

Adsorption properties of Friedel's salt for the nitrate in the landfill

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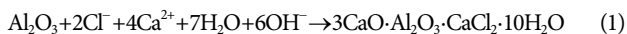
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Abstract—Adsorption characteristics of nitrate on Friedel's salt under the landfill circumstance were investigated to explore the effect of Friedel's salt on the migration of nitrate in the landfill. Friedel's salt was synthesized by a coprecipitation method and characterized by XRD and FTIR spectroscopy. The kinetics and isotherm of the adsorption were studied. The effect of the variation of landfill circumstance on the adsorption was also discussed. The result showed that the adsorption capacity of Friedel's salt for nitrate was 2.494 mg g⁻¹. The adsorption process was exothermic and could be well described by pseudo-second-order kinetics and Langmuir-Freundlich equation. Cl⁻ could enhance the adsorption, while SO₄²⁻, PO₄³⁻ and organic matter could restrict the adsorption. The results suggested that the migration of nitrate in the landfill could be altered by Friedel's salt, which was related to the variation of the landfill circumstance.

Keywords: Adsorption, Friedel's Salt, Landfill, Migration, Nitrate

INTRODUCTION

Landfills continue to be the mainstays of waste management in numerous countries. For instance, in China, more than 70% of municipal solid waste (MSW) is disposed by landfill [1]. Among the solid waste received in the landfill, the construction and demolition (C&D) waste and municipal solid waste incinerator (MSWI) bottom ash frequently accounts for 10%-30% [2-7]. Friedel's salt is identified as one of the most abundant compounds in the C&D waste and MSWI bottom ash [8-10]. Furthermore, the neoformation of Friedel's salt is expected in the landfill, due to the prevalence of reactive alumina, calcium ion and chloride ion (Eq. (1)) [9,11].



Friedel's salt (3CaO·Al₂O₃·CaCl₂·10H₂O) belongs to the family of layered double hydroxides (LDHs), which consist of cationic brucite layers and exchangeable interlayer anions. The Cl⁻ occupied in the interlayer can be replaced by other anions. Due to the high anion exchange capacity, Friedel's salt has been explored as adsorbent to remove anion contaminants in recent years [12,13]. Several reports have showed that it could remove CrO₄²⁻, AsO₃⁻ and silicates from the waste water [14-16]. The Friedel's salt in the landfill may adsorb NO₃⁻ from the leachate. Thus, the migration of NO₃⁻ will be affected. In the landfill, the nitrogen removal mainly depends on the denitrification of NO₂⁻ and NO₃⁻ [17-21]. Our previous study demonstrated that Friedel's salt possessed a high affinity toward NO₂⁻ [22]. However, the effect of the Friedel's salt on the

migration of nitrate in the landfill was still unclear. Therefore, it is necessary to study the effect of Friedel's salt on the migration of nitrate in the landfill, to reveal its effect on the nitrate release and nitrogen degradation.

In this study, the adsorption characteristics of nitrate on Friedel's salt under the landfill circumstance were investigated. Kinetics and isotherms of the adsorption were studied. The effects of the variation of the pH, temperature and anions competition on the adsorption were also examined. We aim to reveal the effect of Friedel's salt on the migration of nitrate in the landfill.

MATERIALS AND METHODS

1. Preparation and Characterization of Friedel's Salt

Friedel's salt was prepared by a coprecipitation method [22]. The synthesized Friedel's salt sample was characterized by XRD and FTIR spectroscopy, as described in our previous study [22].

2. Batch Adsorption Studies

Batch adsorption experiments were conducted and equilibrated using a model KYC-1102 air-temperature-controlled shaker at 100 rpm. The solution was continually flushed with N₂ to avoid contact with the atmosphere. Batch experiments were conducted in triplicate to ensure the accuracy of the obtained data.

