Titanium(IV) hydrate based on chitosan template for defluoridation from aqueous solution

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ABSTRACT

A cost effective bio-adsorbent, titanium(IV) hydrate based on chitosan template (Ti-CHI), was synthesized using $\text{Ti}(\text{SO}_4)_2$ and chitosan for defluoridation from aqueous solutions. The Ti-CHI material was characterized using FTIR, SEM with EDX, XRD, XPS and Zeta potential. The adsorption kinetics of fluoride onto Ti-CHI followed pseudo-second-order and intra-particle diffusion models. The Ti-CHI was effective for defluoridating systems with low fluoride concentrations (4.52 mg/L), exhibiting a 87.50% removal rate and permitting a residual fluoride concentration (0.55 mg/L). The most stable pH range for fluoride removal was from 4 to 9. After combining the results of pH effects, FTIR and Zeta potential, the $-\text{NH}$ groups and $\text{Ti}-\text{OH}$ groups were revealed as the fluoride adsorption sites on Ti-CHI. In addition, the carbonate ions present in the aqueous solutions adversely impact the fluoride adsorption. The Langmuir, Freundlich, and Langmuir–Freundlich models were used to illustrate the isotherms of the adsorption process. The adsorption of fluoride onto Ti-CHI fits the Langmuir and Langmuir–Freundlich isotherm models well. The maximum adsorption capacity for fluoride on the Ti-CHI was 16.12 mg/g. Thermodynamic studies revealed that the adsorption process was spontaneous.

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1. Introduction

High fluoride levels are a major threat to drinking water production in many countries worldwide [1]. Consuming too much fluoride-contaminated drinking water can cause endemic fluorosis. Individuals suffering from fluorosis may develop symptoms that include periosteal proliferation, osteoporosis and dental illnesses [2,3]. A comprehensive literature review reveals that defluoridation through adsorption onto various materials is promising because it is cost effective in the context of the medium and running costs and it is characterized by easy operation, high adsorption capacity, recyclability, numerous useful cycles, and possible regeneration [4].

Titanium-derived adsorbents are widely used to treat arsenic-contaminated underground water and known to have potential for defluoridation. Yuchi and Matsuo used titanium (IV) that was

chemically immobilized in a gel-phase for fluoride sorption but discovered that this material has a limited adsorption capacity due to its tendency to hydrolyze [5]. Wajima and Umeta et al. prepared a gel-like titanium hydroxide-derived adsorbent for defluoridation. They found that the adsorption behavior of fluoride ions on this adsorbent was pH-dependent. When $3 \leq \text{pH} \leq 9$, the fluoride ion content linearly decreased to zero as the pH increased [6]. The Fe–Ti oxide nano-adsorbent synthesized by Chen et al. showed a high affinity for fluoride ions, but the effects of pH on its sorption were not reported in their work [7].

The applications of titanium-derived adsorbents in defluoridation are limited when exposed to both a low pH and fluoride ions in solution because these conditions accelerate the titanium release [8]. Chitosan has the highest metal coordinating ability among the natural polymers [9]. Modifying titanium-derived adsorbents with chitosan would overcome the limitations of these adsorbents. Thakre et al. prepared a chitosan-based mesoporous Ti–Al binary metal oxide to adsorb fluoride. Their study revealed obvious enhancements in the adsorption capacity after integrating the chitosan. Jagtap et al. used titanium isopropoxide as a raw material for preparing chitosan-based adsorbents for defluoridation [10]. The adsorbents reduced the fluoride concentration from 5 mg/L to 1.27 mg/L but still could not achieve the acceptable limit for

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fluoride in drinking water in most fluoride damaged countries (1 mg/L) [4]. Therefore, titanium-derived adsorbents should be improved in terms of their cost effectiveness and should have stable defluoridation performance under different pH conditions.

In this study, we use chitosan as a template and $\text{Ti}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ as a titanium(IV) source to prepare a new defluoridation adsorbent for fluoride-contaminated aqueous solutions to meet the drinking water standard. $\text{Ti}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is much cheaper than titanium isopropoxide [11]. This work evaluated the defluoridation capacity (DC) of this adsorbent and investigated its surface characteristics and fluoride adsorption mechanism using surface examination techniques. Moreover, a nonlinear method was applied to the experimental data to determine the best-fitting isotherm and kinetic models.

