Fluoride ion adsorption from wastewater using magnesium(II), aluminum(III) and titanium(IV) modified natural zeolite: kinetics, thermodynamics, and mechanistic aspects of adsorption
Zhijun Ma, Qi Zhang, Xingyuan Weng, Changye Mang, Liwei Si, Zhihao Guan and Liang Cheng

ABSTRACT
Natural zeolite was modified using metal ions, including magnesium(II), aluminum(III) and titanium(IV). The modified zeolite was then used as an adsorbent for the investigation of the adsorption kinetics, isotherms, and thermodynamic parameters of fluoride ions in wastewater at various pHs and temperatures. The kinetics and thermodynamics for the removal of the fluoride ions onto the modified zeolite have also been investigated. The fluoride ion adsorption capacity of the three types of modified zeolites exhibited an increase, then decrease, with rising pH. The fluoride adsorption capacity of the modified zeolites decreased with an increase in temperature. The pseudo-second-order model is more suitable for describing the adsorption kinetic data than the pseudo-first-order model for modified zeolite and the adsorption process of the fluoride ions reveals pseudo-second-order kinetic behavior, respectively. It was found that the adsorption equilibrium data fit the Freundlich isothermal equation better than that of the Langmuir isothermal and Dubinin–Radushkevich (D–R) isothermal equations. Thermodynamic analysis suggests that the negative values of $\Delta G^0$ and $\Delta H^0$ further indicate that the fluoride adsorption process is both spontaneous and exothermic. The results of competitive adsorption tests suggest that the modified metal zeolite materials adsorb fluoride ions with high selectivity.

Key words | adsorption, fluoride, kinetics, modified natural zeolite, thermodynamics

INTRODUCTION
As a trace element, fluoride is essential to prevent dental cavities, but an excessive intake of the element can be detrimental to human health. Indeed, excess ingestion of fluoride can cause dental/skeleton fluorosis (Mahranmanlioglu et al. 2002). It not only affects the teeth and skeleton, but its accumulation over a long period of time can lead to cancer, osteosclerosis (brittle bones and calcified ligaments), as well as neurological impairment in human beings (Harrison 2005). According to World Health Organization (WHO) norms, the acceptable fluoride concentration in drinking water is generally 0.5–1.5 mg/L (World Health Organization 1993). In China, the industrial standards of fluoride concentration in wastewater discharge are under 10 mg/L, and 1.0 mg/L in drinking water. The need to effectively reduce the fluoride concentration in industrial wastewater has become a vital task in contemporary society.

Fluoride water pollution mainly occurs via two ways, both of which are related to natural and human activities. Fluoride is often present in minerals and it can be leached...
out due to erosion by rainwater, leading to contamination of ground and surface waters. Conversely, fluoride contamination occurs in a wide range of industrial wastewater generated by aluminum and steel production, metal finishing and electroplating, glass and semiconductor manufacturing, ore beneficiation, and fertilizer operation (Paulson 1977).

Currently, there are several methods to remove fluoride ions from industrial wastewater at home and abroad. Some successful defluoridation methods under investigation include chemical precipitation (Huang & Liu 1999; Yang et al. 2001), ion exchange (Ku et al. 2002), adsorption (Bishop & Sansoucy 1978; Ku & Chiu 2002; Liao & Shi 2005), electrolysis (Adhikary et al. 1989; Sahli et al. 2007), reverse osmosis (Joshi et al. 1992) and nanofiltration (Simons 1993). Among these techniques, adsorption is the most suitable process for treating drinking water. Different adsorbents have been tested for fluoride removal, such as activated alumina (Meenakshi & Maheshwari 2006), activated carbon (Li et al. 2003; Sivasamy et al. 2010), calcite (Yang et al. 1999), clay, and modified zeolite (Cengeloglu et al. 2006). One study was directed at investigating industrial wastewater in the base of the fluoride chemical industry in Fuxin. There are rich natural zeolite mineral resources in this region, so the modified zeolite adsorption method not only reduces the cost, but also makes good use of the resources at hand. Zeolite is an aqueous frame structure made up of aluminum silicate minerals, the chemical formula for which is (Na, K)\(_x\)(Mg, Ca, Sr or Ba)\(_y\)(Al\(_{1-x-2y}\)Si\(_{1-x-2y}\))O\(_{2n} \cdot mH_2O\). The lattice is characterized by many pores and channels; therefore, it possesses a large specific surface area and exhibits good adsorption performance. Making the adsorbent with natural zeolite treated with the appropriate modification methods has always been a hot area of research both at home and abroad. Naturally occurring low-cost zeolites used as an ion adsorbent offer great potential for removing fluoride from industrial wastewater.

