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# Removal of Fluoride from water by Al(III)-loaded and $Al(OH)_3$-coated chelating resin

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**ABSTRACT**

An Al(III)-loaded and $Al(OH)_3$-coated chelating resin Lewatit TP 260 was utilized for the removal of $F^-$ from aqueous solutions. Both forms of resin showed superior properties in the removal of $F^-$. Removal performances of such resins were investigated extensively by adsorption isotherms and kinetic tests. It was revealed that maximum adsorption capacity of $Al(OH)_3$-coated resin (0.55 mg/g) was higher than Al(III)-loaded resin (0.40 mg/g). The adsorption kinetics of both resins fitted well with the pseudo-second-order equation. The initial adsorption rate of $Al(OH)_3$-coated resin was approximately seven times greater than Al(III)-loaded resin. The equilibrium isotherms have been investigated by using Langmuir and Freundlich isotherm equations and the obtained experimental data were best described by Langmuir model. The removal of $F^-$ by both forms of resin was accomplished by an anion-exchange mechanism. In the presence of $Cl^-$ and $SO_4^{2-}$, removal performances of resins did not vary however, when the Al(III)-loaded resin was used, the presence of $NO_3^-$ species reduced the removal efficiency of such resin.

*Keywords:* Aminomethylphosphonic acid; Anion exchange; Chelating resin; Fluoride; Lewatit TP 260

## 1. Introduction

Fluoride exists in various forms, and the type of the $F^-$ species plays an important role on the effects of such species in living organism. Depending on its concentration, the fluoride in drinking water is known for both beneficial and detrimental effects on health, particularly to infants and young children [1]. When fluoride is ingested by humans and animals, a part of $F^-$ is absorbed up by body tissues with long-term deposition in teeth and bones. Low concentrations of fluoride in drinking water have been considered beneficial to prevent dental carries [2]. It has long been known that chronic intake of excessive fluoride can lead to severe dental and skeletal fluorosis. It does not only affect teeth and skeleton, but its accumulation over a long period could also lead to change in the DNA structure [2]. In view of the health impacts of fluoride, its concentration must be reduced from drinking water down to reference level. The World Health Organization has set a guideline value of 1.5 mg/L as

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the maximum permissible level of fluoride for drinking water [3]. Various methods are available for the removal of fluoride from drinking water such as coagulation–precipitation, adsorption, ion exchange, electrochemical process, and membrane process [4–8].

In the literature, it is reported that fluoride removal by means of ion-exchange technology using anion-exchange resins is challenging, since the order of selectivity for anionic species by anion-exchange resins is as follows: citrate > $SO_4^{2-}$, oxalate > $I^-$ > $NO_3^-$ > $CrO_4^{2-}$ > $Br^-$ > $SCN^-$ > $Cl^-$ > formate > acetate > $F^-$ [9]. Consequently, the conducted research on fluoride removal consist of using metal-loaded inorganic cation exchangers such as silica gel, alumina gel, or chelating resins where high-valence metals such as Fe(III), La(III), Ce (IV), and Zr(IV) have been used as loaded metals. Considering the loaded metal ions and functional groups of the sorbents are different, their fluoride removal performances are divergent. Due to its high electronegativity and small size, fluoride ion is classified as a hard base, which has a good affinity towards multivalent metal ions including Fe(III), Al(III), Zr(IV), and a series of lanthanide metal ions such as La(III), Ce(IV). Therefore, it is expected that using these resins could be a useful tool in terms of developing high efficiency low cost materials for the removal of fluoride [10–14].

In this study; removal of fluoride was carried out by aminomethylphosphonic acid-containing chelating resin (Lewatit TP260). In order to obtain high removal efficiency; resin was loaded with Al(III) or coated by $Al(OH)_3$. Experiments for the removal of $F^-$ in different resin levels, pH of the solution, adsorption mechanism, and kinetic performances of resins were also carried out.

## 2. Experimental

### 2.1. Materials

Lewatit TP 260 macroporous, aminomethylphosphonic acid-containing chelating resin was provided by Lanxess–Lewatit and their distributor in Turkey; Ökotek Environmental Technologies and Chemical Industries. The properties of resin are shown in Table 1.