2. Materials and methods

2.1. Chemicals

All chemicals were of analytical grade. The experimental equipment was washed with deionized water. When required, the experimental reagents were diluted with ultra-pure water. The chitosan was purchased from Zhejiang Aoxing Biotechnology Co. Ltd., Zhejiang, P. R. China and had a 90% degree of deacetylation. The nano TiO_2 , titanium(IV) sulfate ($\text{Ti}(\text{SO}_4)_2$), sodium fluoride (NaF), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium nitrate (NaNO_3), sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3), sodium phosphate (Na_3PO_4), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), urea, acetic anhydride, sodium citrate and oxalic acid were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Preparation of adsorbents

Adsorbent 1: 5 g of titanium(IV) sulfate and 6 g of urea were dissolved in 100 mL of deionized water in a 3-necked flask and stirred for 1 h at 333 K. Chitosan-acetic anhydride solution (2%) was subsequently added to the flask, and the pH was adjusted to 7 using 2 M ammonia. After 3 h, the deposits in the flask were centrifuged and washed with deionized water until all sulfate ions were removed. Finally, the deposits were dried at 353 K for 6 h and ground. The titanium(IV) hydrate based on the chitosan template (Ti-CHI) was obtained.

Adsorbent 2: The Ti-CHI was calcined in a muffle furnace at 450 for 2 h to obtain the cTi-CHI.

Adsorbent 3: The nano TiO_2 and chitosan were magnetically stirred in a 10 M NaOH solution. After the mixture was well mixed, it was placed in a high pressure reactor and heated at 160–180 °C for 24 h. Afterward, the mixture was centrifuged and washed with deionized water until the washings were neutral. Finally, the mixture was dried at 353 K for 6 h and ground to obtain the nTi-CHI.

2.3. Characterization

The Ti-CHI was identified using several non-destructive techniques: scanning electron microscopy (SEM, Quanta 200, FEI Co.) with energy dispersive X-ray spectroscopy (EDX, accessories of Quanta 200, FEI Co.), Fourier transform infrared spectroscopy (FTIR, 5700 FTIR, Nicolet Co.), X-ray diffraction (XRD, D/MAX-γ instrument), X-ray photoelectron spectroscopy (XPS, KRATOS XSAM800, Shimadzu Co.) and Zeta potential (zen 3600, Malvern Co.). The surface charges were measured using Zeta-Sizer; these values were based on the electrophoretic mobility of the adsorbents in aqueous media at different pHs. Each measurement was performed in an aqueous solution with a constant ionic strength (0.1 M NaNO_3); the pH was adjusted using NaOH or HNO_3 . Each Zeta potential

was measured 4 times; the average values were used in the Zeta potential–pH plot.

The fluoride analysis was carried out using a fluoride-selective electrode method (ASTM D1179-B). Total ionic strength adjustment buffer (I) (TISAB (I)) solution was used as a buffer, maintaining the pH and background ion concentration while analyzing the F^- concentration. This medium was prepared by dissolving 58.5 g of NaCl, 0.3 g of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 57 mL of glacial acetic acid in DI water before adjusting the pH to 5.0–5.5 with 10 M NaOH and adding DI water until the solution reached 1000 mL.

2.4. Adsorption of fluoride onto adsorbents

A stock solution of 1000 mg NaF/L was prepared for the various aqueous fluoride dilutions. The experiments for DC evaluation of the adsorbents were carried out as follows: 1 g of adsorbent was added in 1000 mL (40 mg NaF/L) of aqueous fluoride solution without adjusting the pH; the mixture was stirred for 3 h at room temperature. At selected time intervals, approximately 8 mL of the suspension was withdrawn to assess the F^- concentration. The equilibrium sorption experiment was carried out as follows: after adding 0.1 g of adsorbent and 50 mL of a fluoride aqueous solution with a known concentration to a flask, the mixtures were oscillated in a shaking water bath at 283, 293, 303, 313, and 323 K under 200 rpm for 3 h, respectively; the residual F^- concentration was tested. The pH effects were studied using equilibrium sorption experiments at known pH values. The pH values were adjusted using aqueous 1 M HCl or NaOH solutions. The impact of the co-anions was studied by adding NaCl, Na_2SO_4 , NaNO_3 , Na_2CO_3 , NaHCO_3 and Na_3PO_4 during equilibrium sorption.

