<sub>2</sub>O<sub>3</sub> was characterized by XRD, FTIR and TEM and used for fluoride adsorption. The adsorption capacity increased with increasing initial fluoride concentration and reaction time. Fluoride-removal performance of PAN-oxime-nano Fe<sub>2</sub>O<sub>3</sub> was also tested in the presence of various competing anions usually found in drinking water. Competitive sorption between fluoride and competing anions showed a minimum preference for chloride counterions. Carbonate was the greatest competitor for fluoride removal followed by phosphate and sulphate. Counterion presence decreased fluoride adsorption capacity in order of CO<sub>3</sub><sup>2-</sup> > PO<sub>4</sub><sup>3-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup>. The presence of anions at various concentrations decreased fluoride adsorption capacity on PAN-oxime-nano Fe<sub>2</sub>O<sub>3</sub> by 1.22 to 6.51 mg g<sup>-1</sup>. Effects of each two anions exist simultaneously in aqueous solution on fluoride adsorption was investigated using Tukey's test (called also a pairwise comparison). Tukey's HSD results indicate that the differences between various pairs of anions are significant ( $P < 0.05$ ), except for chloride-sulphate ( $P = 0.08$ ). In the design of PAN-oxime-nano Fe<sub>2</sub>O<sub>3</sub> for environmental applications, the strong influence of the counter ions must be considered.

## KEY WORDS

Fluoride, PAN-oxime- nano Fe<sub>2</sub>O<sub>3</sub>, counterion, adsorption.

## 1. Introduction

One of the major classes of aquatic pollutants is inorganic anions, which pose serious health and environmental threats when present even at low concentrations. A number of inorganic anions have been found in harmful concentrations in numerous drinking water resources.<sup>1,2</sup> The inorganic anionic contaminants can be present at the same time at various levels, thus leading to the emerging issue of their control and removal from drinking water supplies. The major inorganic anions of great concern includes: fluoride (F<sup>-</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>) and chloride (Cl<sup>-</sup>).<sup>3</sup> Dental fluorosis, also called 'mottled enamel' and skeletal fluorosis occurs when the fluoride concentration exceeds 1 mg L<sup>-1</sup>.<sup>4</sup> Taking health effects into consideration, the World Health Organization (WHO) has set a guideline value of 1.5 mg L<sup>-1</sup> as the maximum permissible level of fluoride in drinking waters.<sup>5</sup> Various technologies are currently available to remove fluoride from water, including coagulation and precipitation,<sup>6,7</sup> membrane processes,<sup>8</sup> electrochemical treatments,<sup>9,10</sup> and ion-exchange and its modification,<sup>11,12</sup> and among them, adsorption has been found as one of the cheapest and effective way to remove a wide range of pollutants from water.<sup>13-15</sup> Adsorption mechanism of the anions onto adsorbents is significantly dependent on the physico-chemical properties of anions and their interaction with the adsorbent surface.<sup>16</sup> Properties of anions such as the solubility, ionic radius, hydration

energy and bulk diffusion coefficient are of great importance for the selective adsorption of anions.<sup>17</sup> In our earlier study the equilibrium and thermodynamics of fluoride adsorbed on the selected adsorbent were investigated.<sup>18</sup> However, to our knowledge, very little appears in literature on the question of co-existing ions on adsorption. Counterions affect not only the bulk and interfacial self-assembly of ions but also they compete with the adsorption. Counterion effects are crucial as aqua ions are present at the same time in natural waters. The adsorption isotherm and its behaviour would change as the type and concentration of ions varies. The studies of the effects of counterions on fluoride adsorption are very limited. Moreover, models are lacking that can accurately predict fluoride adsorption under different field of water quality conditions, especially in the presence of competing anions. The present study was designed to determine fluoride adsorption behaviour in the presence of competing elements, and to quantify fluoride adsorption under different water quality conditions. This information will be useful when designing and operating fluoride-removal systems based on varying local water anions.

## 2. Materials and Methods

### 2.1. Materials

Sodium carbonate, hydroxylamine hydrochloride and sodium fluoride were purchased from the Merck Company. Fluoride stock solution was prepared by dissolving sodium fluoride in

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deionized (DI) water. The solution was stored in the dark at 4 °C. Standards various nitrate concentrations were prepared by appropriate dilution of the stock solution with DI water. All reagents used were of analytical reagent grade.