In recent years, considerable attention has been devoted to developing new adsorbents loaded with metal ions (Zhang et al. 2003). These metal ions, such as sodium, magnesium, aluminum, titanium, zirconium, and lanthanum, exhibit promising results for the removal of fluoride when they are loaded on zeolite. Rahmani found that the adsorption capacity of Al(III)-loaded zeolite for removing fluoride is larger than that of Fe(III)-loaded zeolite; this adsorbent performs desorption and regeneration processes well (Rahmani et al. 2010). In another investigation, Zhao et al. studied the combined removal of fluoride and arsenic by Fe(III)-loaded ligand exchange cotton cellulose and found that the adsorbent could simultaneously remove As(V) and F\(^-\) efficiently from the aqueous solution (Han et al. 2014). Moreover, research on rare earth metal-loaded zeolite has also made progress, but the operating costs are typically high. Therefore, the long-term interests, low adsorption capacity, and high costs are problems restricting their wide application. In this paper, three types of modified zeolite were prepared by loading magnesium, aluminum, and titanium, respectively. The aim was to investigate and characterize the effect of different metal ion valences loaded on zeolite for the removal of fluoride ions. Other factors including adsorption equilibrium, adsorption kinetics, effect of various pHs, initial fluoride concentration, solution temperature, reaction time, and coexisting anions on fluoride removal were also investigated to evaluate the adsorption performance of the modified zeolites.

### MATERIALS AND METHODS

#### Materials

The natural zeolite used in this experiment was obtained from Fuxin, Liaoning Province, China. The zeolite was crushed and ground to provide ore with a particle size of 0.25–0.38 mm. The chemical compositions of the natural zeolite are shown in Table 1. The fluoride ion solution (80 mg/L) was obtained from Fuxin Specialty Chemicals Co. Ltd. Chemicals used in this experiment include sodium hydroxide (NaOH), magnesium sulfate (MgSO\(_4\)),

<table>
<thead>
<tr>
<th>Species</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>TiO(_2)</th>
<th>K(_2)O</th>
<th>MgO</th>
<th>Na(_2)O</th>
<th>CaO</th>
<th>FeO</th>
<th>H(_2)O</th>
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</thead>
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<td>The mass fraction %</td>
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<td>11.5</td>
<td>0.66</td>
<td>0.10</td>
<td>2.25</td>
<td>0.39</td>
<td>0.79</td>
<td>3.74</td>
<td>0.09</td>
<td>11.17</td>
<td>11.83</td>
</tr>
</tbody>
</table>
aluminum sulfate \((\text{Al}_2\text{(SO}_4)_3)\), and titanium sulfate \((\text{Ti(SO}_4)_2)\). All the chemicals were of analytical grade. The experiments were conducted in distilled water.

**Adsorbent preparation**

The natural zeolite samples were washed with deionized water and dried below 378 K. Three types of modified zeolite to be employed as an adsorbent were separately prepared with 20 wt% \(\text{MgSO}_4\), 15 wt% \(\text{Al}_2\text{(SO}_4)_3\), and 10 wt% \(\text{Ti(SO}_4)_2\) at 313 K for 6 h using a magnetic stirrer at 40 rounds per minute (rpm). Before the modification experiments, the natural zeolites were first dipped in 1.0 mol/L \(\text{NaOH}\) at 313 K for 2 h. The natural zeolites without modification used in the adsorption experiments as comparison were also dipped in 1.0 mol/L \(\text{NaOH}\) at 313 K for 2 h. The natural zeolites without modification and three modified zeolite materials were then obtained following washing, filtering, and drying procedures.

