Characterization of quintinite particles in fluoride removal from aqueous solutions

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Abstract

The aim of this study was to characterize quintinite in fluoride removal from aqueous solutions using batch experiments. Experimental results showed that the maximum adsorption capacity of fluoride to quintinite was 7.71 mg/g. The adsorption of fluoride to quintinite was not changed at pH 5–9 but decreased considerably at the highly acidic (pH < 3) and alkaline (pH > 11) solution conditions. Kinetic model analysis showed that the pseudo second-order model was the most suitable for describing the kinetic data among the three (pseudo first-order, pseudo second-order, Elovich) models. From the nonlinear regression analysis, the pseudo second-order parameter values were determined to be $q_e = 0.18$ mg/g and $k_2 = 28.80$ g/mg/h. Equilibrium isotherm model analysis demonstrated that among the three (Langmuir, Freundlich, Redlich-Peterson) models, both Freundlich and Redlich-Peterson models were suitable for describing the equilibrium data. In the model analysis, the Redlich–Peterson model fit was superimposed on the Freundlich fit. The Freundlich model parameter values were determined from the nonlinear regression to be $K_F = 0.20$ L/g and $1/n = 0.51$. This study demonstrated that quintinite could be used as an adsorbent for the removal of fluoride from aqueous solutions.

Keywords: Adsorption, Batch experiment, Fluoride, Hydrotalcite-like particles, Quintinite
1. Introduction

Quintinite is a carbonate mineral with hexagonal crystal system. It has a chemical formula of \( \text{Mg}_4\text{Al}_2(\text{OH})_12\text{CO}_3 \cdot 3\text{H}_2\text{O} \), which is included in the family of hydrotalcite-like (HTL) particles [1]. Hydrotalcite is a carbonate mineral and rare in nature with a general formula of \( \text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4(\text{H}_2\text{O}) \). Hydrotalcite mineral is a layered double hydroxide with carbonate anions lying between the structural layers [2]. The HTL particles are similar to hydrotalcite mineral, which can be easily synthesized in the laboratory. They have a general formula of \( [\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x^+}[\text{An}^{n-x/n}]^{x^-} \cdot m\text{H}_2\text{O} \), where \( \text{M}(\text{II}) \) is the divalent cation (Mg, Ni, Zn, Co, Mn, etc), \( \text{M}(\text{III}) \) is the trivalent cation (Al, Fe, Cr, V, etc), \( \text{An}^- \) is the interlayer anion (Cl\(^-\), NO\(_3^-\), CO\(_3^{2-}\), SO\(_4^{2-}\), etc) of valence \( n \), and \( x \) is the molar ratio of \( \text{M}(\text{III})/[\text{M}(\text{II})+\text{M}(\text{III})] \). They consist of positively charged brucite[\( \text{Mg}(\text{OH})_2 \)]-like layers \( [\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x^+} \) and negatively-charged interlayers \( [\text{An}^{n-x/n}]^{x^-} \cdot m\text{H}_2\text{O} \). They are a class of anionic clays with high surface area and large anion exchange capacity [3, 4]. The HTL particles have been used as adsorbents for the removal of oxyanions including chromate, phosphate, nitrate, borate, arsenate/arsenite, selenite/selenite [5].

Fluoride is an essential micronutrient for human health preventing dental caries and helping dental enamel calcification. At concentrations greater than 1.5 mg/L, however, fluoride can cause dental/skeletal fluorosis and neurological damage [6]. The contamination of fluoride in drinking water resources is a serious environmental problem around the world. Fluoride contamination in surface and ground water can come from natural geological sources (fluorite, biotites, granite, basalt, etc) and from industrial wastewaters (semiconductor manufacturing, electroplating, glass and ceramic production, etc) [7]. In many countries, fluoride occurs naturally in groundwater at concentrations exceeding the guidelines of the
World Health Organization (1.5 mg/L), causing serious health problems [8]. Adsorption is used widely for the fluoride removal from aqueous solutions, due to its cost effectiveness and simplicity of operation. Various adsorbents have been applied for fluoride removal, including activated alumina, activated carbon, granular ferric hydroxide, limestone, fly ash, and clay [9, 10].