2.5. Data processing methods

The equilibrium sorption capacity could be calculated using the following expression:

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where q_e is the equilibrium adsorption capacity of fluoride adsorbed per unit mass of Ti-CHI (mg/g); c_0 and c_e are the initial (mg/L) and equilibrium fluoride concentrations (mg/L), respectively; V is the volume of the fluoride solution (L); and m is the mass of the Ti-CHI (g). For the remainder of the present work, q_e is the defluoridation capacity used to evaluate the defluoridation performance of Ti-CHI.

In this work, the Langmuir, Freundlich and Langmuir–Freundlich isotherm models were adopted to model the adsorption equilibrium data [18]. The pseudo-first-order, pseudo-second-order and intra-particle diffusion [19,20] models were employed while assessing the adsorption kinetics. A nonlinear method was used to find the best-fitting isotherms through a trial-and-error procedure using Origin 8.6.

In general, based on the magnitude of the coefficient of determination for the linear or nonlinear regression, the accuracy of the fit of the experimental equilibrium data to an isotherm model could be assessed [21]. The coefficient of determination (r^2) was obtained:

$$r^2 = \frac{\sum (q_m - \bar{q}_e)^2}{\sum (q_m - \bar{q}_e)^2 + \sum (q_m - q_e)^2} \quad (2)$$

where q_m is the equilibrium capacity obtained from the isotherm model, q_e is the equilibrium capacity obtained from experiment, and $\bar{q}_e$ is the average of the q_e values.

Table 1
Different synthetic processes for Ti-CHI, cTi-CHI and nTi-CHI and their defluoridation capacities.

Adsorbent no.	Adsorbent name	Ti resource	Reactants	Thermal treatment (°C)	Defluoridation capacity (mg/L)
1	Ti-CHI	Ti(SO ₄) ₂	Chitosan, urease, acetic anhydride	80	12.11
2	cTi-CHI	Ti(SO ₄) ₂	Chitosan, urease, acetic anhydride	450	6.81
3	nTi-CHI	Nano TiO ₂	Chitosan, NaOH	160–180	4.31

3. Results and discussion

3.1. Optimal adsorbent

The optimal adsorbent should have a high affinity to the sorbate and a high specific surface area. We either used nano TiO₂ and Ti(SO₄)₂ as Ti sources while synthesizing the Ti-CHI and nTi-CHI bio-adsorbents for fluoride sorption. We also calcined the Ti-CHI bio-adsorbent at 450 °C to compare the function of the chitosan. These three adsorbents were exposed to aqueous F[−] ions for 24 h. Table 1 shows the DC of the adsorbents. The Ti-CHI had the highest DC of the three adsorbents, followed by cTi-CHI and nTi-CHI. While synthesizing Ti-CHI (Eqs. (3)–(5)), urea uniformly heated Ti(SO₄)₂ and titanium hydrate generated on the chitosan template. Therefore, the titanium hydrate has a better affinity for F[−]. The DC of the cTi-CHI is lower than that of nTi-CHI due to the absence of chitosan, which would enhance the surface porosity of the adsorbents [12]. The Ti-CHI was selected as the fluoride adsorbent because it has the advantages of both titanium hydrate and chitosan.

3.2. Characterization

3.2.1. SEM with EDX

The surface morphology and elemental constituents of Ti-CHI were confirmed using SEM with EDX analysis. Fig. 1(a and b) shows the SEM photographs of chitosan and Ti-CHI, respectively. Compared to the chitosan, the Ti-CHI had a very different morphology; it changed from being long strips of irregular, scattered flakes into aggregated, spherical particles. Furthermore, the particle size of new adsorbent was much smaller than that of the original chitosan. The Ti-CHI particle size was 200 nm, which was approximately 1/125 that of chitosan, and could reach submicron levels. Fig. 2

Table 2
Elemental constituents of Ti-CHI.