**Batch experiments**

All experiments were conducted in 100 mL of fluoride solution, which had been diluted into different concentrations from fluoride-containing wastewater with deionized water in a 250 mL conical flask and shaken in a thermostatic shaker at 200 rpm. Several parameters were then investigated, such as pH, temperature, adsorption time, initial concentration of the fluoride solution, and adsorbent dosage. The pH value of the fluoride solution was adjusted from 2 to 12 by adding 0.1 mol/L HCl or 0.1 mol/L \(\text{NaOH}\), and the temperature of the aqueous solution was controlled from 293 K to 323 K for a contact time of 300 minutes. The adsorption isotherm experiments were conducted with the initial concentration of the fluoride solution of 10, 20, 30, 40, 50, 60, 70 and 80 mg/L, and an adsorbent dosage of 1.0 g. After adsorption, the residual fluoride concentration in the solution was measured by an ion-selective electrode method. The specific amount adsorbed was calculated using the following equation (Equation (1)).

\[
Q_e = (C_0 - C_e) \times \frac{V}{M}
\]  

and the fluoride removal rate expression (Equation (2)),

\[
S = \frac{C_0 - C_e}{C_0} \times 100\%
\]

where \(Q_e\) is the adsorption capacity (mg/g) at equilibrium; \(S\) is the fluoride removal rate (%); \(C_0\) and \(C_e\) are the initial and equilibrium concentration of fluoride (mg/L) in the wastewater sample, respectively; \(V\) is the volume of the wastewater sample (L); and \(M\) is the adsorbent dosage (g) used in the experiments.

The adsorption kinetics were determined by analyzing the adsorptive uptake of fluoride ions from aqueous solutions at different time intervals. The fluoride solution was agitated with a known dosage of the adsorbent at a fixed pH and temperature after 300 minutes. The thermodynamic experiments were performed using different temperatures of the fluoride solution under other constant parameters. Each experiment was replicated three times, and the mean values were used in the analyses.

**Regeneration**

The exhausted adsorbents were regenerated using 1.0 mol/L \(\text{NaOH}\) solution as the eluent at 313 K for 2 h with a solid/solution ratio of 1:5 under stirring. The three samples were treated three times in 20 wt% \(\text{MgSO}_4\), 15 wt% \(\text{Al}_2\text{(SO}_4)_3\), and 10 wt% \(\text{Ti(SO}_4)_2\) at 313 K for 6 h with a solid/solution ratio of 1:5 on a magnetic stirrer at 40 rpm. Subsequently, the three samples were washed, filtered, and dried to obtain the regenerated samples. Similar regeneration procedures were undertaken until the adsorbents were recycled consecutively five times for adsorption-desorption experiments.

**RESULTS AND DISCUSSION**

**Effect of pH**

A set of wastewater solutions with different pHs was used in the adsorption experiment. The fluoride removal process was studied over the pH range of 2 to 12, the results for which are shown in Figure 1. It was found that the pH of
the wastewater plays a significant role in the adsorption process. The fluoride ion adsorption capacity of the three kinds of modified zeolite materials first showed an increase, then decrease, with rising pH. The Mg(II)-zeolite exhibited an adsorption capacity of 0.80 mg/g when the pH of the solution was 7, while that of the Al(III)-zeolite was 0.88 mg/g at neutral pH. The Ti(IV)-zeolite reached a maximum adsorption capacity of 1.64 mg/g at the optimum pH of 6. In contrast to this was the adsorption capacity of natural zeolite, which was 0.42 mg/g at pH = 7. It can therefore be seen that the adsorption capacity of the modified zeolite is greater than that of the natural zeolite.