Recently, some researchers used Mg/Al, Zn/Al, and Mg/Al/Fe type HTL particles for fluoride removal [11, 12]. Batistella et al. [13] evaluated the effect of acid activation on the removal of fluoride by Mg/Al type particles. Mandal and Mayadevi [14] performed the kinetic, equilibrium, and thermodynamic studies for the fluoride removal by Zn/Al type particles. Others used mixed metal oxides (MMO) derived from the various HTL particles via calcination for fluoride removal [15–20]. Cai et al. [7] examined the competitive adsorption of fluoride and phosphate by Mg/Al MMO. Zhou et al. [21] analyzed the characteristics of Li/Al MMO in fluoride adsorption in water. In addition, Mandal and Mayadevi [22] used Zn/Al MMO for fluoride adsorption.

The aim of this study was to characterize quintinite in fluoride removal from aqueous solutions. The characteristics of synthetic quintinite particles were elucidated using Transmission electron microscopy (TEM), X-ray diffractometry (XRD), nitrogen gas (N₂) adsorption-desorption experiment, and X-ray photoelectron spectroscopy (XPS). Batch experiments were performed to examine the effect of adsorbent dosage, reaction time, initial fluoride concentration, and initial solution pH on the adsorption of fluoride to quintinite. Kinetic and equilibrium isotherm models were used to analyze the batch experimental data.
2. Materials and Methods

2.1. Synthesis and characterization of quintinite particles

All chemicals used for the experiments were purchased from Sigma Aldrich. Quintinite particles were prepared by the following procedures. The particles were synthesized by co-precipitating mixtures of magnesium nitrate \([\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}]\) and aluminum nitrate \([\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}]\). A 700 mL solution (Mg/Al molar ratio = 2) of \(\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) (1 mol) and \(\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\) (0.5 mol) was added dropwise using a peristaltic pump (QG400, Fasco, Springfield, MO, USA) at 3 mL/min into 1000 mL of alkali solution (pH = 13) consisting of sodium hydroxide (NaOH) and sodium carbonate (Na\(_2\)CO\(_3\)) with intensive stirring at room temperature. The resulting precipitates were aged at 65 °C for 18 h in mother liquor. The precipitates were washed thoroughly with deionized water to remove excess sodium, and then final suspensions were centrifuged at 8,500 rpm for 20 min. The washed precipitates were oven-dried again at 65 °C for 24 h and then pulverized in a ball mill. The pulverized precipitates were passed through US Standard Sieve No. 100 (grain size: 0.149 mm). The particles used for the experiments were finally obtained through oven dry at 105 °C.

TEM (JEM-1010, JEOL, Tokyo, Japan) was used to take images of the particles. The particle size was determined by the analysis of the TEM image (number of particle = 71) using ImageJ 1.43u software (National Institutes of Health, Bethesda, MD, USA). The mineralogical and crystalline structural properties were examined using XRD (D8 Advance, Bruker, Germany) with a CuK\(\alpha\) radiation of 1.5406 Å at a scanning speed of 0.6°/sec. \(\text{N}_2\) adsorption-desorption experiments were performed using a surface area analyzer (BELSORP-max, BEL Japan Inc., Japan) after the sample was pretreated at 120 °C. From the \(\text{N}_2\) adsorption-desorption isotherms, the specific surface area, total pore volume, and
mesopore volume were determined by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses. XPS (XPS Sigma Probe, Thermo VG, UK) measurement was performed with monochromatic Al Kα radiation.

2.2. Fluoride adsorption experiments

The desired fluoride solution was prepared by diluting the stocking fluoride solution (1000 mg/L), which was made from sodium fluoride (NaF). The first batch experiments were performed at the different dosages of adsorbent (quintinite) ranging from 0.1 to 2.0 g in 30 mL solution. Adsorbent was added to 30 mL of fluoride solution (initial concentration = 10 mg/L) in 50 mL polypropylene conical tubes. The tubes were shaken at 25 °C and 100 rpm using a culture tube rotator (MG-150D, Mega Science, Korea). The samples were collected 6 h after the reaction and were filtered through a 0.45-μm membrane filter. The fluoride concentration was measured using a fluoride ion selective electrode (9609BNWP, Thermo Scientific, USA). For the fluoride measurement, total ionic strength adjustment buffer solution (58 g of NaCl, 57 mL of CH₃COOH, 150 mL of 6 M NaOH in 1000 mL of deionized water) was used to prevent the interference of other ions.