Element	Wt%	At.%
C	24.23	35.71
N	13.76	17.39
O	31.53	34.89
S	04.14	02.28
Ti	26.34	09.73

shows the energy dispersive X-ray analysis diagram of the chitosan and the modified material. Ti-CHI contained C, N, O, S, and Ti. The Ti and S came from the titanium sulfate, whereas N came from the urea. In Table 2, the elemental constituents of Ti-CHI reveal that Ti-CHI was rich in titanium.

3.2.2. XRD

XRD was used to determine the crystalline structure of the materials. The XRD patterns of the CHI and Ti-CHI are shown in Fig. 3. The XRD pattern of chitosan contains a dominant crystalline peak at a 2 theta value of 10°. This major crystalline peak is also observed in the pattern for Ti-CHI, but the peaks for titanium oxide are not observed, suggesting that the titanium oxide had an amorphous Ti(OH)₄ structure [9,11].

3.2.3. XPS

The XPS technique has been applied to further identify the chemical status of the biocomposite. Using the curve-fitting program (XPSPEAK v4.1), curve fitting of the Ti 2p peak was performed by using a Shirley background, Gauss-Lorentzian character, and a full width at half maximum (FWHM). As can be seen from Fig. 4, Ti 2p_{3/2} and 2p_{1/2} peak position were measured at 458.50 [13] and 464.32 eV [14], respectively. The Ti 2p spectrum of the Ti-CHI is dominated by species in the Ti (IV) oxidation state with the presence of a small contribution of reduced species Ti(III) [15]. This Ti(III) species can be assigned to TiN formation by bonding of Ti(III) and NH groups on chitosan.

Fig. 1. SEM image of the chitosan (a) and the Ti-CHI (b).

Fig. 2. EDX spectrum of the chitosan and the Ti-CHI.

3.2.4. FTIR

FTIR spectroscopy can analyze the organic groups on the surface of these particles. Spectral variations could be observed before and after the fluoride sorption, revealing the adsorption groups on the adsorbents. Fig. 5 shows the FTIR spectra of Ti-CHI before and after fluoride sorption. In the Ti-CHI spectrum, the characteristic bands (3440 and 1635 cm^{-1}) represent the stretching vibrations of the OH group and molecular H_2O , respectively. The band at 2913 cm^{-1} is assigned to the symmetric stretching of the aliphatic CH_2 groups on chitosan [16]. The bands at 1452 and 1328 cm^{-1} can be assigned to the C–N stretching vibration and C–H bending modes. The band at 1101 cm^{-1} is attributed to the Ti–OH bond on the OH groups that coordinate with metal ions [17]. The broad band from 760 to 455 cm^{-1} is due to the envelope of phonon bands generated by the Ti–O–Ti in the CHI [16]. The FTIR data for Ti-CHI are similar to

the data reported for Khan's research. Therefore, the Ti–O–Ti was bonded with CHI macromolecules through hydrogen and covalent bonding in the Ti-CHI composite. Major variations in the FTIR spectra appear after fluoride sorption at 3376 , 1529 and 1411 cm^{-1} . Because the band for the amino ($-\text{NH}$) groups at 3440 cm^{-1} is masked by the broad adsorption band from the OH group [18], the shift in the band from 3440 to 3376 cm^{-1} suggests that the F^- interacts with the $-\text{NH}$ group. The band at 1529 cm^{-1} assigned to the $-\text{NH}$ group was revealed after fluoride sorption; the intensity of the band at 1635 cm^{-1} decreases precipitously, suggesting that the OH group interacted with F^- . The band at 1452 cm^{-1} (C–N stretch) shifts to 1411 cm^{-1} , indicating that the surface structure of Ti-CHI changes after interacting with F^- . Therefore, F^- ions adsorb on the $-\text{NH}$ and $-\text{OH}$ groups.