According to our previous research, the level of NO₃⁻ in landfill leachate ranged from 87.0 to 238.0 mg L⁻¹ (see Fig. S1). Thus, the initial nitrate concentration used in this study was 200.0 mg L⁻¹. Besides, the dosage study showed that the removal efficiency of NO₃⁻ reached the platform when the dosage of Friedel's salt increased to 2.0 g (see Fig. S2). Therefore, 2.0 g of Friedel's salt was added during the adsorption experiments.

The kinetics of the adsorption was studied by adding 50 mL nitrate

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solution and 2.0 g Friedel's salt to 100 mL beaker for the contact time ranging from 5 to 150 min at 298 K.

Isotherm studies were conducted with a constant Friedel's salt dosage (2.0 g) and 50 mL nitrate solution with the initial concentrations varying from 3.0 to 1,000.0 mg L⁻¹. The mixture was equilibrated at 298 K for 120 min.

The effect of pH on the adsorption was conducted at the range from 5.0 to 10.0, which was corresponding to the variation of leachate pH [23]. 50 mL nitrate solution (200.0 mg L⁻¹) and 2.0 g Friedel's salt were added and equilibrated at 298 K for 120 min.

The effect of the temperature on the adsorption was studied at 293 to 318 K according to the previous study [17]. 50 mL nitrate solution and 2.0 g Friedel's salt were added and equilibrated at the desired temperature for 120 min.

Coexisting ions such as Cl⁻, SO₄²⁻ and PO₄³⁻ were imposed to explore the impact of anion competition on the adsorption. The concentration of Cl⁻, SO₄²⁻ and PO₄³⁻ ranged from 0 to 5,000 mg L⁻¹, 0 to 2,000 mg L⁻¹ and 0 to 8 mg L⁻¹, respectively, which was in accordance with our previous research (see Fig. S3-S4) and the literature report [24]. The mixture was equilibrated at 298 K for 120 min.

Landfill leachate contains high level of organic matter. The highest COD concentration of the landfill leachate could be up to 40,000 mg L⁻¹, which is usually observed at the acidogenic stage of the landfill. In this study, the acetic acid with the concentration varying from 0 to 40,000 mg L⁻¹ was imposed to investigate the effect of organic acid on the adsorption. The concentration of the acetic acid was generally in agreement with the variation of COD in the leachate (see Fig. S5, 1.0 mg L⁻¹ acetic acid equal to 1.06 mg L⁻¹ COD). The mixture was equilibrated at 298 K for 120 min.

After the adsorption, the samples were centrifuged and NO₃⁻ concentration in supernatant was determined immediately by ion chromatograph (Dionex ICS-2000, USA). The setup of the experiment can be seen in Fig. 1.

3. Calculation and Statistical Analysis

The amount of nitrate adsorbed on the Friedel's salt (q_t) and the removal percentage of nitrate ($r\%$) were calculated according to Eqs. (2) and (3), respectively.

$$q_t = (C_0 - C_t) \times V / m \quad (2)$$

$$r\% = (C_0 - C_t) \times 100 / C_0 \quad (3)$$

where q_t is adsorption capacity (mg g⁻¹); C_0 and C_t are initial and instantaneous concentrations of nitrate (mg L⁻¹), respectively; V is the volume of the solution (L) and m is the mass of Friedel's salt (g).

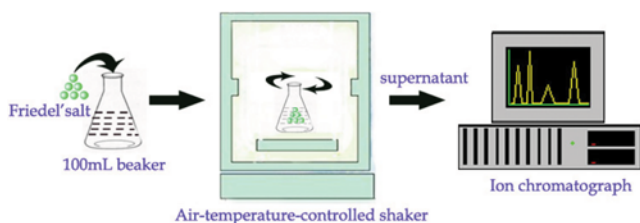


Fig. 1. Setup of the experiment.