Table 1
Physicochemical properties of resin

| Resin | LEWATİT TP 260 |
|---|---|
| Matrix | Cross linked polystyrene |
| Functional group | Aminomethylphosphonic acid |
| Ionic form | $Na^+$ |
| Total capacity | 2.3 (min) eq/L |
| Water retention | 59–61% |

NaF, KCl, $K_2SO_4$, and $KNO_3$ were of analytical grade, obtained from Merck.

### 2.2. Preparation of Al(III)-loaded resin

Prior to loading to Al(III), the resin was needed to be prewashed with 2 M HCl, followed by 2 M NaOH. The Na form of resin was finally washed with pure water. Prewashed resin (100 mL of wet resin) was kept in contact with 100 mL 1 M $Al(NO_3)_3$ solution (pH < 2.5) for 24 h. The amount of loaded Al(III) was calculated by measuring the Al(III) concentration in the solution before and after its contact with resins. Concentration determination of Al(III) was carried out by spectrophotometric Alizarin Red S method [15]. After loading with Al(III); resin was rinsed with distilled water, and air dried. 0.06 equivalents Al(III) loaded to 100 mL resin of resin. The calculated capacity for Al(III) was 0.08 equivalents Al(III).

### 2.3. Preparation of $Al(OH)_3$-coated resin

100 mL of prewashed resin was contacted with 125 mL of 1 M Al(III) solution. 24 h later, the resin and the solution were transferred to a beaker and $NH_3/NH_4^+$ buffer solution (pH 8.5) was added dropwise to a beaker and $Al(OH)_3$ precipitate formed on the surface of the resin. This solution was mixed for 48 h and pH of solution was controlled in order to keep the solution pH at 8.5, buffer solution was added. 48 h later the resin was removed from the solution and dried in the oven at 50˚C for 3 d.

### 2.4. Solubility of $Al(OH)_3$

The solubility of precipitate may increase dramatically in the presence of reagents that form complexes with the anion or the cation of the precipitate. Many precipitates react with excess levels of the related precipitating reagent to form soluble complexes, in this case Al(III) is precipitated as $Al(OH)_3$. The effect of excess reagent ($OH^-$) is complex, as revealed by the following set of equations (Eqs. (1)–(9)) that describes the system:

$$Al(OH)_3 \leftrightarrows Al^{3+} + 3OH^- \quad (1)$$

$$Al(OH)_3 + OH^- \leftrightarrows Al(OH)_4^- \tag{2}$$

Equilibrium, in Eq. (2) shifts to the right with the added hydroxide ion. The result of such opposing effects is that a plot of $Al(OH)_3$ solubility as a function of pH that exhibits a minimum. This can be explained as follows.

The molar solubility (S) of $Al(OH)_3$ is equal to the sum of the concentrations of the $Al^{3+}$-containing species [16]:

$$S = [Al^{3+}] + [Al(OH)_4^-] \tag{3}$$

Equilibrium constants available in the literature are shown in Eqs. (4) and (5).

$$K_{SP} = [Al^{3+}][OH^-]^3 = 3 \times 10^{-34} \tag{4}$$

$$\beta_4 = \frac{[Al(OH)_4^-]}{[Al^{3+}][OH^-]^4} = 2.5 \times 10^{33} \tag{5}$$

where $K_{sp}$ is the solubility product constant and $\beta_4$ is formation constant for $Al(OH)_4^-$.

Rearrangement of Eq. (4) is equal to Eq. (6):

$$\frac{K_{SP}}{[OH^-]^3} = [Al^{3+}] \tag{6}$$

On the other hand, rearrangement of Eq. (5) is equal to Eq. (7):

$$\beta_4 [Al^{3+}][OH^-]^4 = [Al(OH)_4^-] \tag{7}$$

$$\beta_4 [Al^{3+}][OH^-]^4 = \beta_4 K_{sp} [OH^-] \tag{8}$$

Substitution of Eqs. (5) and (8) in to Eq. (3) permits us to express the solubility in terms of the hydroxide ion concentration and the constants (Eq. (9)):

$$S = \frac{K_{SP}}{[OH^-]^3} + \beta_4 K_{SP} [OH^-] \tag{9}$$

The relationship between the solubility and the analytical concentration of $OH^-$ is observed clearly after obtaining such results which are given above.