3.3. Effect of the F^- initial concentration on sorption

At the sorbent and sorbate interface, increasing the initial aqueous fluoride concentration could strengthen the ability of the sorbent to capture the sorbate. Therefore, sorption experiments were performed using Ti-CHI in aqueous fluoride solutions with different concentrations at constant temperatures (Fig. 6). The initial concentrations were 4.52 , 9.05 , 13.57 and 18.09 mg/L ; the sorption primarily occurred within the first 10 min , and the Ti-CHI reached adsorption equilibrium of fluoride in 180 min . Based on these findings, the shaking time in all the further experiments was set as 180 min . The fluoride adsorption capacity of Ti-CHI increased from 4.31 to 11.44 mg/g as the initial concentration increased. The removal rate was from 63.98% to 87.50% , showing a high removal efficiency of fluoride on the Ti-CHI. Additionally, at a relatively low

Fig. 3. XRD patterns of the chitosan and the Ti-CHI.

Fig. 4. XPS patterns of the Ti-CHI: curve-fitted as-measured Ti 2p.

Fig. 5. FTIR spectra of the Ti-CHI before and after the fluoride sorption.

Fig. 6. (a and b) Effects of the initial fluoride concentration on adsorption.

initial fluoride concentration of 4.52 mg/L, residue fluoride concentration decreased to 0.55 mg/L, which is below the standard of fluoride permitted concentration in drinking water of China (1.0 mg/L). This suggests that the Ti-CHI may be used for fluoride purification in drinking water.

3.4. Effect of different coexisting anions on defluoridation

In natural water, various ions coexist alongside fluoride that may compete for the adsorption sites [16]. To study the effects of different anions on the defluoridation capacity, the Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , NO_3^- and PO_4^{3-} ions that are common in natural water bodies were added to the fluoride aqueous solution as coexisting anions [20,21]. The initial concentrations of the coexisting anions were either 20 mg/L, 60 mg/L and 100 mg/L. The DC of Ti-CHI (Fig. 7) showed that the carbonate, bicarbonate and phosphate reduced

Fig. 7. Defluoridation capacity of Ti-CHI exposed to different anions without adjusting the pH.

Fig. 8. The effects of fluoride adsorption onto Ti-CHI with different pH values and the surface charges as determined by the Zeta potential.

the F^- sorption capacity, while the other anions had few adverse effects on the fluoride uptake. The adverse effects on the adsorption capacity were as follows: $\text{CO}_3^{2-} > \text{HCO}_3^- > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. These results were similar to the results reported for a previous study [22]. For CO_3^{2-} , HCO_3^- and PO_4^{3-} , the fluoride removal efficiency declined as the coexisting ion concentration increased. However, Cl^- , SO_4^{2-} and NO_3^- did not display the same regularity; the regularity was not applicable for all coexisting ions because the competition capacity of the coexisting anions is usually determined by the changes in the pH, concentration, charge and size of the anions or by a combination of these factors [23].

3.5. Effect of pH on defluoridation

3.5.1. Evaluation of defluoridation capacity

The pH of the solution is critical and controls the adsorption at the water–sorbent interface. Acidic or alkaline solutions can determine the charge of the sorbent directly, affecting the adsorption capacity of the sorbate. Fig. 8 shows the following: (1) the impact of different pH conditions on the DC and (2) the Zeta potential of the Ti-CHI at various pHs before and after fluoride sorption. The DC in 16.69 mg/L F^- changed slightly as the initial pH increased, showing a declining trend overall. The optimal fluoride adsorption occurred at pH 4.0 because at a lower pH, the adsorbent surface was highly protonated, increasing the attractive forces between the positively charged surface and the negatively charged fluoride ions [23]. The DC did not decrease until pH = 5, but then declined more slowly when pH larger than 7. This was because the extra hydroxyl ions will compete with fluoride ions for adsorption sites in the adsorbent surface [24,25]. The highest adsorption capacity occurs at pH = 4 (13.39 mg/L). Because the defluoridation performance of Ti-CHI remains stable from pH 4 to 9, the Ti-CHI should be an effective defluoridation adsorbent in natural fluoride-contaminated underground water that has a pH of approximately 8.