## 2.2. Methods

### 2.2.1. Preparation of PAN-oxiamide-nano Fe<sub>2</sub>O<sub>3</sub>

The preparation and synthesis of selected PAN-oxiamide-nano Fe<sub>2</sub>O<sub>3</sub> was described in our earlier research.<sup>18</sup> Hydroxylamine hydrochloride (16 g), sodium carbonate (12 g), and 0.4 g of PAN powder were added to a 250 mL bottle to which 100 mL of deionized water was added and shaken. The reaction was carried out at 70 °C for 120 min. After reaction, the resultant was filtered and dried at room temperature. Fe<sub>2</sub>O<sub>3</sub> was coated on PAN functionalized by adding 0.2 g of selected Fe<sub>2</sub>O<sub>3</sub> and 100 mL deionized water in a sealed bottle. The solution was shaken at 70 °C for 120 min and the product was filtered and dried in a vacuum oven at 60 °C. PAN-functionalized Fe<sub>2</sub>O<sub>3</sub> was used as an adsorbent. Fig. 1 represents the hypothesized reaction of hydroxylamine hydrochloride and iron oxide nanoparticles with the PAN nitrile group.<sup>18</sup>

### 2.2.2. Characterization of the Adsorbent

The functional group and iron oxide nanoparticles on PAN were detected by Fourier transform infrared (FT-IR) spectrometer (FT-IR Bruker Tensor 27 spectrometer). The size and structure of the synthesized functionalized-PAN coated with Fe<sub>2</sub>O<sub>3</sub> nanoparticles were analyzed by transmission electron microscopy (TEM) (ARA TEM Model No: 0201/A, ARA research company, Iran). X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Philips PW 1800 diffractometer.

### 2.2.3. Batch Adsorption Experiments

A stock solution (1000 mg L<sup>-1</sup>) was prepared by dissolving sodium fluoride in 1000 mL of deionized water. The prepared stock solution was diluted to obtain the required concentrations for further use. All batch adsorption experiments were carried out in 50 mL sealed plastic tubes with the working volume of 25 mL. After adding a known weight of the adsorbent, the flask was shaken (150 rpm) for 24 h in a temperature-controlled (25 ± 2 °C) water bath shaker for predetermined time intervals. The liquid samples then centrifuged and residual fluoride was analysed by the use of a fluoride-specific ion-indicating elec-

trode. The amount of fluoride uptake was calculated from the following equation:<sup>7</sup>

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $q_e$  is the fluoride adsorbed (mg g<sup>-1</sup>),  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of fluoride in solution (mg L<sup>-1</sup>), respectively.  $V$  is the volume of solution and  $m$  is mass of the adsorbent (g). The effects of adsorption time and initial fluoride concentration were analysed by Sigma Plot 12.5 software (Published by Systat Software 2003–2013).

### 2.2.4. Coexisting Ions Experiments

The effects of different anions on fluoride removal were studied in batch experiment. Pure grade salts Na<sub>2</sub>SO<sub>4</sub>, NaCl, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub> and deionized water were used to prepare the desired anion concentration of 30 and 50 mg L<sup>-1</sup>. The aliquots were stirred in the presence of fluoride with initial concentration of 30 mg L<sup>-1</sup> for 24 h. Fluoride removal was measured spectrophotometrically and its removal percentage were compared with absence of ions (referred as control groups). The concentrations of competing anions were analyzed using a Dionex chromatograph.

## 3. Results and Discussion

### 3.1. Adsorbent Characteristic

The FT-IR spectrum of PAN (Fig. 2a) exhibited characteristic bands of nitrile (2238 cm<sup>-1</sup>), carbonyl (1728 cm<sup>-1</sup>) and ether (1229 and 1070 cm<sup>-1</sup>) groups; carbonyl and ether bands originate from methylacrylate comonomer. The FT-IR spectra of functionalized PAN (Fig. 2b) showed all the characteristic bands of the functional groups of PAN with additional peaks at 910 and 1662 cm<sup>-1</sup> which are due to the stretching vibration of N-O and C=N groups in functionalized PAN,<sup>18</sup> respectively; furthermore, the intensity of the nitrile peak of functionalized PAN decreased, all of these changes confirm the introduction of amidoxime groups on PAN.<sup>18</sup> Fig. 3. shows the XRD patterns functionalized PAN Fe<sub>2</sub>O<sub>3</sub>. The XRD patterns of functionalized PAN Fe<sub>2</sub>O<sub>3</sub> (Fig. 3) show a broad non-crystalline peak (2θ = 20–30 °) and a crystalline peak (2θ = 18 °) corresponding to the orthorhombic PAN reflection,<sup>18</sup> and besides the diffraction peaks of the PAN phase, other peaks appeared corresponding to the above peaks, indicating that the Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the PAN have the same crystal diffraction as pure Fe<sub>2</sub>O<sub>3</sub>. All of the peaks in the