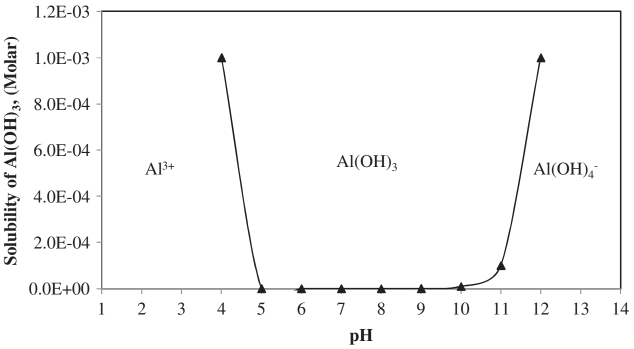

Fig. 1. Solubility of $Al(OH)_3$ vs. pH.

To find the minimum solubility (S), we set the derivative of S with respect to $OH^-$ equal to zero (Eq. (10)):

$$\frac{dS}{d[OH]} = 0 = -3\frac{K_{SP}}{[OH^-]^4} + \beta_4 K_{SP} \tag{10}$$

Fig. 1 illustrates the effect of hydroxide ion concentration on the solubility of $Al(OH)_3$; data of the curve were obtained by substituting various hydroxide concentrations into Eq. (9).

### 2.5. Concentration measurement of fluoride

The analysis of fluoride was performed spectrophotometrically using Alizarin Red S method. Fluoride-containing solution was transferred into a polypropylene volumetric flask. 1.25 mL of zirconyl solution ($1.0 \times 10^{-3}$ M), 1–2 drops of sodium arsenite solution (0.183%), and 1.25 mL of Alizarin Red S solution (0.075%) were added to a volumetric flask and then diluted to 25 mL with distilled water. One hour later, after the color development, fluoride concentration was measured with double beam spectrophotometer (PG T80+) at 625 nm.

### 2.6. Batch-mode removal of fluoride

#### 2.6.1. Effect of resin dose on the removal of fluoride

In this set of experiments various resin dosages (varied from 0.01 to 0.2 g) contacted with 25 mL of fluoride-containing solution. Initial fluoride concentration in the solution was 2mg F/L (pH 6.5). The resins were equilibrated with fluoride solution for 24 h at 25°C. The resin was then filtered off and the concentration of fluoride in the filtrate was determined as explained in Section 2.5.

#### 2.6.2. Effect of solution pH on the removal of fluoride

In order to examine the influence of pH on fluoride removal, batch-wise experiments were carried out by shaking 25 mL test solution containing 2.0 mg F/L together with optimum resin amounts (0.15 g Al(III)-loaded resin and 0.10 g $Al(OH)_3$-coated resin) at different pH. The pH of the solutions was varied from 4 to 9. Resins were equilibrated with fluoride solution for 24 h at 25°C. After the equilibration, the resin was removed from the solution and fluoride concentration in filtrate was measured.

#### 2.6.3. *Removal of fluoride in the presence of foreign ions*

The experiments were conducted with 25 mL of fluoride solution (2.0 mg F/L pH 6.5) paired with chloride, nitrate, or sulfate. The equivalent ratios of ionic species in the mixture were adjusted as 1:1, 1:5, and 1:10 in binary mixtures (F:Cl, F:$NO_3^-$, and F:$SO_4^{2-}$). After equilibration of resins with solution, resins were removed from solution and fluoride concentration in filtrate was analyzed.

## 3. Results and discussions

### 3.1. *Effect of resin dose on the removal of fluoride*

Resin dosage is a significant parameter because that concludes the capacity of an adsorbent for given initial concentration of the fluoride at the operating conditions.

Fig. 2 shows the effect of resin dose on the removal of fluoride. As it can be seen in Fig. 2, when the resin dosage was increased the removal of the fluoride was increased. Such result was expected because for a fixed initial fluoride concentration, increasing the resin amount provides greater ion-exchange sites. The optimum resin amounts are 0.15 g for Al(III) loaded and 0.10 g for $Al(OH)_3$-coated resin.