The pH of the wastewater can affect the amount of fluoride ions retrieved. At low pH, F\(^-\) combines with H\(^+\) to form HF (K\(_1\) = 1.5 × 10\(^3\)) or HF\(_2\) (K\(_2\) = 3.9). This leads to low adsorption capacity, as F\(^-\) cannot be adsorbed by both the natural and modified zeolites. There is also some debate over the nature of the zeolite structure. Because the zeolite surface has groups of −Al–OH and −Si–OH, the variable surface charges are generated by associating and desorbing these groups for H\(^+\) ions. At lower pHs, the concentration of H\(^+\) ions in the aqueous solution is higher; therefore, the −Al–OH and −Si–OH groups can adsorb more H\(^+\) ions to decrease the active point and the negative charges on the surface of the zeolite, thereby decreasing the association capacity of the zeolite and fluoride ions. In the same vein, the fluoride ion removal decreases at higher pHs due to the abundance of OH\(^-\) ions and the electrostatic repulsion between the negatively charged surface of the adsorbent and the F\(^-\) ions. There are also no exchangeable anions on the outer surface of the adsorbent at higher pH values due to the presence of excess OH\(^-\) ions competing with F\(^-\) anions for adsorption sites. As a result, adsorption decreases (Wu et al. 2004; Alkan et al. 2007; Dogan et al. 2007). Similar observations have been reported for other fluoride absorption investigations, indicating that the adsorbent had a net positive charge on its surface (Bousher et al. 1997; Pang et al. 2007; Janas et al. 2009). Moreover, as the pH increases from 7 to 12, metal hydroxide complexes are generated and cover the surface of the modified zeolites. These complexes enter the pores of the zeolite, thereby reducing the number of fluoride ions that can participate in the diffusion adsorption of the internal zeolite structure.

**Effect of temperature**

The effect of temperature on fluoride ion adsorption was investigated by varying the temperature from 293 K to 323 K, while keeping all other factors constant. The results are shown in Figure 2. The adsorption capacity of the
various zeolites decreased with an increase in wastewater temperature. The adsorption experiment can be adopted at room temperature (293 K) to reduce energy consumption. The adsorption capacity of the zeolites exhibited large differences when their temperature was held at 293 K. While the adsorption capacity of Al(III)-zeolite is greater than that of Mg(II)-zeolite, Ti(IV)-zeolite’s is largest. Despite this, the absorption capacity of the natural zeolite is smallest.

Effect of adsorbent dosage

The adsorbent dosage was varied in the following amounts: 0.5, 1, 2, 5, 10, and 20 g. It was then placed in the wastewater solution with 80 mg/L constant initial concentration, 100 mL solution volume, at 293 K temperature. After 300 min, the residual fluoride concentration was obtained, and the removal rate and adsorption capacity were calculated. Table 2 shows the effects of the adsorbent dosage on fluoride removal. From Table 2, it can be seen that the fluoride removal rate of the modified zeolite increases with increasing adsorbent dosage. The removal effect of Ti(IV)-zeolite is much greater than that of Mg(II)-zeolite and Al(III)-zeolite. When the adsorbent dosage reached 20 mg, the removal rate of the Ti(IV)-zeolite achieved 94.78%. Bearing these values in mind, the fluoride concentration successfully meets the emission standards of national industrial wastewater in China.

Adsorption kinetics

The adsorption data was applied to three different kinetic models: pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. In both the pseudo-first-order and pseudo-second-order models, the adsorption steps, including external diffusion, internal diffusion, and adsorption are lumped together. Linear forms of the pseudo-first-order and pseudo-second-order equations are given in Equations (3) and (4), as well as intraparticle diffusion in Equation (5) (Ho & McKay 1998; Ozacar & Sengil 2005).