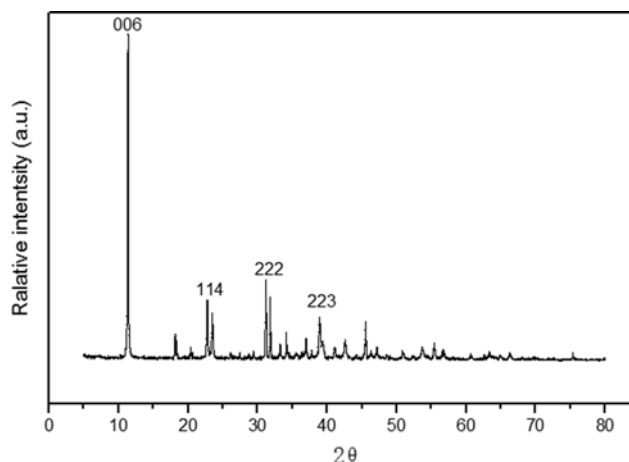


Fig. 2. XRD pattern of Friedel's salt.

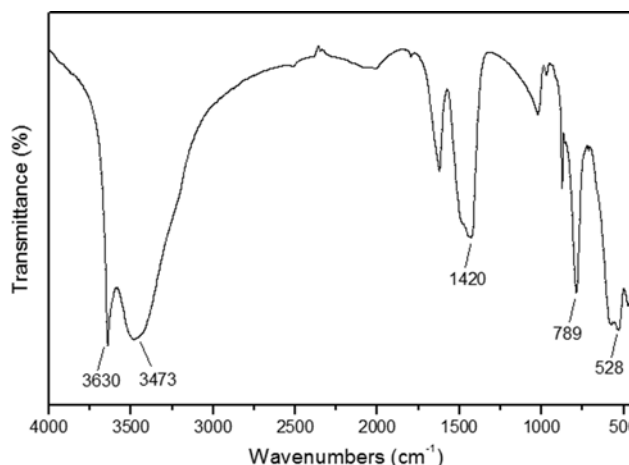


Fig. 3. FTIR spectrum of Friedel's salt.

Statistical analysis was conducted by SPSS software (version 18.0) to understand the statistical difference between the results.

RESULTS AND DISCUSSION

1. Characterization of Friedel's Salt

The XRD pattern of the synthesized Friedel's salt is shown in Fig. 2. All the peaks in the XRD pattern are in good agreement with the literature value of the pure Friedel's salt (Joint Committee on Powder Diffraction Standards File Card No. 78-1219). Such a mineral phase was corresponding to the FTIR spectrum (Fig. 3). The features at 528 and 789, 3,473 and 3,630 cm⁻¹ were due to the stretching vibration of Al-OH, lattice water and structural OH groups, respectively [25]. The band at 1,420 cm⁻¹ was the stretching vibration of CO₃²⁻, indicating the incorporation of CO₂ during the synthesis.

2. Adsorption of Nitrate on Friedel's Salt

2-1. Adsorption Kinetics

The nitrate adsorption on Friedel's salt was rapid during the first 30 min (Fig. 4), when about 30% of the adsorption occurred. Then, the adsorption showed a gradual increase. The equilibrium was

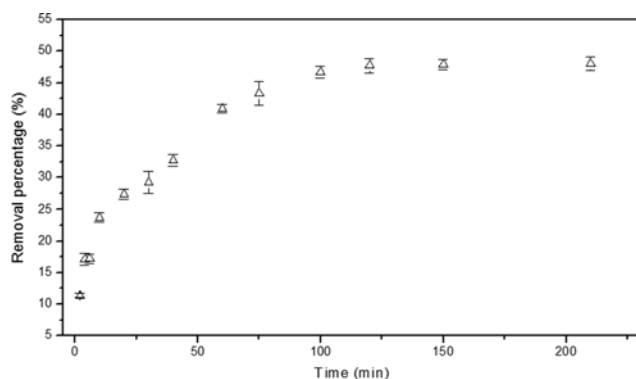


Fig. 4. Nitrate removal percentage as a function of shaking time (conditions: $V=50$ mL; nitrate concentration= 200 mg L^{-1} ; Friedel's salt dosage= 2.0 g; $T=298$ K).

established since 120 min, when 48.0% of removal percentage was observed.