### 3.2. *Effect of solution pH on the removal of fluoride*

The effect of results shown in Fig. 3 indicated that both forms of resins removed fluoride ion effectively between pH 5.0 and 9.0.

It should be noted that pH limitation comes from the solubility of $Al(OH)_3$ and formation of HF (hydrofluoric acid) which has a p$K_a$ value of 3.17 [16]. If the pH is lower than 3.17, the molecular form of HF becomes dominant in the solution; so we did not work with more acidic medium. The other limitation is the solubility of $Al(OH)_3$. Solubility vs. pH depicted in Fig. 1. As can be seen in Fig. 1, the lowest solubility of $Al(OH)_3$ is between 5 and 10. At higher pH $Al(OH)_3$ dissolves as $Al(OH)_4^-$ (Aluminate) which may reduce the removal performance.

### 3.3. *Removal of fluoride in the presence of foreign ions*

In the presence of chloride, nitrate, and sulfate ions, separation of fluoride by ion-exchange resin was investigated. The experiments were conducted with 25 mL of fluoride solution (2.0 mg F/L pH 6.5) paired with chloride, nitrate, or sulfate. The equivalent ratios of ionic species in the mixture were adjusted as 1:1; 1:5, and 1:10 in binary mixtures (F:Cl, F:$NO_3^-$, and F:$SO_4^{2-}$). Effect of other ionic species on separation of fluoride is shown in Fig. 4. It can be seen from Fig. 4 that, when the $Al(OH)_3$-coated resin was used; other anionic species did not affect the removal of $F^-$. The removal mechanism of $F^-$ by $Al(OH)_3$-coated resin is

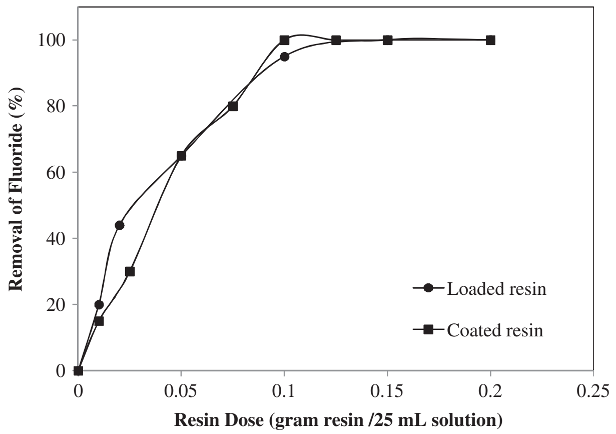

Fig. 2. Effect of resin amount on the removal of fluoride from aqueous solution (loaded resin: Al(III) loaded; coated resin $Al(OH)_3$-coated resin).

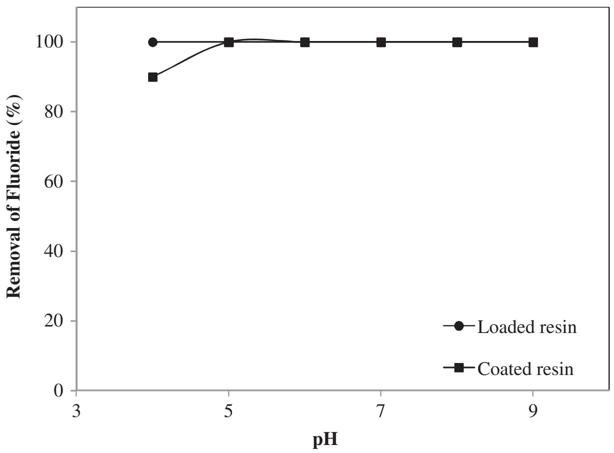

Fig. 3. Effect of pH on the removal of fluoride from aqueous solution (loaded resin: Al(III) loaded; coated resin $Al(OH)_3$-coated resin).