Based on the results from the above tests, further batch experiments were conducted at the adsorbent dose of 1.5 g in 30 mL solution. The second batch experiments were performed at the initial fluoride concentrations of 10 mg/L to examine the effect of contact time on fluoride removal. In the experiments, the samples were collected 1, 2, 3, 6, 9, 12, and 24 h after the reaction. The third batch experiments were conducted at fluoride concentrations of 10–1000 mg/L to examine the effect of initial fluoride concentrations on fluoride removal. The samples were collected 6 h after the reaction for the fluoride measurement. The fourth
batch experiments were performed to examine the effect of initial solution pH, which was
adjusted to the desired value with 0.1 M NaOH and/or 0.1 M HCl. All experiments were
performed in triplicate.

2.3. Data analysis

All of the parameters of the models were estimated using MS Excel 2010 with the solver
add-in function incorporated into the program. The model parameter values were determined
by nonlinear regression. The determination coefficient ($R^2$), chi-square coefficient ($\chi^2$) and
sum of square error (SSE) were used to analyze the data and confirm the fit to the model. The
expressions of $R^2$, $\chi^2$ and SSE are given below:

$$R^2 = \frac{\sum_{i=1}^{m} (y_c - \bar{y}_e)^2}{\sum_{i=1}^{m} (y_c - \bar{y}_e)^2 + \sum_{i=1}^{m} (y_c - y_e)^2}$$  \hspace{1cm} (1)

$$\chi^2 = \sum_{i=1}^{m} \left[ \frac{(y_e - y_c)^2}{y_c} \right]_i$$  \hspace{1cm} (2)

$$\text{SSE} = \sum_{i=1}^{m} (y_e - y_c)^2$$  \hspace{1cm} (3)

where $y_c$ is the calculated adsorption capacity from the model, $y_e$ is the measured adsorption
capacity from the experiment, and $\bar{y}_e$ is the average of the measured adsorption capacity.
3. Results and Discussion

3.1. Characteristics of quintinite particles

The characteristics of quintinite particles are presented in Fig. 1 and Fig. 2. The TEM image (Fig. 1a) demonstrates that the particles were nano-sized. The particle size distribution (Fig. 1b) determined from the TEM image shows that the particle size was in the range from 20 to 120 nm with the mean particle size of 59 nm. According to the XRD pattern (Fig. 2a), the particle had a layered structure with sharp and intense lines at low 2θ and less intense lines at high 2θ. The peaks observed at 2θ = 11.673, 23.469, 34.437, 35.978, 38.428, 41.652, 45.520, 60.675 and 62.025 (JCPDS 87-1138) were corresponded well to quintinite particles found in the literature [1]. The particle had a chemical formula of Mg₄Al₂(OH)₁₂CO₃·3H₂O with hexagonal crystal system (a = 5.283 Å; c = 15.159 Å). Based on the XRD pattern, the average crystal size (d) of the particle was estimated by the Debye-Scherrer formula [23]:

\[ d = \frac{0.9\lambda}{\beta \cos \theta} \]  

(4)

where \( \lambda \) is the wavelength of the X-ray (= 1.5406 Å), \( \beta \) is full width at half maximum width of diffraction peak (= 0.369 °), and \( \theta \) is the diffraction angle (= 11.673 °/2). From the Debye-Scherrer analysis (inset in Fig. 2a), the value of \( d \) was calculated to be 21.6 nm. N₂ adsorption and desorption isotherms are presented in Fig. 2b. According to the BET analysis (inset in Fig. 2b), the particles had the specific surface area of 49.8 m²/g and total pore volume of 0.4582 cm³/g. From the BJH analysis, the mesopore volume was determined to be 0.4522 cm³/g.