To analyze the adsorption rate of nitrate on Friedel's salt, three widely used kinetic models including the Lagergren-first-order model (Eq. (4)), pseudo-second-order kinetic model (Eq. (5)) and intra-particle mass transfer diffusion model (Eq. (6)) were utilized to understand the dynamics of the adsorption process.

The Lagergren-first-order model is based on the assumption of proportionality between the adsorption rate and the number of free adsorption sites [26,27]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

where q_e and q_t are the amount of nitrate adsorbed (mg g^{-1}) on the adsorbents at the equilibrium and at time t , respectively; k_1 is the rate constant of adsorption ($L \text{ min}^{-1}$). Values of k_1 are calculated from the plots of $\log(q_e - q_t)$ versus t .

The pseudo-second-order kinetic model assumes that the chemical sorption is the rate-limiting step [28,29]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k_2 is the rate constant of the pseudo-second-order adsorption ($g \text{ mg}^{-1} \text{ min}^{-1}$). Values of k_2 are obtained from plotting (t/q_t) versus t .

The intra-particle mass transfer diffusion model stipulates that the adsorption process is influenced by several steps such as film or external diffusion, pore diffusion and adsorption on the pore surface [30]:

$$q_t = k_{id} t^{1/2} + c \quad (6)$$

where c is the intercept (mg g^{-1}) and k_{id} is the intra-particle diffu-

sion rate constant ($mg \text{ g}^{-1} \text{ min}^{-1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$.

The kinetic parameters (k_1 , k_2 , k_{id} , q_e , c) and correlation coefficients (R^2) are summarized in Table 1. Compared with the Lagergren-first-order model and intra-particle mass transfer diffusion model, the value of the correlation coefficient (R^2) of the pseudo-second-order kinetic model was closer to 1.0 and the adsorption capacities calculated by the model ($q_{e,cal}$) were also closer to those determined by experiments ($q_{e,exp}$). It showed that the pseudo-second-order kinetic model was more suitable to describe the adsorption process. The pseudo-second-order model is based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and sorbate [31]. As a matter of fact, Cl^- occupied in the interlayer of Friedel's salt was able to exchange with other anions. The nitrate adsorption on Friedel's salt was probably through the exchange of Cl^- with NO_3^- . This result was consistent with several researches regarding the adsorption characteristics of anions on Friedel's salt [12,14].

2-2. Adsorption Isotherms

The adsorption data of this study were fitted by three adsorption models: Langmuir, Freundlich and Langmuir-Freundlich model [32]. The Langmuir model is based on the assumption that the adsorbed layer is one molecule in thickness and all sites are equal. It is often used for modeling the adsorption occurring on homogeneous surface sites. The Freundlich model assumes an exponential decay energy distribution function inserted in the Langmuir equation. The amount adsorbed is the summation of adsorption on all sites with different bond energies. It is often used for modeling the adsorption occurring on heterogeneous surface sites. The Langmuir-Freundlich model is established by the introduction of a power law expression of Freundlich form [33]. The Langmuir (Eq. (7)), Freundlich (Eq. (8)) and Langmuir-Freundlich (Eq. (9)) model are represented by the following equations:

$$q_e = \frac{b q^0 C_e}{1 + b C_e} \quad (7)$$

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

$$q_e = \frac{q^0 (K_{LF} C_e)^v}{1 + (K_{LF} C_e)^v} \quad (9)$$

where C_e is the equilibrium concentration ($mg \text{ L}^{-1}$); q^0 is the maximum amount of the nitrate ion per unit weight of Friedel's salt ($mg \text{ g}^{-1}$); q_e is the amount adsorbed per unit mass of adsorbent, and b is the binding energy constant ($L \text{ mg}^{-1}$). For Freundlich model, n is the heterogeneity factor and K_F is the Freundlich constant ($L \text{ mg}^{-1}$). For Langmuir-Freundlich model, K_{LF} is the Langmuir-Freundlich constant ($L \text{ mg}^{-1}$) $^{1/v}$, and v is the Langmuir-Freundlich heterogeneity constant.