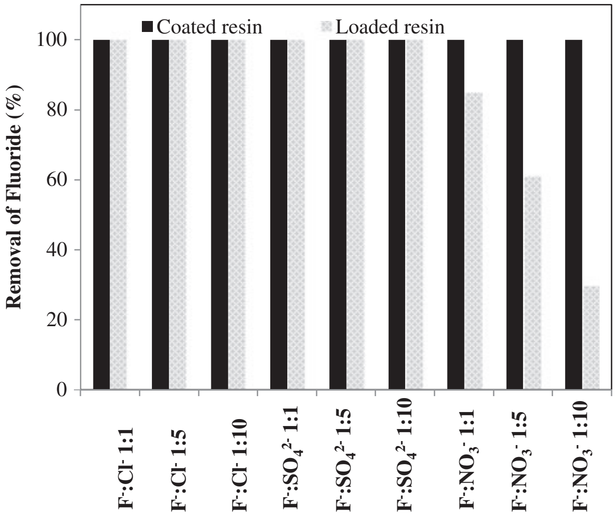

Fig. 4. Removal of fluoride in the presence of foreign ions by Al(III)-loaded and $Al(OH)_3$-coated resins.

ion exchange. As it can be seen from Fig. 5 ion exchange may occur on the surface of $Al(OH)_3$-coated resin [17]. However when the Al(III)-loaded resin was utilized; only the nitrate ions affected the fluoride removal. When the nitrate concentration was increased, the removal of fluoride decreased. The reaction of $F^-$ with Al(III)-loaded resin was accomplished by anion-exchange mechanism as shown in Fig. 6.

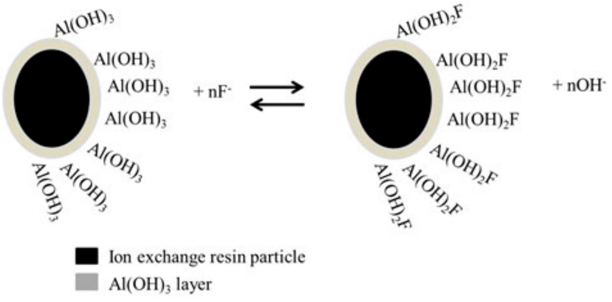

Fig. 5. Removal mechanism of fluoride by $Al(OH)_3$-coated resin.

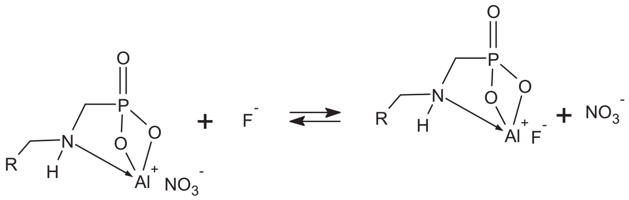

Fig. 6. Removal mechanism of fluoride by Al(III)-loaded resins.

According to the Le Chatelier's principle, when $NO_3^-$ concentration was increased the equilibrium shifts to left-hand side so that removal rate of fluoride decreased.

### 3.4. Sorption isotherms

To quantify the sorption capacity of the resins investigated for the removal of fluoride ions, the two most commonly used isotherms, Freundlich and Langmuir, have been adopted. In this set of experiment, optimum resin amount was contacted 25 mL of fluoride-containing solution at different concentrations (1.0–16.0 mg F/L) for 24 h at 25°C.

#### 3.4.1. Langmuir isotherm

The Langmuir model assumes that the adsorption of ions occurs on a homogeneous surface by monolayer adsorption without any interaction with adsorbed ions. The linear form of the Langmuir equation can be represented as Eq. (11) [18].

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \tag{11}$$

In which $Q_e$ is the adsorption capacity at equilibrium, $C_e$ is the equilibrium concentration, and $Q_0$ and $b$ are the Langmuir constants related to the maximum adsorption capacity and the adsorption energy, respectively.

#### 3.4.2. Freundlich isotherm

A Freundlich adsorption isotherm equation can be written as Eq. (12) [18]:

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e \tag{12}$$

The constants in the Freundlich isotherm are determined by plotting log $Q_e$ vs. log $C_e$.

Table 2 shows the Freundlich and Langmuir sorption isotherm constants and the correlation coefficients.

According to the results presented in Table 2, the sorption of fluoride on ion-exchange resins is more of monolayer sorption rather than sorption on a surface having heterogeneous energy distribution.