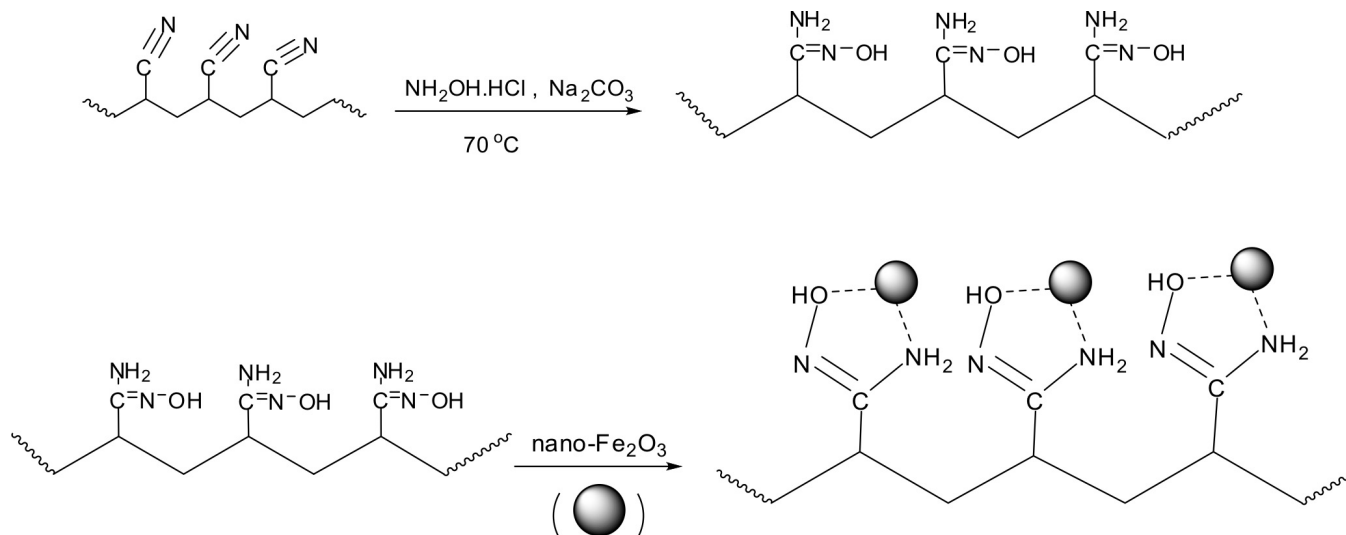
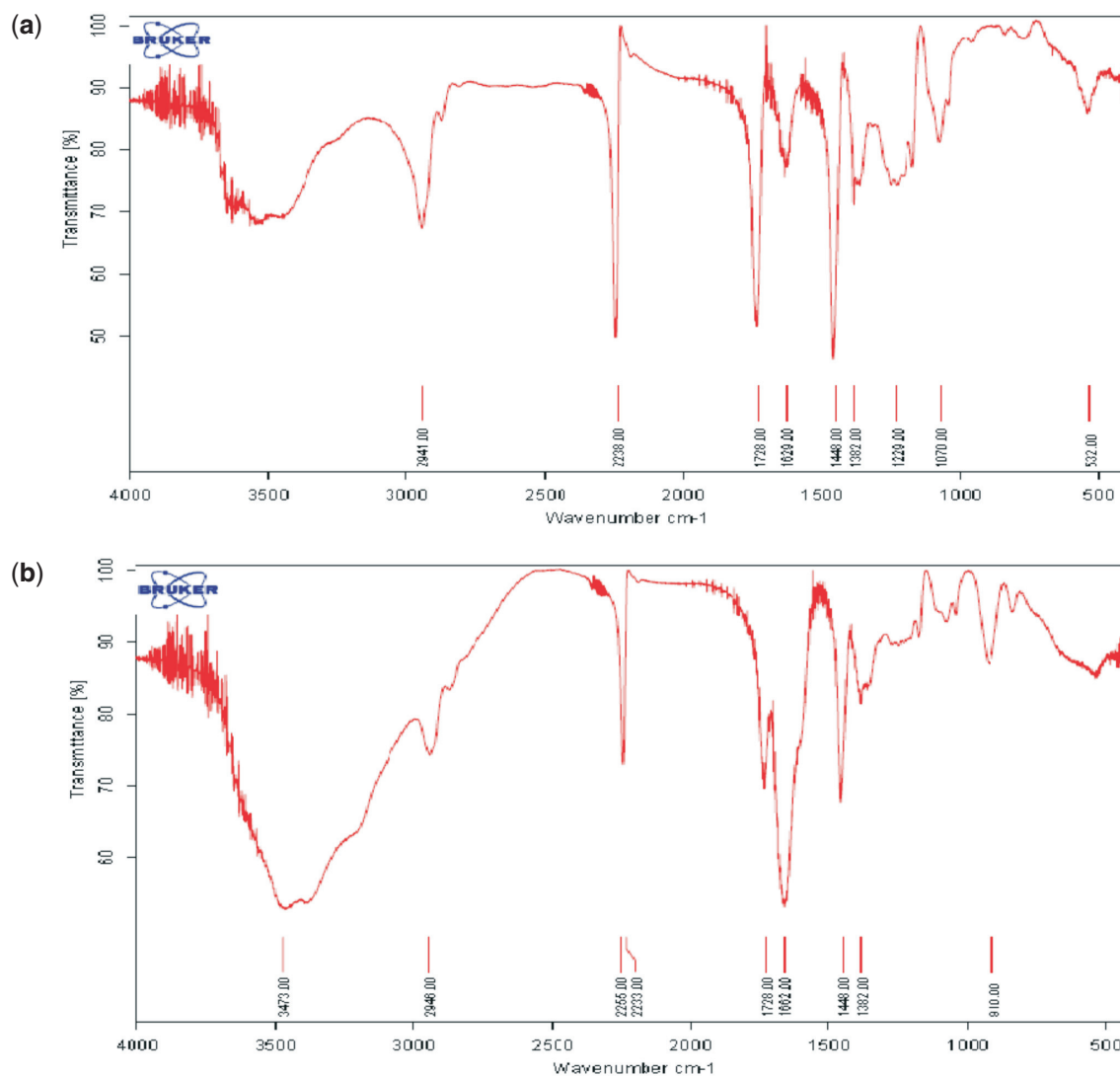