\[
\ln \left( \frac{Q_e}{Q_t} \right) = \ln Q_t - k_1 t \\
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \\
Q_t = k_p t^{1/2} + C
\]

where \(Q_e\) and \(Q_t\) are the amount of dye adsorbed (mg/g) on the adsorbents at equilibrium and at time \(t\), respectively, \(k_1\) is the rate constant of adsorption (1/h), \(k_2\) is the rate constant of pseudo-second-order adsorption (g/mg h), \(k_p\) is the rate constant for intraparticle diffusion (1/h), and \(C\) is the intercept. The linear plots of \(\ln(Q_e - Q_t)\) versus \(t\) for the first-order reaction and \(t/Q_t\) against \(t\) for the second-order reaction for the adsorption of fluoride ions onto modified zeolites have also been tested to obtain the rate parameters. The kinetics plot (a), plot (b), and plot (c) show the linear fitting of different kinetics data for the three types of modified zeolite materials (Figure 3). The kinetic parameters of the fluoride ions under different conditions were calculated from these plots and are provided in Table 3.

According to these correlation coefficient values, the second-order model is better suited to describe the

<table>
<thead>
<tr>
<th>Adsorbent dosage (g)</th>
<th>Initial concentration (mg/L)</th>
<th>Solution volume (mL)</th>
<th>Residual concentration (mg/L)</th>
<th>Removal rate (%)</th>
<th>Adsorption capacity, (mg/g)</th>
</tr>
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<tbody>
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<td>100</td>
<td>22.68</td>
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adsorption kinetic data than the first-order model and the intraparticle diffusion model for the adsorption of fluoride ions on modified zeolites.

Adsorption isotherms

Figure 4 exhibits the adsorption capacity of three modified zeolites under different fluoride equilibrium concentrations. It can be seen that the adsorption capacity of the Ti(IV)-zeolite is 1.35 mg/g at the wastewater concentration of 80 mg/L, the Al(III)-zeolite is 0.9 mg/g, and the Mg(II)-zeolite is 0.82 mg/g.

The adsorption isotherms of three types of modified zeolite materials are described by the Langmuir, Freundlich, and Dubinin–Radushkevich isothermal equations. The equations for the three models are given as follows (Equations (6)–(8)).

Langmuir model: \[ \frac{C_e}{Q_e} = \frac{1}{Q_m \times b} + \frac{C_e}{Q_m} \] (6)

Freundlich model: \[ \lg Q_e = \frac{1}{n} \lg C_e + \lg K_f \] (7)

Dubinin–Radushkevich (D–R) model: \[ \ln Q_e = \ln X_m - K_c e^2 \] (8)

In the Dubinin–Radushkevich isothermal equation, the energy of adsorption, \( E \) (kJ/mol), was \( E = (2K)^{-1/2} \). \( Q_e \) is the amount absorbed at equilibrium (mg/g), \( C_e \) is the

Table 3 | Constant parameters and correlation coefficients based on different kinetics models for fluoride adsorbed on three types of modified zeolites at different temperatures

<table>
<thead>
<tr>
<th>Adsorbent types</th>
<th>T(K)</th>
<th>( k_1 ) (1/h)</th>
<th>( Q_{e,calc} ) (mg/g)</th>
<th>( R_1^2 ) (1/h)</th>
<th>( k_2 ) (1/h)</th>
<th>( Q_{e,exp} ) (mg/g)</th>
<th>( Q_{e,calc} ) (mg/g)</th>
<th>( R_2^2 )</th>
<th>( k_3 ) (1/h)</th>
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<td>Mg-Zeolite</td>
<td>293</td>
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<td>0.82</td>
<td>0.9773</td>
<td>0.0447</td>
<td>0.89</td>
<td>0.82</td>
<td>0.9995</td>
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<td>Al-Zeolite</td>
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equilibrium concentration (mg/L), $Q_m$ is the adsorption capacity (mg/g), and $b$ is the Langmuir constant (L/mg). $K_f$ and $n$ are the Freundlich constants and were calculated from the slope and intercept of the Freundlich plots. $\epsilon$ is the Polanyi potential, which can be found from $E = RTln(1 + 1/C_0)$, $X_m$ is the ultimate capacity per unit area in the adsorption micropores, $K_c$ is a constant related to the adsorption energy (mol$^2$/kJ$^2$), and $R$ is the gas constant (J/kmol) (Yousef et al. 2001). Adsorption isotherm model parameters for the Mg(II)-zeolite, Al(III)-zeolite, and Ti(IV)-zeolite are shown in Table 4. The linear fitting figures of the adsorption isotherm are revealed in Figure 5.