### 3.5. Ion-exchange kinetics

Kinetic tests were performed by contacting 6.0 g for Al(III) loaded and 4.0 g for $Al(OH)_3$-coated resin

Table 2
Isotherm constants for fluoride sorption on the ion-exchange resin

| | Langmuir isotherm constants | | | Freundlich isotherm constants | | |
|---|---|---|---|---|---|---|
| Resin form | $Q_0$ (mg/g) | $b$ (L/mg) | $r^2$ | $K_f$ (mg/g) | $n$ | $r^2$ |
| Al(III) loaded | 0.40 | 8.99 | 0,99 | 0.30 | 14.84 | 0.40 |
| $Al(OH)_3$ coated | 0.55 | 3.13 | 0.99 | 0.41 | 21.98 | 0.18 |

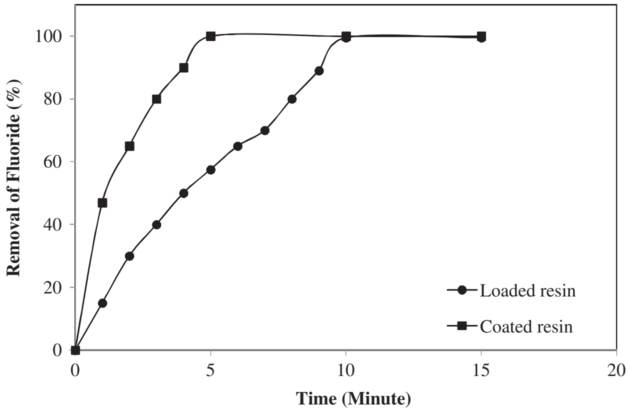

Fig. 7. Removal of fluoride vs. time (loaded resin: Al(III) loaded; coated resin $Al(OH)_3$-coated resin).

with 1.0 L of fluoride solution (2.0 mg F/L, pH 6.5) at 25˚C. Solution was stirred with overhead mixer. Fluoride concentrations were monitored by taking the samples at prescribed time intervals, and these samples were analyzed and obtained results are depicted in Fig. 7. Initially, the ion-exchange kinetic rates were found to be quite rapid and then it reached the equilibrium for both forms of resin. As can be seen in Fig. 7; kinetics of $Al(OH)_3$-coated resin are faster than Al(III)-loaded resin. The reason for that could be when the $Al(OH)_3$-coated resin was used; ion-exchange reaction occurs on the surface of resin but in case of Al (III)-loaded resin; $F^-$ transport inside resin.

The two main types of sorption kinetic models, reaction-based and diffusion-based, were adopted to fit the experimental data.

### 3.5.1. Reaction-based models

In order to investigate the sorption mechanism of resins; pseudo-first-order and pseudo-second-order kinetic models have been used. The pseudo-first-order rate constant was given by following Eq. (13) [19]:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{13}$$

where $q_t$ and $q_e$ represent the amount of adsorbed species (mg/g) at any time $t$ and at equilibrium time, respectively, and $k_1$ represents the sorption rate constant ($min^{-1}$). Integrating Eq. (13) with respect to boundary conditions.

$q = 0$ at $t = 0$ and $q = q$ at $t = t$, one equation obtain (14)

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{14}$$

Sorption rate constant $k_1$ ($min^{-1}$) can be calculated from the plot of $\log(q_e - q_t)$ vs. time.

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as Eq. (15) [20]:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{15}$$

where $k_2$ is the pseudo-second-order rate constant (g/mg min), $q_e$ and $q_t$ are the amount of adsorbed species (mg/g) at equilibrium and at time $t$. By changing the variables in Eq. (15) one get Eq. (16):

$$\frac{dq}{(q_e - q_t)^2} = k_2 dt \tag{16}$$

$t = 0$ to $t = t$ and $q = 0$ and $q = q_e$ one obtains the final form (17):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{17}$$