Figure 1 Expanded molecular formula of functionalized PAN coated with iron oxide nanoparticles.<sup>18</sup>



**Figure 2** FTIR pattern of PAN (a), functionalized PAN (b).

diffraction diagram indicated by vertical lines could be assigned to the hematite phase  $\text{Fe}_2\text{O}_3$ . The crystallographic phase is in good agreement with the standard data form JCPDS card No. 01-072-0469.

TEM images of as-prepared nanomaterial presented in Fig. 4. TEM image of PAN-oxime- $\text{Fe}_2\text{O}_3$ , show that  $\text{Fe}_2\text{O}_3$  nanoparticles are well dispersed with an average diameter of around 50 nm. The morphology also indicates that the nanoparticles are clearly well identified and spherical.

The mean crystallite size was also evaluated using XRD analysis based on the well-known Scherrer formula:<sup>19</sup>

$$d = \frac{k\lambda}{(\text{FWHM}\cos\theta_{\max})} \quad (2)$$

where  $k$  denotes the shape factor,  $\lambda$  is the X-ray wavelength, (FWHM) shows line broadening at half of the maximum intensity, and  $\theta$  designates the Bragg angle. In the above formula, 'd' is the mean size of the crystalline domains, which may be equal to the size of the grains.<sup>19,20</sup> In our research the average  $\text{Fe}_2\text{O}_3$  crystallite size was found to be 41.4 nm.

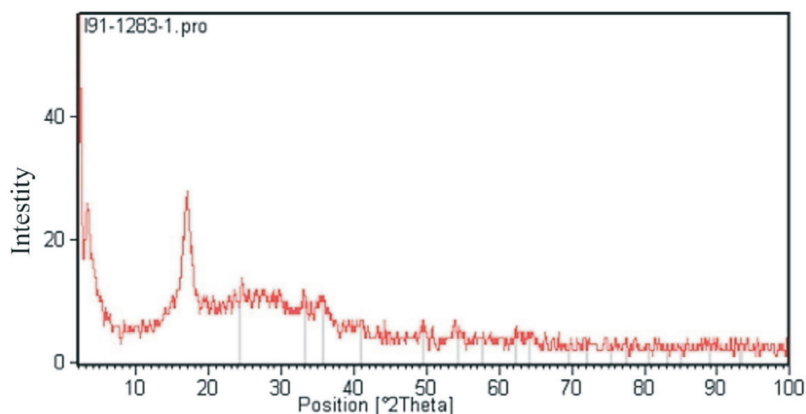
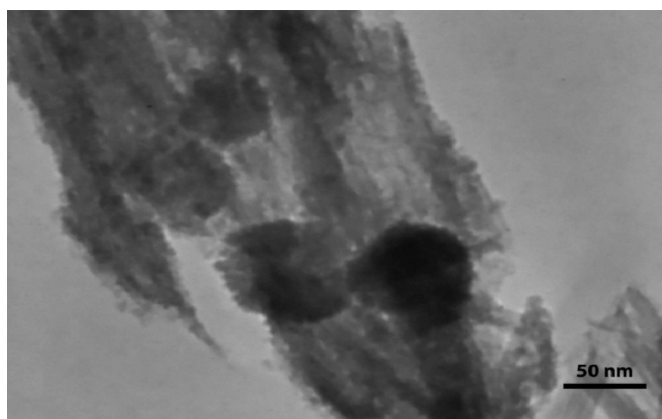
### 3.2. Adsorption Kinetics