Table 1. Kinetic parameters of nitrate adsorption on Friedel's salt

Lagergren-first-order			Pseudo-second-order			Intra particle diffusion		
q_e (mg g^{-1})	k_1	R^2	q_e (mg g^{-1})	k_2	R^2	k_{id}	c	R^2
2.749	0.0048	0.988	2.286	0.7362	0.996	5.006	3.357	0.914

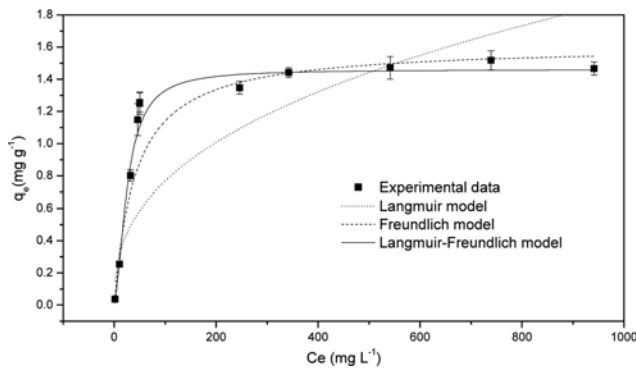


Fig. 5. Isotherm for adsorption of nitrate on Friedel's salt (conditions: $V=50$ mL; Friedel's salt dosage=2.0 g; $T=298$ K).

The results of the experimental data were fitted to the three equations and the parameters shown in Fig. 5 and Table 2. The correlation coefficients (R^2) of Freundlich, Langmuir and Langmuir-Freundlich models were 0.776, 0.937 and 0.985 respectively. In addition, the q^0 value of Langmuir-Freundlich model was 2.494 mg g^{-1} , which agreed well with the experimental value. Therefore, the Langmuir-Freundlich model was more suitable to describe the adsorption compared with the Langmuir and Freundlich model. This result was consistent with our previous research concerning the adsorption of nitrite on Friedel's salt [22]. Although the adsorption capacity of Friedel's salt for nitrate is not at a high level compared with other adsorbents [34,35], it could still be deduced that the migration of nitrate in the landfill could be affected by Friedel's salt.

2-3. Effect of pH on the Adsorption

As shown in Fig. 6(a), the adsorption of nitrate on Friedel's salt was greatly affected by pH. The removal percentage increased significantly from 6.1% to 36.7% when the pH increased from 5.0 to 9.0. As Friedel's salt was alkaline, the low pH could affect the stability of the structure of Friedel's salt. This assumption was confirmed by the test of Cl^- leaching from Friedel's salt, which showed the leaching of Cl^- was much higher in the acidic condition than in the neutral or alkaline condition (Fig. S6). Therefore, the adsorption was restricted in the acidic condition. The removal percentage showed a decrease when the pH further increased from 9.0 to 10.0. This might be due to the fact that the high level of OH^- could compete for active adsorption sites with NO_3^- [36,37].

2-4. Effect of Temperature on the Adsorption

As shown in Fig. 6(b), the removal efficiency decreased significantly from 35.4% to 27.8% when the temperature increased from 293 to 318 K, indicating the exothermic nature of the adsorption process. This result was consistent with the result concerning the adsorption of nitrite on Friedel's salt [22]. The Gibbs free energy