If pseudo-second-order kinetics is applicable, the plot of $t/q_t$ against $t$ of Eq. (17) should provide a linear relationship, from which $q_e$ and $k_2$ (g/mg min) can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand. Constant $k_2$ is used to calculate the initial sorption rate $r$; at $t \to 0$, as shown in Eq. (18) [21]:

$$h = k_2 q_e^2 \tag{18}$$

The calculated parameters of pseudo-first- and second-order kinetic models were summarized in Table 3. As can be seen from Table 3 that $k_2$ and $q_e$ values of $Al(OH)_3$-coated resin is higher than Al(III)-loaded resin. It means that ion-exchange kinetics is faster and equilibrium capacity is higher for the $Al(OH)_3$-coated resin. When the linear correlation coefficients were compared, it was observed that the sorption kinetics for resin agreed well with the pseudo-second-order mechanism.

### 3.5.2. Diffusion-based models

In a solid–liquid sorption process, the solute transfer is usually characterized either by particle diffusion or by pore diffusion control. A simple equation for the particle-diffusion-controlled sorption process is shown in Eq. (19) [9]:

$$\ln\left(1 - \frac{C_t}{C_e}\right) = -k_p t \tag{19}$$

where $k_p$ is the particle diffusion coefficient (mg/g min). The value of the particle diffusion coefficient is obtained by the slope of ln $(1 - C_t/C_e)$ against $t$. If the plot of 1n $(1 - C_t/C_e)$ against time yields a straight-line, then the rate-limiting step is particle diffusion controlled.

The Weber and Morris equation is given in Eq. (20) [9,22]:

$$q_t = k_d t^{1/2} \tag{20}$$

A plot of solute sorbed ($q_t$) against square root of contact time, ($t^{1/2}$), yielding a straight line; will confirm the rate-limiting step as pore diffusion controlled.

The experimental data fitted in the Eqs. (19) and (20) and the results are summarized in Table 3. The $r^2$ revealed that the retention process is pore-diffusion-controlled mechanism, since such plot provides a better straight-line plot than the particle-diffusion-controlled mechanism.

Batch kinetic studies have also been evaluated by using diffusion and reaction models. The models for process dynamics include both the diffusion steps (in bulk solution, in external surface layer, in pores) and the exchange reaction on the active sites. Since the resistance in the bulk solution is easily controlled and negligible, three resistances, such as film diffusion, particle diffusion, and the chemical reaction usually determine the overall rate of the ion-exchange process. One approach uses the infinite solution volume (ISV) model, whereas the other method uses the unreacted core model (UCM) to express the rate-determining steps in the ion-exchange process [23,24].

According to the ISV model, the rate is controlled by the film diffusion process. However, according to the UCM, chemical reaction is the rate-determining step in both forms of the resin (see Table 4).

Previously in the literature, various research studies were conducted on modified resin for fluoride removal. The obtained results in such research studies are summarized in Table 5.

Various high-valence metal ions were used for removal of fluoride. The removal performance of these materials strongly depends on experimental conditions and loaded metal. As can be seen from Table 5 the maximum capacity of these materials varies from 0.13 to 49.02 mg/g of sorbent.

Table 3
Calculated parameters of kinetic models

| Kinetic model | Parameter | Al(III) loaded | $Al(OH)_3$ coated |
|---|---|---|---|
| Pseudo-first order | $k_1$ ($min^{-1}$) | 0.23 | 0.56 |
| | $q_e$ (mg/g) | 0.40 | 0.50 |
| | $r^2$ | 0.93 | 0.98 |
| Pseudo-second order | $k_2$ (g/mg min) | 0.12 | 0.67 |
| | $q_e$ (mg/g) | 0.67 | 0.70 |
| | $h$ (mg/gmin) | 0.05 | 0.33 |
| | $r^2$ | 0.96 | 0.99 |
| Particle diffusion model | $k_p$ (mg/g min) | 3.63 | 2.07 |
| | $r^2$ | 0.97 | 0.95 |
| Pore diffusion model | $k_d$ (mg/g $min^{0.5}$) | 0.07 | 0.072 |
| | $r^2$ | 0.99 | 0.99 |