3.2. Characteristics of fluoride sorption to quintinite particles

The effect of adsorbent dose on fluoride removal is shown in Fig. 3a. The percent
removal increased from 41.7±0.3 to 89.8±0.2% with increasing adsorbent doses from 0.1 to 2.0 g in 30 mL of solution. Meanwhile, the sorption capacity decreased from 1.26±0.01 to 0.14±0.01 mg/g with increasing adsorbent doses. Results indicate that initial fluoride concentration of 10 mg/L could be reduced to < 1.5 mg/L at the adsorbent dose ≥ 1.5 g. The effect of reaction time on the removal of fluoride is provided in Fig. 3b. The fluoride concentrations decreased rapidly with increasing reaction time until the equilibrium was reached at 6 h. At 1 h of reaction time, the fluoride concentration dropped sharply to 2.7 mg/L (initial fluoride concentration =10 mg/L), and further decreased to 1.4 mg/L at 6 h. Then, the fluoride concentration reached to 1.2 mg/L at 24 h of reaction time. Meanwhile, the sorption capacity increased from 0.15 to 0.18 mg/g with increasing reaction time from 1 to 24 h.

The effect of initial fluoride concentration on fluoride removal is presented in Fig. 3c. At the lowest concentration of 10 mg/L, the percent removal was 87.6% and then decreased to 68.0% at the fluoride concentration of 100 mg/L. The percent removal further decreased to 27.8% at the highest concentration of 1000 mg/L. Meanwhile, the sorption capacity increased from 0.18 to 5.75 mg/g with increasing fluoride concentrations from 10 to 1000 mg/L. The effect of initial solution pH on fluoride removal is demonstrated in Fig. 3d. The sorption capacity at pH 3 was 0.10 mg/g and increased to 0.17 mg/g at pH 5. Between pH 5 and pH 9, the sorption capacity remained relatively constant at 0.17–0.18 mg/g. At pH 10, the sorption capacity dropped to 0.16 mg/g and then further decreased sharply to 0.09 mg/g.

Results demonstrate that fluoride sorption in quintinite particles was not much varied at initial pH 4–10. This result could be related to the fact that the final (equilibrium) pH converged to 8.1–8.8 during the sorption experiments (initial pH 4–10). Similar findings were reported in the literature by Kim et al. [15] showing that the fluoride sorption capacity of calcined Mg/Al LDH was not greatly varied between pH 4 and pH 9; the sorption capacity
changed from 15.6 to 14.1 mgP/g with increasing pH from 4 to 9. Han et al. [24] also reported that the removal of phosphate in the alginate beads containing calcined Mg/Al LDH was not sensitive to solution pH. They demonstrate that the percent removal of phosphate decreased slightly from 98.6% to 95.5% as solution pH increased from 4.9 to 8.9.

In our experiments, the fluoride sorption capacity decreased considerably at highly acidic (pH < 3) and alkaline pH (pH > 11) conditions. At highly acidic pH, the fluoride sorption could decrease due to the formation of HF (hydrofluoric acid), which is not favorable for adsorption to the surfaces of adsorbent. According to MINTEQ calculation (Visual MINTEQ 3.0), HF species is formed at 35% of total F species (HF and F\textsuperscript{−}) at pH 3. In addition, metal cations in quintinite might be dissolved at highly acidic pH, which results in the decrease of fluoride sorption [12]. At highly alkaline pH, the fluoride sorption could decrease due to the competition between F\textsuperscript{−} and OH\textsuperscript{−} on the sorption sites. The contribution of NaF formation to the decrease of fluoride sorption might be negligible at highly alkaline pH. According to MINTEQ calculation, NaF species is only 0.2% of total F species (F\textsuperscript{−} and NaF) at pH 11. Note that alkaline pH was obtained by adding 0.1 M NaOH in the experiments. Lv et al. [12] reported that phosphate removal in Mg/Al HTL decreased sharply from 110 to 5 mg/g with increasing pH from 5 to 10. Mandal and Mayadevi [22] showed that phosphate removal in Zn/Al HTL had an increasing tendency between 2.5 and 6.2 but a decreasing one between 6.2 and 9.8.