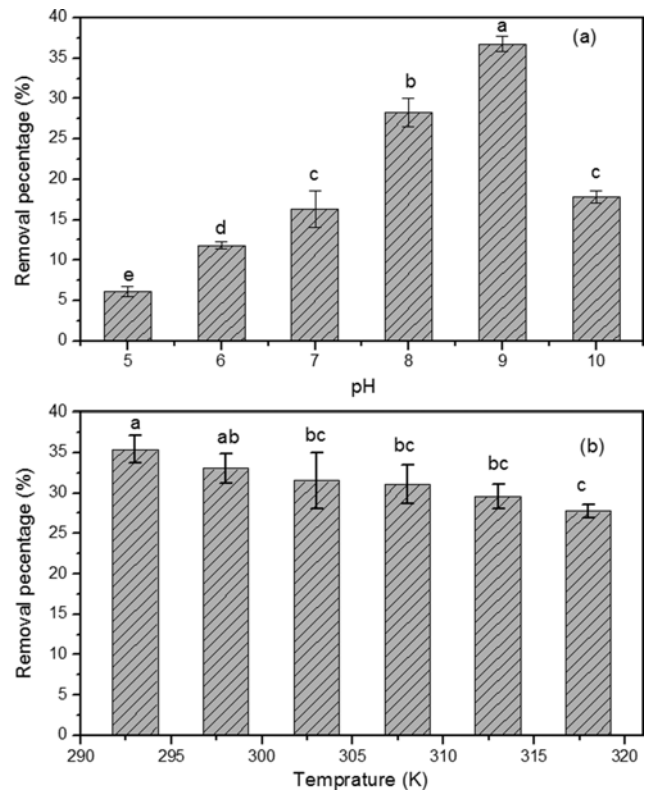


Fig. 6. Effect of pH (a) and temperature (b) on the adsorption of nitrate on Friedel's salt.

change (ΔG^0) was studied for a better understanding of the effect of temperature on the adsorption. The results showed ΔG^0 increased with the increase of temperature, indicating that the adsorption was more spontaneous at the low temperature (Table S1). Therefore, the low temperature was beneficial to the adsorption process.

2-5. Effect of Coexisting Anions

Landfill leachate contains abundant anions. In this study, Cl^- , SO_4^{2-} and PO_4^{3-} were chosen to represent the single valence anion, dianion and trivalent anion, respectively. The effect of Cl^- on the adsorption was shown in Fig. 7(a). The removal percentage of nitrate increased significantly from 36.5% to 58.8% when the concentration of Cl^- increased from 0 to $5,000 \text{ mg L}^{-1}$. This result suggested that the presence of Cl^- could enhance the adsorption of nitrate on Friedel's salt. Cl^- is an ingredient of Friedel's salt. It can be incorporated in the interlayer of Friedel's salt and exchange with other anions. The increase of Cl^- could promote the ion exchange capacity of Friedel's salt.

Different from Cl^- , the presence of SO_4^{2-} and PO_4^{3-} could restrict the adsorption. The presence of $2,000 \text{ mg L}^{-1}$ of SO_4^{2-} and 8 mg L^{-1}

Table 2. Langmuir, Freundlich and Langmuir-Freundlich isotherm parameters and correlation coefficients for the adsorption of nitrate on Friedel's salt at 298 K

Freundlich model constants			Langmuir model constants			Langmuir-Freundlich model constants			
$K_F (\text{L mg}^{-1})$	n	R^2	$q^0 (\text{mg g}^{-1})$	$b (\text{L mg}^{-1})$	R^2	$q^0 (\text{mg g}^{-1})$	$K_{LF} (\text{L mg}^{-1})^{1/\nu}$	ν	R^2
0.417	3.512	0.776	2.811	0.0185	0.937	2.494	0.0214	2.450	0.985