Table 4
Linear regression analysis data related to diffusion models on sorption kinetics of fluoride from water resin

| Method | Equation | $k$ | Rate-controlling step | $R^2$ value | |
|---|---|---|---|---|---|
| | | | | Al(III) loaded | $Al(OH)_3$ coated |
| ISV | $-\ln(1-X) = k_{li}t$ | $k = 3DC/r_o\delta\ C_r$ | Film diffusion | 0.99 | 0.99 |
| | $-\ln(1-X^2) = \mathrm{k}t$ | $k = Dr\pi^2/r_o^2$ | Particle diffusion | 0.98 | 0.96 |
| UCM | $X$ | $k = 3C_{Ao}K_{MA}/ar_oC_{So}$ | Liquid film | 0.98 | 0.98 |
| | $3–3(1-X)^{2/3–2}X = \mathrm{k}t$ | $\mathrm{k} = 6D_{eR}C_{Ao}/ar_o^2\ C_{So}$ | Reacted layer | 0.95 | 0.98 |
| | $1-(1-X)^{1/3} = kt$ | $k = K_sC_{Ao}/r_o$ | Chemical reaction | 0.99 | 0.99 |

Table 5
Fluoride removal using different resins

| Resin/Sorbent | Loaded metal | Capacity (mg/g) | Refs. |
|---|---|---|---|
| Na-Attapulgite | Zr(IV) | 24.55 | [10] |
| Amberlite 200CTNA | La(III) | 24.51 | [11] |
| Amberlite IR124 | | 41.99 | |
| Diaion WK11 | | 26.79 | |
| Readf-(PG) | Hydrated zirconium(IV) oxide | 39.90 | [12] |
| Readf-(HG) | Hydrated cerium(IV) oxide | 44.65 | |
| AMB200CT | La(III) | 24.51 | [9] |
| | Ce(III) | 24.51 | |
| | Y(III) | 19.00 | |
| | Fe(III) | 49.02 | |
| | Al(III) | 24.70 | |
| Amberlite IRA 400 | Pr(Ill) complex of alizarin fluorine blue | 0.5 | [13] |
| Alumina | La(III) | 0.35 | [25] |
| | Y(III) | 0.13 | |
| Polystyrene | Zr(IV) | 6.14 | [26] |
| Collagen fiber | Zr(IV) | 43,51 | [27] |
| IDA | Zr(IV) | 19.95 | [28] |
| CMA | | 21.85 | |
| Indion FR 10 | La(III) | 1.931 | [29] |
| | Fe(III) | 1.704 | |
| | Ce(III) | 1.799 | |
| | Zr(IV) | 2.825 | |
| Natural zeolite | Al(III) | 2.35 | [30] |
| | La(III) | 2.63 | |
| | Zr(IV) | 4.13 | |
| Lewatit TP 260 | Al(III) loaded | 0.40 | This work |
| | $Al(OH)_3$ coated | 0.55 | |

## 4. Conclusions

Removal of fluoride from water by Al(III)-loaded and $Al(OH)_3$-coated resin was performed. Efficiency of fluoride removal was increased by increasing the resin amount. Experimental data reveal that capacity and kinetic performance of $Al(OH)_3$-coated resin are more efficient than Al(III)-loaded resin. Additionally, the ion-exchange kinetics of the resins could be described by pseudo-second-order kinetic model. It is feasible to achieve complete removal of fluoride for solution of pH between 5 and 9. It has also been found that the resin is effective even in the presence of other anions such as $Cl^-$ and $SO_4^{2-}$; however when the Al(III)-loaded resin was used, $NO_3^-$ ions affected the fluoride removal performance of the resin. In case of $Al(OH)_3$-coated resin $NO_3^-$ ions did not affect the fluoride removal performance.

The ion-exchange kinetics of such resins is very fast. When the $Al(OH)_3$-coated resin was used, complete removal of fluoride was achieved in 5 min.

According to diffusion-based model, pore diffusion controls the ion-exchange reaction. On the other hand the UCM expresses that chemical reaction is the rate-determining step which may be related to in the ion-exchange process. The ion exchange of fluoride by such resins in batch systems can be described by the Langmuir isotherm, and the adsorption capacity was 0.40 mg F/g for Al(III)-loaded and 0.55 mg/g dry resin for $Al(OH)_3$-coated resin.

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