Response surface plots describe the relationship between the response and experimental levels of each variable. These plots also depict the type of interaction between test variables. Figure 5 shows the contour plots for interaction of initial concentration

and contact time on fluoride adsorption in  $\text{pH } 9 \pm 0.5$ . As both the time and initial fluoride concentration increased, fluoride uptake by adsorbent rose. The equilibrium time was independent of initial fluoride concentrations, as can be seen from Fig. 5. The adsorption capacity increased nearly two-fold (from 9 to 18  $\text{mg g}^{-1}$ ) as fluoride concentration increased from 20 to 40  $\text{mg L}^{-1}$ . Adsorption of fluoride on adsorbent increased quickly within the first 80 min. Initially the adsorption proceeded quickly, due to the greater availability of binding sites on the adsorbent surface. After 100 min of reaction, fluoride uptake did not change; therefore, the equilibrium time was selected as 120 min. A second-order polynomial model with interaction terms fitted to the experimental data was conducted on the basis of Box-Behnken experimental design model. The goodness of fit of the model was calculated using coefficient of determination ( $R^2$ ) and analysis of variance. Sigma plot software was used for statistical analysis of the data obtained. The application of the response surface methodology based on the estimated parameters indicated an empirical relationship between the response and the input variables which is well expressed by the following fitted second-order polynomial equation:<sup>21</sup>

$$Y = -4.58 + 0.14 X_1 + 0.165 X_2 - 0.001 X_2^2 + 0.003 X_1 X_2 \quad (3)$$

where  $Y$  is the amount of fluoride adsorbed ( $\text{mg g}^{-1}$ ),  $X_1$  is initial fluoride concentration ( $\text{mg L}^{-1}$ ) and  $X_2$  is the time of reaction

Figure 3 XRD pattern of oxime-nano-Fe<sub>2</sub>O<sub>3</sub>.Figure 4 TEM image of PAN-oxime-Fe<sub>2</sub>O<sub>3</sub>.

(min). The Student *t*-distribution and the corresponding *P*-values, along with the estimated parameters, are given in Table 1. A larger *t*-value and smaller *P*-value identifies the effects that appear to be very significant. According to Equation 3 and Table 1 it is clear that the first-order effects of fluoride concentration and time are strongly significant due to their respective small *P*-values. The quantities of  $X_1$  and  $X_2$  have positive influence while  $X_2^2$  showed negative influence on adsorption. The second-order fluoride concentration showed no effect on adsorption (Table 1).

Table 1 The significance of each parameter on fluoride adsorption.

Variables	<i>P</i> -value	<i>t</i> -value	Probability
Intercept	0.02	2.78	0.021
$X_1$	0.01	3.03	0.014
$X_2$	0.0003	5.65	0.0003
$X_2^2$	0.00004	7.25	0.00004
$X_1X_2$	0.0002	5.98	0.0002
$X_1^2$	0.09	1.03	–

(*n* = 30) and residual standard error = 0.78

### 3.3. Fluoride Adsorption Model

Fluoride has different species in water, including F<sup>-</sup>, HF and HF<sub>2</sub><sup>-</sup> in an aqueous. The reactions can be written as:<sup>22</sup>

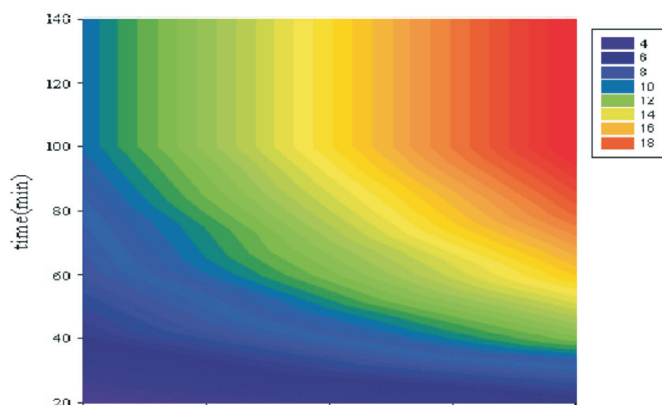
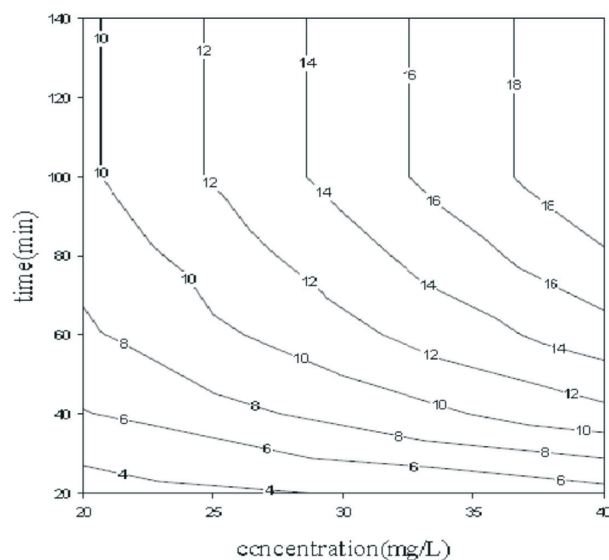
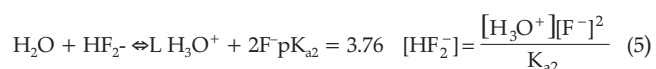
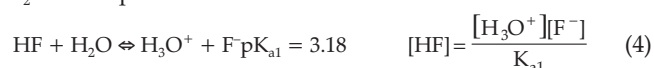