3.5.2. Surface charge measured using the Zeta potential

The surface charge of the adsorbents governs the interactions between the adsorbents and the sorbate [26]. The Zeta potential of Ti-CHI with and without F^- sorption as the pH varies from 4 to 10 is shown in Fig. 8. The Zeta potential plots of Ti-CHI before and after fluoride sorption reveal that the pH value at the zero point of charge (pH_{ZPC}) was approximately 7.8. After exposing the Ti-CHI to F^- , the Zeta potential decreases as the pH values increase and the DC values decrease. The correlation between the DC and the Zeta potential occurs because the adsorption process is governed by electrostatic adsorption [27]. At pH values below the pH_{ZPC} , the adsorbent is positive charged, favoring the adsorption of anionic species [28,29]. At the pH_{ZPC} , the adsorbent is electronically neutral and the

Table 3

Kinetic parameters for adsorption of fluoride onto Ti-CHI.

Initial concentration (mg/g)	Pseudo first order model			Pseudo second order model		
	k_1 (h ⁻¹)	q_{e1} (mg/g)	r^2	k_2 (g h/mg)	q_{e2} (mg/g)	r^2
4.52	97.99	3.66	0.83	32.30	3.79	0.88
9.05	135.79	6.46	0.96	49.07	6.55	0.97
13.57	118.88	8.98	0.96	27.78	9.13	0.97
18.09	119.11	10.61	0.94	-7.70E+44	10.50	0.92

sorbate with negative charge and is predominantly adsorbed at pHs below the pH_{ZPC} . At pHs above the pH_{ZPC} , the adsorbent is negative charged and OH^- competes for the adsorption sites. Consequently, the adsorption capacity decreases as pH increases because the electrostatic repulsion is strengthened by the increased negative charge at the surfaces of the adsorbents.

3.5.3. FTIR of the pH effect

Based on the Zeta potential analysis, the Ti-CHI showed different affinity toward H^+ , OH^- and F^- . Therefore, we could identify the adsorption sites on Ti-CHI by comparing the FTIR spectra of Ti-CHI after fluoride sorption at pH values from 4 to 11. In Fig. 9, variations are observed at 1687, 1633, 1521, 1033 cm^{-1} that can be assigned to interactions of Ti ions with the $-NH$ group, the OH bond, the $-NH$ bond and the Ti–OH bonds on the three OH groups, and five CH_2OH groups on chitosan [16], respectively. As the pH increases, the band intensities at 1687 and 1521 cm^{-1} decrease and disappear, respectively; at pHs above 9 and 11, the band intensity at 1033 cm^{-1} increases accordingly. These variations imply that the adsorption sites on the surface of the Ti-CHI are $-NH$ and OH groups. The $-NH$ groups are protonated under acidic conditions and exhibit a band at 1687 cm^{-1} ; therefore, the intensity of this band decreases as the pH increases. Moreover, the increased pH generates more OH^- ions in the aqueous solution, forming more Ti–OH groups and increasing the absorbance intensity of the band at 1033 cm^{-1} . Therefore, the F^- adsorption sites on Ti-CHI operate using electrostatic adsorption and are the $-NH$ and Ti–OH groups.

3.6. Kinetic studies

To investigate the mechanism of the adsorption process, the Weber and Morris intra-particle diffusion model, the pseudo-first-order model and the pseudo-second-order model were fitted to the experimental data. The pseudo-first-order model [30] is one of the most popular reaction kinetic models for the liquid–solid adsorption system. It is summarized as follows:

$$q = q_{e1}(1 - e^{-k_1 t}) \quad (6)$$

Fig. 9. FTIR spectra of Ti-CHI after fluoride sorption at different pH values.

where k_1 is the rate constant of the pseudo-first-order model (h⁻¹); q is the amount of fluoride ions adsorbed per unit mass of Ti-CHI (mg/g); q_{e1} is the adsorption at equilibrium (mg/g); and t is the adsorption time (h). The pseudo-second-order model [31,32] is based on the adsorption capacity on the solid phase. The adsorption capacity is proportional to the number of active sites occupied on the adsorbent:

$$q = \frac{q_{e2}^2 k_2 t}{1 + q_{e2} k_2 t} \quad (7)$$

where k_2 is the rate constant of the pseudo-second-order equation (g h/mg); q is the amount of fluoride ions adsorbed per unit mass of Ti-CHI (mg/g); q_{e2} is the adsorption at equilibrium (mg/g); and t is the adsorption time (h).