X-ray photoelectron spectroscopy (XPS) spectra were presented in Fig. 4. In the wide scan before and after fluoride sorption experiments (Fig. 4a), the peaks at binding energy of 49.15 and 73.20 eV are assigned to Mg 2p and Al 2p, respectively. In the high-resolution scan of the F 1s region after fluoride sorption experiment (Fig. 4b), the peak at 683.4 eV is ascribed to adsorbed fluoride ion on the surfaces of quintinite [21]. It is known that two
mechanisms including interlayer anion exchange and surface adsorption could contribute to the removal of fluoride by quintinite particles [5]. In anion exchange process, the charge balancing anion (carbonate) in the interlayer region is replaced by fluoride ion. In surface adsorption, the negatively charged fluoride could adsorb to the positively charged brucite-like layer via electrostatic interaction [5].

3.3. Kinetic and equilibrium model analyses

The reaction time data (Fig. 3b) were analyzed using the following nonlinear forms of pseudo first-order (Eq. 5), pseudo second-order (Eq. 6), and Elovich (Eq. 7) kinetic models:

\[
q_t = q_e (1 - e^{-k_1 t})
\]  (5)

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}
\]  (6)

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t
\]  (7)

where \(q_t\) is the amount of fluoride removed at time \(t\), \(q_e\) is the amount of fluoride removed per unit mass of adsorbent at equilibrium, \(k_1\) is the pseudo first-order rate constant, \(k_2\) is the pseudo second-order velocity constant, \(\alpha\) is the initial adsorption rate constant, and \(\beta\) is the Elovich adsorption constant.

The kinetic data and model fits for fluoride sorption to quintinite are shown in Fig. 5. Model parameters for the pseudo first-order, pseudo second-order, and Elovich models are provided in Table 1. In the pseudo first-order model, the value of \(q_e\) was 0.17 mg/g, and the value of \(k_1\) was 1.85 (1/h). The value of \(q_e\) from the pseudo second-order model was similar
to that from the pseudo first-order model. The value of $q_e$ was 0.18 mg/g, and the value of $k_2$ was 28.80 g/mg/h, respectively. In the Elovich model, the values of $\alpha$ and $\beta$ were 1.90E+06 mg/g/h and 125.0 g/mg, respectively. The values of $R^2$, $\chi^2$, and SSE indicate that the pseudo second-order model was the most suitable for describing the data. This finding indicates that chemisorption is involved in the adsorption of fluoride to quintinite. In the literature, Cai et al. [7] reported that the kinetic data for fluoride sorption to calcined Mg/Al LDH were found to fit very well the pseudo second-order model. Zhou et al. [21] also reported that the pseudo-second-order model was suitable for describing the adsorption kinetics of fluoride on calcined Li/Al LDH.

The fluoride concentration data (Fig. 3c) were analyzed using the following nonlinear forms of Freundlich (Eq. 8), Langmuir (Eq. 9), and Redlich-Peterson (Eq. 10) isotherm models:

$$ q_e = K_F C_e^{1/n} \quad (8) $$

$$ q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (9) $$

$$ q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (10) $$

where $C_e$ is the concentration of fluoride in the aqueous solution at equilibrium, $K_F$ is the distribution coefficient, $1/n$ is the Freundlich constant, $Q_m$ is the maximum mass of fluoride removed per unit mass of adsorbent (removal capacity), $K_L$ is the Langmuir constant related to the binding energy, $K_R$ is the Redlich-Peterson constant related to the adsorption capacity, $a_R$ is the Redlich-Peterson constant related to the affinity of the binding sites and $g$ is the Redlich-Peterson constant related to the adsorption intensity.
The equilibrium data and isotherm model fits for fluoride sorption to quintinite are shown in Fig. 6. The equilibrium isotherm parameters for the Langmuir, Freundlich, and Redlich-Peterson models are summarized in Table 2. The values of $R^2$, $\chi^2$, and $SSE$ indicate that both Freundlich and Redlich-Peterson models were suitable for describing the data. Note that the Redlich–Peterson model fit was superimposed on the Freundlich fit (Fig. 6). The Redlich–Peterson model can be reduced to the Freundlich model if $K_R$ and $a_R$ are much greater than unity [25]. In the Freundlich model, the value of $K_F$ was 0.20 L/g, which corresponded well to the value of $K_R/a_R$ in the Redlich–Peterson model. The value of $1/n$ was equivalent to the value (0.51) of $(1-g)$. The adsorption capacity ($q_m$) was calculated from $K_F$ and $1/n$ using the following equation [26]:

$$q_m = K_F C_0 \frac{1}{n}$$  \hspace{1cm} (11)

The value of $q_m$ was calculated to be 6.78 mg/g.

The fluoride sorption capacities of hydrotalcite-like particles or mixed metal oxides from in the literature are summarized in Table 3. The maximum adsorption capacity ($q_m$) of quintinite in this study was determined to be 7.71 mg/g from the Langmuir model, which was in the low range of adsorption capacity in Table 3. In order to improve the fluoride sorption capacity of quintinite, thermal treatment of quintinite at high temperatures ($\geq 300$ °C) is recommended, which results in the increase of the BET surface area and fluoride sorption capacity [15]. Consequently, it is expected that the cost effectiveness of the adsorbent in fluoride removal can be improved.
4. Conclusions

In this study, the sorption of fluoride to quintinite was examined using batch experiments. Results showed that the maximum adsorption capacity of fluoride to quintinite was 7.71 mg/g. The adsorption of fluoride to quintinite was not changed at pH 5–9 but decreased considerably at the highly acidic (pH < 3) and alkaline (pH > 11) solution conditions. Kinetic model analysis showed that the pseudo second-order model was the most suitable for describing the kinetic data. Equilibrium isotherm model analysis demonstrated that both Freundlich and Redlich-Peterson models were suitable for describing the equilibrium data. This study demonstrated that quintinite could be used as an adsorbent for the removal of fluoride from aqueous solutions.

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Table 1. Kinetic model parameters obtained from model fitting to experimental data

|                | Pseudo first-order model |                | Pseudo second-order model |                | Elovich model |
|----------------|--------------------------|----------------|---------------------------|----------------|---------------|
|                | q_e (mg/g)               | k_1 (1/h)     | R^2                       | \chi^2         | SSE           |
|                | 0.17                     | 1.85          | 0.92                      | 2.75E-04       | 4.62E-05      |
|                | q_e (mg/g)               | k_2 (mg/g)    | R^2                       | \chi^2         | SSE           |
|                | 0.18                     | 28.80         | 0.98                      | 9.19E-05       | 1.50E-05      |
|                | \alpha (mg/g/h)          | \beta (g/mg)  | R^2                       | \chi^2         | SSE           |
|                | 1.90E+06                 | 125.0         | 0.78                      | 8.39E-03       | 1.36E-03      |
Table 2. Equilibrium model parameters obtained from model fitting to experimental data

|                    | Freundlich model | Langmuir model | Redlich-Peterson model |
|--------------------|------------------|----------------|------------------------|
|                    | $K_F$            | $Q_m$          | $K_L$                  | $K_R$                  |
|                    | $(L/g)$          | $(mg/g)$       | $(mg/g)$               | $(L/g)$                |
|                    | $1/n$            | $K_F$          | $K_L$                  | $K_R$                  |
|                    | $(mg/g)$         | $R^2$          | $R^2$                  | $R^2$                  |
|                    | $q_m$            | $\chi^2$       | $\chi^2$               | $\chi^2$               |
|                    | $R^2$            | SSE            | SSE                    | SSE                    |
|                    | $\chi^2$         | SSE            | SSE                    | SSE                    |