![Figure 4](image_url)  
**Figure 4** | The adsorption isotherms of three types of modified zeolite (pH value of wastewater: pH = 6; reaction temperature: T = 293 K) at different fluoride concentrations.

and the relevant data were obtained by using Equations (4)–(6). It is seen that the coefficient of determination ($R^2$) obtained from the Freundlich isotherm model is higher than that obtained using the Langmuir and D-R models for Mg(II)-zeolite and Al(III)-zeolite. The $R^2$ obtained from the Langmuir model is close to the $R^2$ obtained using the Freundlich isotherm model for Ti(IV)-zeolite. At room temperature (293 K), the Freundlich isotherm model $R^2$ values of the Mg(II)-zeolite, Al(III)-zeolite, and Ti(IV)-zeolite are 0.9400, 0.9848, and 0.9423.

According to Freundlich theory, in a solid-liquid adsorption system, the $K_f$ value decreases with an increase in temperature. In this manner, the relative adsorption quantity tends to decrease; the increasing value of $1/n$ also indicates a reduction in the adsorption strength. Because all values of $1/n$ are less than 0.5, this result explains that the adsorption of the modified zeolite is better for chemical adsorption. As Figure 5(c) shows, the D-R model fits the data more closely than the Langmuir and Freundlich models. In the D-R isotherm model, the average free activation energy of adsorption, $E$, can determine whether the adsorption process is physical adsorption or chemical adsorption. If this value is between 8 and 16 kJ/mol, the adsorption is classified as chemical adsorption; for the value of $E < 8$ kJ/mol, the adsorption process is said to be physical in nature. The values of $E$ in this study were found to be 9.8372, 9.5996, and 11.7053 kJ/mol at 293 K for the Mg(II)-zeolite, Al(III)-zeolite and Ti(IV)-zeolite. These numbers suggest that the adsorption proceeds mainly by chemical adsorption.

| Table 4 | Constant parameters and correlation coefficients based on different adsorption models for $F^-$ adsorbed on three modified zeolites at different temperatures |
|---------|-----------------|-----------------|-----------------|-----------------|
| Adsorbent types | Langmuir | Freundlich | Dubinin–Radushkevich |
| | $Q_m$ (mg/g) | $b$ (L/mg) | $R^2$ | $K_f$ | $1/n$ | $R^2$ | $K_c$ (mol$^2$/kJ$^2$) | $X_m$ (mmol/g) | $E$ (kJ/mol) | $R^2$ |
| Mg-Zeolite | 293 | 1.0827 | 0.0350 | 0.9214 | 0.1332 | 0.4102 | 0.9400 | 5.17×10$^{-9}$ | 0.1033 | 9.8372 | 0.9133 |
| | 303 | 1.0858 | 0.0278 | 0.8712 | 0.1042 | 0.4498 | 0.9210 | 5.30×10$^{-9}$ | 0.1047 | 9.7141 | 0.8906 |
| | 313 | 0.9155 | 0.0331 | 0.9017 | 0.1081 | 0.4153 | 0.9288 | 4.60×10$^{-9}$ | 0.0869 | 10.4273 | 0.9019 |
| | 323 | 0.8368 | 0.0350 | 0.9284 | 0.1040 | 0.4077 | 0.9294 | 4.24×10$^{-9}$ | 0.0797 | 10.8559 | 0.9025 |
| Al-Zeolite | 293 | 1.1787 | 0.0269 | 0.9756 | 0.1443 | 0.4277 | 0.9848 | 5.43×10$^{-9}$ | 0.1266 | 9.5996 | 0.9755 |
| | 303 | 1.1994 | 0.0212 | 0.9597 | 0.1232 | 0.4595 | 0.9558 | 5.45×10$^{-9}$ | 0.1332 | 9.5774 | 0.9448 |
| | 313 | 1.0292 | 0.0382 | 0.9492 | 0.1311 | 0.4096 | 0.9598 | 4.54×10$^{-9}$ | 0.1017 | 10.4963 | 0.9392 |
| | 323 | 1.0291 | 0.0270 | 0.8627 | 0.0963 | 0.4532 | 0.9199 | 4.70×10$^{-9}$ | 0.0991 | 10.3113 | 0.8892 |
| Ti-Zeolite | 293 | 1.5113 | 0.0629 | 0.9462 | 0.3507 | 0.2940 | 0.9423 | 3.65×10$^{-9}$ | 0.1253 | 11.7053 | 0.9153 |
| | 303 | 1.3892 | 0.0706 | 0.9663 | 0.3530 | 0.2786 | 0.9651 | 3.24×10$^{-9}$ | 0.1142 | 12.4267 | 0.9431 |
| | 313 | 1.3736 | 0.0576 | 0.9528 | 0.2947 | 0.3085 | 0.9384 | 3.36×10$^{-9}$ | 0.1158 | 12.2015 | 0.9103 |
| | 323 | 1.2154 | 0.0690 | 0.9754 | 0.3017 | 0.2832 | 0.9619 | 2.91×10$^{-9}$ | 0.1009 | 13.1149 | 0.9379 |
Thermodynamic analyses