Figure 5 Response surface counter plots showing the effects of reaction time and initial concentration on fluoride adsorption capacity. Experiments were conducted under a pH of 9 ± 0.1 and adsorbent mass of 0.2 g.

where  $\text{p}K_{a1}$  is an acid dissociation constant. Total dissolved fluoride is expressed as:

$$F_{\text{total}} = [\text{HF}] + 2[\text{HF}_2^-] + [\text{F}^-] \quad (6)$$

HF is the dominant species at pH 1–3.18, while F<sup>-</sup> is the dominant species at pH above 3.18.<sup>11</sup> Increase in HF<sub>2</sub><sup>-</sup> species were observed as total fluoride concentration increases. However, when the total dissolved fluoride is below 50 mg L<sup>-1</sup>, the maximum fraction of HF<sub>2</sub><sup>-</sup> is less than 10%.<sup>22</sup> Therefore, it is expected that, under practical water quality conditions, the adsorption of

HF<sub>2</sub> is insignificant. As a result, there are only two soluble fluoride species considered, HF and F<sup>-</sup>. Based on previous study HF<sub>2</sub><sup>-</sup> is not adsorbed.<sup>22</sup> Therefore, the amount of fluoride adsorbed on the surface site of adsorbent can be expressed as:



where

$$F^- = \frac{K_{a1} F_{\text{Total}}}{K_{a1} + [H_3O^+]} \quad (8)$$

In this research, natural pH of fluoride-containing water (30 mg L<sup>-1</sup>) was 9, indicating only F<sup>-</sup> exists. In our earlier study, the adsorption of fluoride ion on PAN-oxime-nano Fe<sub>2</sub>O<sub>3</sub> was well defined by the Langmuir isotherm model,<sup>23</sup> in which each type of surface site is assumed to have the properties of a single-site system.

### 3.3. Effects of Competitive Ions

The effects of interfering ions on fluoride adsorption were assessed by adding a mixture of commonly occurring anions in deionized water, such as carbonate (CO<sub>3</sub><sup>2-</sup>), chloride (Cl<sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>) and phosphate (PO<sub>4</sub><sup>3-</sup>) to the fluoride solutions at pH 9. The initial fluoride concentration was 30 mg L<sup>-1</sup>, while the initial concentrations of other anions varied from 20 mg L<sup>-1</sup> to 40 mg L<sup>-1</sup>. At 30 mg L<sup>-1</sup> initial F<sup>-</sup> concentration and other anions' absence, the adsorption capacity of fluoride was 14 mg g<sup>-1</sup>. The presence of anions at various concentrations decreased the adsorption capacity by 1.22 to 6.51 mg g<sup>-1</sup>. The anions reduced fluoride adsorption on adsorbent in the order of CO<sub>3</sub><sup>2-</sup> > PO<sub>4</sub><sup>3-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup>; suggesting that the affinity of adsorbent for these anions (Fig. 6). From the box plots it appears that the mean effect of chloride on relative percentage removal of fluoride is lower than that for sulphate, phosphate and carbonate. Carbonate ion had the maximum and chloride showed the minimal effect on the reduction of fluoride removal. The results indicate that carbonate is the greatest competitor for fluoride followed by phosphate, sulphate and chloride. Some anions could enhance coulombic repulsion forces and compete with fluoride for the active sites, readily decreasing adsorption.<sup>24</sup> Generally, multivalent anions are absorbed more readily than monovalent anions.<sup>24</sup> This phenomenon is closely correlated with the Z/r (charge/radius) values of the anions which classified with the order of CO<sub>3</sub><sup>2-</sup>

CO<sub>3</sub><sup>2-</sup> (2/2.1) > PO<sub>4</sub><sup>3-</sup> (3/3.4) > SO<sub>4</sub><sup>2-</sup> (2/2.9) > Cl<sup>-</sup> (1/1.8). A decrease in fluoride adsorption capacity was observed as counterions concentrations decreased from 50 to 30 mg L<sup>-1</sup>. Similar phenomenon has been observed in the case of fluoride removal by nano-magnesia.<sup>24</sup>