| Parameters | Value | Value | Value | Value | Value | Value |
|------------|-------|-------|-------|-------|-------|-------|
| $K_F$      | 0.20  | 0.51  | 0.20  | 0.49  | 0.20  | 0.49  |
| $1/n$      | 6.78  | 6.78  | 6.78  | 6.78  | 6.78  | 6.78  |
| $q_m$      | 1.00  | 1.00  | 0.97  | 0.97  | 0.97  | 0.97  |
| $R^2$      | 0.028 | 0.028 | 1.50  | 1.50  | 1.50  | 1.50  |
| $\chi^2$  | 0.027 | 0.027 | 0.0035| 0.0035| 0.0035| 0.0035|
| $SSE$      | 0.97  | 0.97  | 0.0035| 0.0035| 0.0035| 0.0035|
| $Q_m$      | 7.71  | 7.71  | 0.0035| 0.0035| 0.0035| 0.0035|
| $K_L$      | 0.0035| 0.0035| 0.97  | 0.97  | 0.97  | 0.97  |
| $R^2$      | 1.50  | 1.50  | 1.50  | 1.50  | 1.50  | 1.50  |
| $\chi^2$  | 0.0035| 0.0035| 0.0035| 0.0035| 0.0035| 0.0035|
| $SSE$      | 0.97  | 0.97  | 0.0035| 0.0035| 0.0035| 0.0035|
| $K_R$      | 3.64  | 3.64  | 0.20  | 0.20  | 0.20  | 0.20  |
| $a_R$      | 17.72 | 17.72 | 0.49  | 0.49  | 0.49  | 0.49  |
| $K_R/a_R$  | 0.20  | 0.20  | 1.00  | 1.00  | 1.00  | 1.00  |
| $g$        | 0.67  | 0.67  | 3.64  | 3.64  | 3.64  | 3.64  |
| $R^2$      | 0.0035| 0.0035| 0.20  | 0.20  | 0.20  | 0.20  |
| $\chi^2$  | 0.0035| 0.0035| 0.0035| 0.0035| 0.0035| 0.0035|
| $SSE$      | 0.97  | 0.97  | 0.0035| 0.0035| 0.0035| 0.0035|

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| Adsorbent         | Initial F conc. (mg/L) | Adsorption capacity (mg/g) | References |
|-------------------|------------------------|-----------------------------|------------|
| Quintinite        | 10–1000                | 7.71                        | This study |
| Mg/Al MMO         | 5–50                   | 36.86                       | [7]        |
| Li/Al MMO         | 50–500                 | 128.2–158.7                 | [21]       |
| Mg/Al HTL         | 10–1000                | 416.67                      | [13]       |
| Mg/Al/Fe MMO      | 3–60                   | 14.92                       | [11]       |
| Zn/Al HTL         | 5.6–51.4               | 4.14                        | [14]       |
| Mg/Al MMO         | 3.5–500                | 213.2                       | [16]       |
| Mg/Al HTL         | 5–2500                 | 319.8*                      | [12]       |
| Zn/Al MMO         | 2–60                   | 13.4                        | [19]       |

*Maximum adsorption capacity obtained from the Langmuir-Freundlich isotherm
Figure Captions

Fig. 1. Characteristics of quintinite particles: (a) transmission electron microscopy (TEM) image (bar = 100 nm); (b) particle size analysis based on the TEM image (number of particle = 71).

Fig. 2. Characteristics of quintinite particles: (a) X-ray diffraction (XRD) pattern of quintinite particles (inset = Debye-Scherrer analysis); (b) N$_2$ adsorption-desorption isotherms (inset = BET analysis).

Fig. 3. Fluoride removal by quintinite particles: (a) effect of adsorbent dose; (b) effect of reaction time; (c) effect of initial fluoride concentration; (d) effect of initial solution pH (the numbers in the parenthesis are final (equilibrium) pHs).

Fig. 4. X-ray photoelectron spectroscopy (XPS) spectra: (a) wide scan before and after fluoride sorption experiments; (b) high-resolution scan of the F 1s region after fluoride sorption experiment.

Fig. 5. Kinetic sorption model analysis. Model parameters are provided in Table 1.

Fig. 6. Equilibrium isotherm model analysis. Model parameters are provided in Table 2.
Fig. 1
Fig. 3
Fig. 4

(a) Relative intensity (a.u.)

Binding energy (eV)

(b) Relative intensity (a.u.)

Binding energy (eV)
Fig. 6