Thermodynamic parameters can provide in-depth information regarding the inherent energy changes associated with adsorption. Thermodynamic parameters, including the change in the Gibbs free energy ($\Delta G^0$), enthalpy ($\Delta H^0$), and entropy ($\Delta S^0$) were determined to elucidate the adsorption process using the following equations and the information depicted in Table 5.

The thermodynamic parameters, including the activation free energy change ($\Delta G^0$), activation enthalpy change ($\Delta H^0$), and activation entropy change ($\Delta S^0$), were calculated using the following equations (Equations (9)–(11)) (Onyango et al. 2009; Katal et al. 2012).

\[
K = \frac{Q_e}{C_e} \quad \text{(9)}
\]

\[
\Delta G^0 = -RT \ln K \quad \text{(10)}
\]

\[
\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \text{(11)}
\]

where $K$ is the equilibrium constant; $Q_e$ is the amount of dye adsorbed on the natural sepiolite from the solution at equilibrium (mg/g); $C_e$ is the equilibrium concentration of the dye solutions (mg/L); $R$ is the gas constant (8.3144 J/mol·K); $T$ is the wastewater temperature (K); and $\Delta G^0$ can be calculated through $R$, $T$ and $\ln K$. $\Delta H^0$ and $\Delta S^0$ were calculated from the slope and intercept of van’t Hoff plots of $\ln K$ against $1/T$ (Figure 6).

According to the thermodynamic data, several conclusions can be drawn as follows:

1. The negative $\Delta H^0$ indicates the adsorption process of the fluoride ions on the modified zeolites is exothermic.
2. The negative $\Delta G^0$ shows that the adsorption process is spontaneous and irreversible. With the temperature increasing, the absolute value of $\Delta G^0$ decreases. This phenomenon indicates higher temperature is not conducive to the adsorption reaction.

3. The value of $\Delta S^0$ is negative. After the adsorption process was completed, the free space allowed for the movement of the fluoride ions before adsorption transforms into two-dimensional motion of the zeolites after adsorption. The degrees of freedom of the fluoride ions reduces and the entropy of the whole system decreases.