The intra-particle diffusion model proposed by Weber and Morris [33,34] is determined using the linear equation:

$$q = k_t t^{1/2} + C \quad (8)$$

where q is the amount of fluoride ions adsorbed per unit mass of Ti-CHI (mg/g); k_t is the intra particle diffusion rate constant (h^{-1/2}); C is the intercept (mg/g); and t is the adsorption time (h).

The parameters of these models are presented in Tables 3 and 4. The pseudo-second-order model and the Weber and Morris intra-particle diffusion model described the experimental data well. According to the Weber and Morris model, the plot of q versus $t^{1/2}$ should be linear if intra-particle diffusion is involved in the adsorption process; if these lines pass through the origin, then the intra particle diffusion is the rate controlling step [35]. Because the C was greater than zero, the plot did not pass through the origin. At this circumstance, adsorption process has two stages which are the initial stage with the higher slope corresponds to the external mass transfer process, and the second stage with the lower slope relates the intra-particle diffusion as a rate limiting step [36]. When the plot does not pass through the origin, there is some extent of boundary layer control, indicating that the intra-particle diffusion process is not the only rate controlling step and that other kinetics models may also control the rate of the adsorption process. Therefore, the mechanism of F^- adsorption on Ti-CHI is a combination of chemisorption and electrostatic adsorption.

3.7. The adsorption equilibrium isotherms

Studying the adsorption isotherms is very important for understanding the adsorption process. The Langmuir, Freundlich and Langmuir–Freundlich isotherm models are the most commonly employed isotherms used to describe the experimental data

Table 4

Parameters of the intra-particle diffusion model for fluoride adsorption on Ti-CHI.

Initial concentration (mg/g)	Intra particle diffusion model		
	C (mg/g)	k_t (h ^{-0.5})	r^2
4.52	2.93	0.74	0.94
9.05	5.85	0.61	0.90
13.57	8.04	0.92	0.88
18.09	9.40	1.20	0.84

Table 5

Parameters for the Langmuir, Freundlich and Langmuir–Freundlich isotherms for fluoride adsorption on Ti-CHL.

Temperature (K)	Langmuir			Freundlich			Langmuir–Freundlich			
	$q_{\max}$	k_L	r^2	k_F	n	r^2	$q_{LF-\max}$	k_{LF}	b_{LF}	r^2
283	14.32	0.36	0.997	4.22	2.44	0.936	14.12	−0.60	−0.60	0.996
293	14.16	0.36	0.993	4.20	2.42	0.940	14.16	−0.60	−0.60	0.991
303	15.10	0.60	0.974	5.64	2.74	0.880	15.10	0.78	0.78	0.965
313	15.31	0.62	0.969	5.80	2.79	0.854	15.31	0.80	0.79	0.959
323	16.12	0.77	0.999	5.86	2.58	0.932	16.12	1.03	0.75	0.999

collected during the adsorption process. The Langmuir isotherm model assumes that there is monolayer adsorption onto a surface with a finite number of uniform adsorption sites [37].

$$q_e = \frac{q_{\max} c_e}{1 + k_L c_e} \quad (9)$$

The Freundlich isotherm model is an empirical equation based on adsorption on a heterogeneous surface [38].

$$q_e = k_F c_e^{1/n} \quad (10)$$

where c_e is the equilibrium concentration of F^- in the solutions (mg/L); $q_{\max}$ is the maximum adsorption capacity of fluoride ions

(mg/g); and k_L is the Langmuir constant (L/mg). The terms k_F and $1/n$ are Freundlich constants that indicate the extent of adsorption and the adsorption intensity.

The Langmuir–Freundlich model is a combination of the above models [39–41]. This model could be expressed as follows:

$$q_e = \frac{q_{LF-\max} (k_{LF} c_e) b_{LF}}{1 + (k_{LF} c_e) b_{LF}} \quad (11)$$

where $q_{LF-\max}$ (mg/g), k_{LF} (L/mg) and b_{LF} are the maximum adsorption capacity and Langmuir–Freundlich isotherm constants.