The adsorption mechanism of the anions onto adsorbents is significantly dependent on the physico-chemical properties of anions and their interaction with the adsorbent surface. Properties of anions such as the solubility, ionic radius, hydration energy and bulk diffusion coefficient are crucial for the selective adsorption of anions.<sup>24</sup> Hydrated anions which have larger hydrated radius such as carbonate form only outer sphere complexes and are held by long-range electrostatic forces than anions with smaller hydrated radii.<sup>24</sup> Fluoride, chloride and sulphate form inner-sphere complexes. In comparison, among these anions, chloride has the highest diffusion coefficient, thus the formation of inner sphere complexation is expected. The findings of the current study are consistent with those of Shao-Xiang *et al.* (2009) who examined the effects of coexisting ions on fluoride removal by manganese oxide-coated alumina.<sup>25</sup> NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> (<300 mg L<sup>-1</sup>) showed negligible effect on the removal of fluoride. However, other common coexisting ions affected fluoride removal in the order of PO<sub>4</sub><sup>3-</sup> > SO<sub>4</sub><sup>2-</sup>. The fluoride-removal efficiency was below 10 % in the presence of 300 mg L<sup>-1</sup> PO<sub>4</sub><sup>3-</sup>.<sup>24</sup>

In order to investigate the effect of the two substances on fluoride adsorption, the Tukey's test (called also a pairwise comparison) was applied.<sup>26,27</sup> Tukey test procedures determined which pairs of the six group means differed. The Tukey's HSD results indicate that the differences between various pairs of anions are significant (P < 0.05), while the chloride-sulphate difference is not (P = 0.08). Figure 7 shows the mean difference with 95 % confidence interval for each possible comparison. In Tukey's test, the mean difference confidence interval, which does not span zero indicates a statistically significant difference in that group. The mean differences confidence interval (except for CO<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup>) did not span zero indicating a statistically significant difference in these groups.

### 3.4. Modelling the Effects of Counter-ions on Fluoride Adsorption

In Langmuir isotherm model active sites are independent.

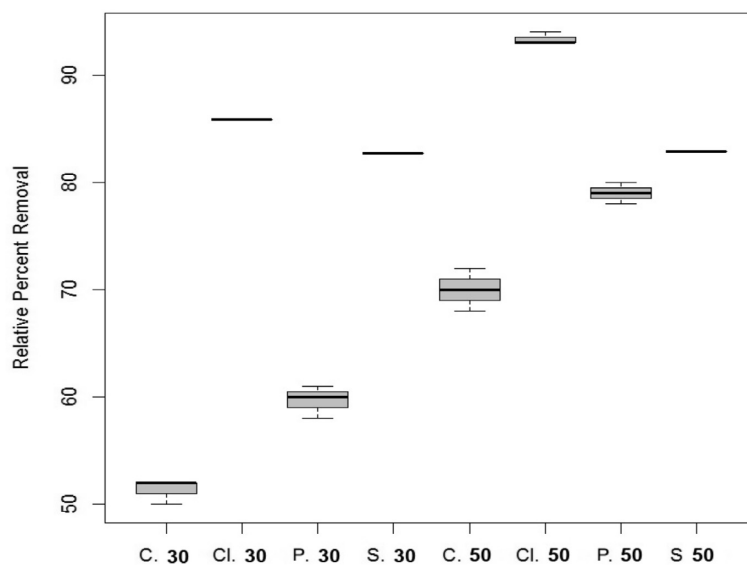
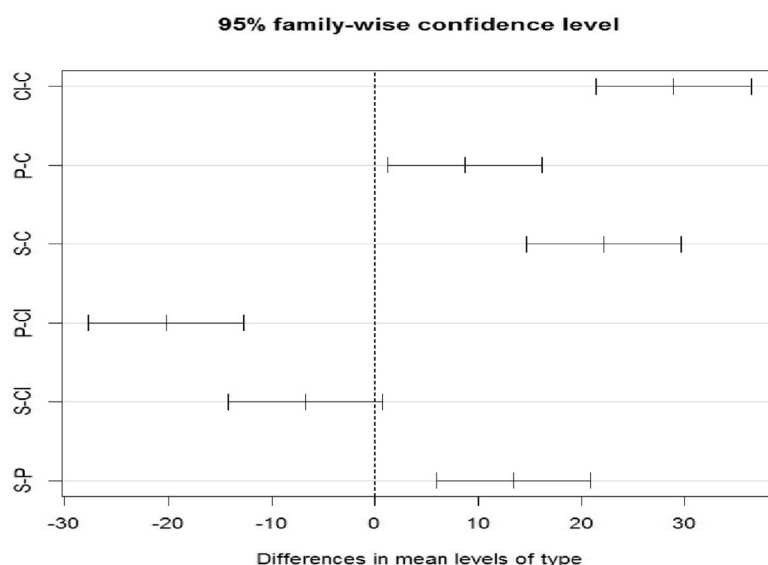


Figure 6 Effects of different anions concentration (30 and 50 mg L<sup>-1</sup>) on fluoride removal C = carbonate, Cl = chloride, N = phosphate, S = sulphate (n = 40).