**Desorption and regeneration**

Any adsorbent is economically viable if the adsorbent can be regenerated and reused in many cycles of operation. The regeneration experiments were performed using 1.0 mol/L NaOH solution as the eluent. After desorption, three kinds of adsorbent were regenerated using 20 wt% MgSO$_4$, 15 wt% Al$_2$(SO$_4$)$_3$ and 10 wt% Ti(SO$_4$)$_2$ solution, respectively. These processes were described in the ‘Materials and methods’ section above. Adsorption tests on the regenerated samples indicate that three kinds of modified zeolites have no apparent reduction in adsorption capacity after five cycles; they reveal only 9%, 6%, and 5% reduction in adsorption capacity.

** ADSORPTION MECHANISM**

The surface of the natural zeolite was coated with a metal hydroxide after modification. While the modified metal (M) zeolite was in contact with the fluoride ions in solution, the fluoride ions can be adsorbed by exchanging with the active hydroxyl groups. The fluoride adsorption onto the neutral solid surface can be described by a ligand or ion exchange reaction mechanism when the pH of the medium remains neutral (~7.00). This process can be expressed by Equations (12) and (13) as follows.

$$\text{Zeo} - \text{MOH} + F^- \rightarrow \text{Zeo} - \text{MF} + \text{OH}^- \quad (12)$$

$$\text{Zeo} - \text{MOH} + F^- \rightarrow \text{Zeo} - \text{MF} + \text{H}_2\text{O} \quad (13)$$

Also, the fluoride ions can undergo non-specific hydrogen bonding interactions (Equation (14)).

$$\text{Zeo} - \text{MOH}_2^+ + \text{F}^- \rightarrow \text{Zeo} - \text{MOH}_2^+ \cdot \text{F}^- \quad (14)$$

The mechanism of the fluoride removal process has been outlined in a similar manner to that discussed for metal oxides by Tor (2006) and Sarkar et al. (2006). In these studies, the exchange between available hydroxide surface groups and fluoride ions occurs because both F$^-$ and OH$^-$ are isoelectronic and therefore have a comparable ionic radius. According to the adsorption effect of different modified metal zeolites, the surface of the Ti(IV)-zeolite may offer more active sites than that of the Mg(II) and Al(III) zeolites. This enables the fluoride ions to approach the zeolites more easily. The mechanism of fluoride adsorption on modified metal zeolites is a complex process, encompassing what may be a chemisorption-controlled process combined with diffusion.

** CONCLUSION**

This manuscript reported the preparation of modified metal zeolite materials and investigated the kinetics and thermodynamics of the adsorption of fluoride ions onto three types of modified zeolites (Mg(II)-loaded, Al(III)-loaded, Ti(IV)-loaded). Several important factors during the adsorption process were discovered. The adsorption capacity of the modified metal zeolites for the fluoride ions in industrial wastewater is larger than that of natural zeolite. Compared with Mg(II) and Al(III) zeolites, the fluoride adsorption capacity of the Ti(IV)-zeolite is greatest. Indeed, the adsorption capacity of the Ti(IV)-zeolite can reach 1.64 mg/g under optimal conditions.

Also studied were the effects of the pH of the wastewater solution, temperature, initial concentration, and the dosage of modified zeolites on fluoride ions adsorption. The experimental results revealed that the adsorption capacity was maximized at a pH of 6 and a temperature of 293 K. The greater the dosage of the modified zeolite, the higher the fluoride ion removal rate.

Fluoride adsorption on the three types of modified zeolite are well described by the Freundlich adsorption model.
The adsorption kinetics were accurately expressed by the pseudo-second-order equation, in which the fluoride adsorption on the modified metal zeolite can be described by a diffusion controlled process combined with chemisorption. The thermodynamic data indicated that the adsorption reaction was both spontaneous and exothermic.

These adsorbents, which were acquired by loading metal ions such as Mg(II), Al(III), and Ti(IV) onto the natural zeolites can be regenerated using 1.0 mol/L NaOH solution as an eluent. The regenerated samples retain their good adsorptive performance, especially the Ti(IV)-loaded adsorbent. The adsorbent is efficient with low chemical consumption and operating costs.

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Conflicts of Interest

The authors declare no conflict of interest.

References


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