Transforming nonlinear isotherms to their linear forms implicitly may alter their error structure and violate the error variance, as

Fig. 10. (a–e) Non linear fits of the experimental data to the adsorption isotherms at 283, 293, 303, 313, 323 K, respectively.

Table 6

Thermodynamic parameters of fluoride adsorption on Ti-CHI.

<i>T</i>	<i>K_L</i>	ΔG°	ΔH°	ΔS°
283	6.84	−4.5	15.7	71
293	6.84	−4.7		
303	11.4	−6.1		
313	11.78	−6.4		
323	14.63	−7.2		

well the normality assumptions of standard least squares [24]. Non-linear optimization is a more complex mathematical method but is more accurate for determining the isotherm parameter values [42]. There is no problem with transforming nonlinear isotherms to linear forms, and they had the same error structures when the best-fitting isotherms are compared [43]. The nonlinear results were presented in Table 5.

According to the r^2 value of the nonlinear regression methods, the Langmuir and the Langmuir–Freundlich isotherms had identical coefficients of determination that exceeded those of the Freundlich isotherm. Fig. 10(a–e) presents the isotherm models of the adsorption process. The data given in Table 4 shows that when the temperature increases from 283 K to 323 K, the F^- adsorption increased from 14.32 to 16.12 mg/g. The high DC of Ti-CHI shows that it could be an effective adsorbent to remove fluoride from drinking water.

3.8. Thermodynamic studies

The increase in DC as the temperature increases may occur because the higher temperature enhances the binding tendency of the F^- ions onto the interface, thus increasing the extent of adsorption [44]. Thermodynamic studies show whether the adsorption process is spontaneous [45]. The thermodynamic spontaneity and feasibility was assessed by calculating the three basic thermodynamic parameters, i.e., standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), using the following equations [46] [47]:

$$\Delta G^\circ = -RT \ln K_L \quad (12)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

where R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), and K_L is the adsorption equilibrium constant of the Langmuir isotherm obtained from the nonlinear method. A plot of ΔG° versus T will be linear, and the values of ΔH° and ΔS° are determined using the slope and intercept of that plot; the linear correlation coefficient of the plot is 0.95 and the data are summarized in Table 6. The ΔG° values are negative from 283 to 323 K. The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption. Moreover, the absolute values of ΔG° increase from 4.5 to 7.2 kJ/mol as the temperature rises, indicating that the fluoride adsorption process on Ti-CHI becomes more favorable at higher temperatures [48]. The ΔH° value given in Table 6 is positive, indicating that the adsorption reaction is endothermic. The positive ΔS° value reflects the affinity of the Ti-CHI for the fluoride and suggests that some structural changes occur in Ti-CHI [49].

4. Conclusions

The titanium(IV) hydrate material based on a chitosan template is a cost effective bio-adsorbent for defluoridating aqueous solutions. Sorption experiments showed the following results: Ti-CHI

could remove fluoride from aqueous solutions with low fluoride concentrations (4.52 mg/L), making water meeting the permitted drinking water standard (0.55 mg/L, below 1 mg/L); the Ti-CHI had an effective defluoridation capacity in a wide pH range (4–9) and is a potential adsorbent for natural fluoride-contaminated water with a basic pH; and finally, the presence of anions had a deleterious effect on the adsorption of fluoride, particularly for CO_3^{2-} , HCO_3^- and PO_4^{3-} . After combining the defluoridation effect, the pH effect and the analysis of the FTIR and Zeta potential data, we found that the adsorption process was governed by both electrostatic adsorption and chemical bonding: the $-NH$ groups and $Ti-OH$ groups were the adsorption sites for F^- on Ti-CHI. The kinetic studies showed that the experimental data fit both the pseudo-second-order and Weber and Morris intra-particle diffusion models. The Langmuir and Langmuir–Freundlich isotherms described the experimental data well, indicating that the maximum adsorption capacity for fluoride on Ti-CHI was 16.12 mg/g. The thermodynamic studies revealed that the fluoride adsorption process on Ti-CHI was spontaneous. Therefore, Ti-CHI is an economical adsorbent free of energy driving.

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