**Figure 7** Pairwise comparisons between anion group means (C = carbonate, Cl = chloride, P = phosphate, S = sulphate) (n = 40).

Probability of one site being occupied is not dependent on the status of adjacent sites. Langmuir isotherm assumes adsorption and desorption as being elementary processes.<sup>22</sup> In this situation the rate of adsorption  $r_{ad}$  and the rate of desorption  $r_d$  for fluoride and carbonate are given by:

$$\begin{cases} r_{ad} = K_{ad}C_F[S] \\ r_d = K_d[F_{ad}] \end{cases} \quad (9)$$

$$\begin{cases} r_{ad} = K_{ad}C_{CO_3}[S] \\ r_d = K_d[CO_{3ad}] \end{cases} \quad (10)$$

where  $C_F$  and  $C_{CO_3}$  are the concentration of fluoride and carbonate at a given temperature,  $[S]$  is the concentration of bare sites in number  $m^{-2}$ ,  $[F_{ad}]$  and  $[CO_{3ad}]$  is the surface concentration of fluoride and carbonate in molecules  $m^{-2}$ , and  $k_{ad}$  and  $k_d$  are constants.

At equilibrium, the rate of adsorption equals the rate of desorption ( $r_{ad} = r_d$ ) and rearranging to:

$$\frac{[F_{ad}]}{C_F[S]} = K_{eq}^F \quad (11)$$

$$\frac{[CO_{3ad}]}{C_{CO_3}[S]} = K_{eq}^{CO_3} \quad (12)$$

The concentration of all sites  $[S_{total}]$  is the sum of the concentration of free sites  $[S]$  and of occupied sites:

$$[S_{Total}] = [S] + [F_{ad}] + [CO_{3ad}] \quad (13)$$

The fraction of the surface sites covered with F and  $CO_3$ , were defined as  $\theta_F$  and  $\theta_{CO_3}$  based on the following equations:

$$\theta_F = \frac{[F_{ad}]}{[S_{Total}]} \quad (14)$$

$$\theta_{CO_3} = \frac{[CO_{3ad}]}{[S_{Total}]} \quad (15)$$

If these equations applied to the previous equations (11 and 12), which combine site balance and equilibrium, then yield to:

$$\theta_F = \frac{K_{eq}^F C_F}{1 + K_{eq}^F C_F + K_{eq}^{CO_3} C_{CO_3}} \quad (16)$$

$$\theta_{CO_3} = \frac{[K_{eq}^{CO_3} C_{CO_3}]}{1 + K_{eq}^{CO_3} C_{CO_3} + K_{eq}^F C_F} \quad (17)$$

Therefore, the fraction of competing anion (m) compete with adsorbate (n) can be expressed as:

$$\theta_n = \frac{[K_{eq}^n C_n]}{1 + K_{eq}^n C_n + K_{eq}^m C_m} \quad (18)$$

Equation 18 incorporates effects of each competing anions on fluoride removal. Using adsorption constants of fluoride and competing anions, the fluoride adsorption can be predicted.

#### 4. Conclusion

A novel adsorbent PAN-oxime-nano  $Fe_2O_3$  was prepared and applied for fluoride removal. The structural properties of as-prepared adsorbent were investigated by FTIR, SEM and XRD analysis. Response surface plots were used to investigate the effects of various parameters on fluoride adsorption, namely initial concentration and reaction time. At higher initial concentration and time of reaction fluoride adsorption capacity increased. Drinking water contains many ions such as sulfate, phosphate, chloride, bromide and nitrate. They will consequently compete with fluoride anions for the adsorption sites on the adsorbents surface. The effects of anions on the adsorption of fluoride were studied in batch mode with the concentration of each anion at 30 and 50  $mg\ L^{-1}$ . The results found that the adsorption capacity of adsorbent decreased when competing anions were present. Multivalent anions adsorbed readily than monovalent anions. The impact of major anions on fluoride adsorption followed the order of  $CO_3^{2-} > PO_4^{3-} > SO_4^{2-} > Cl^-$ . Speciation-based model was quantified impact of coexisting anions on fluoride adsorption. The model provided in this study can be effectively used to predict the removal of fluoride in the presence of strongly competitive elements such as chloride, carbonate, sulphate and phosphate. As competing ions simultaneously exist in water resources, therefore, this model is of great importance in practical applications for designing and operating fluoride-removal systems under different field water quality conditions.

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