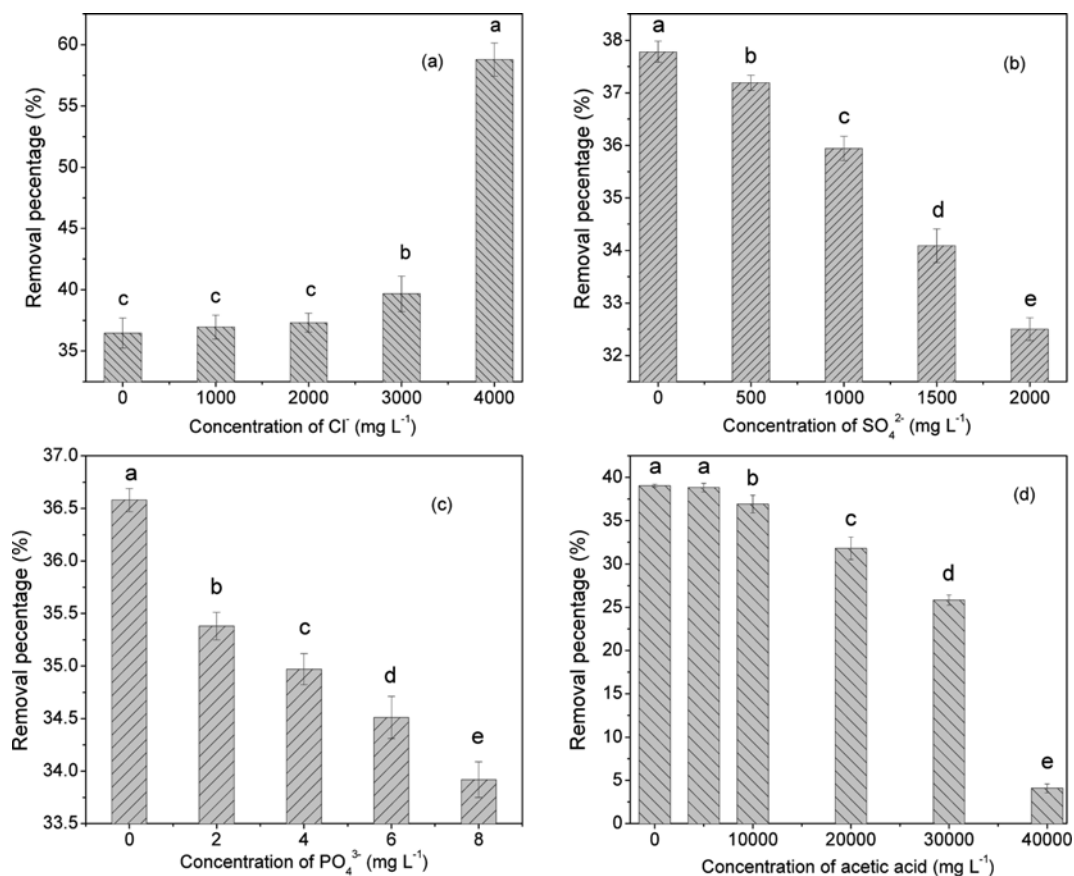


Fig. 7. Effect of Cl⁻ (a), SO₄²⁻ (b), PO₄³⁻ (c) and organic acid (d) on the adsorption of nitrate on Friedel's salt.

of PO₄³⁻ decreased the nitrate removal percentage from 36.5% to 32.5% and 32.9%, respectively (Fig. 7(b), (c)). This might have resulted from the occupation of the active adsorption sites by SO₄²⁻ and PO₄³⁻. The effect of PO₄³⁻ was greater than that of SO₄²⁻. Generally, the affinity of the anions with the LDHs is related to the ionic radius and the anion charge. Several researches have pointed out that the affinity of PO₄³⁻ to LDHs is higher than that of SO₄²⁻ [38,39]. The high affinity of PO₄³⁻ to LDHs resulted in its relatively greater effect on the adsorption.

2-6. Effect of the Organic Matter

In this study, the acetic acid, an important attribution to the COD of landfill leachate, was used to investigate the effect of the organic matter on the adsorption. The result showed the organic matter in the leachate could greatly restrict the adsorption process (Fig. 7(d)). The removal percentage of nitrate decreased significantly from 39.0% to 4.1% when the concentration of the acetic acid increased to 40,000 mg L⁻¹. On one hand, the increase of the acetic acid could reduce the solution pH, which might affect the stability of the structure of Friedel's salt. On the other hand, the acetate could compete for the active adsorption sites with NO₃⁻. As a result, the adsorption of the nitrate on Friedel's salt was restricted.

3. Effect of Friedel's Salt on the Migration of Nitrate

Due to the considerable adsorption capacity of nitrate on Friedel's salt (2.494 mg g⁻¹), the migration of the nitrate could be altered by Friedel's salt in the landfill. The optimum pH for the adsorp-

tion was 9.0. Low temperature was beneficial to the adsorption. The presence of SO₄²⁻, PO₄³⁻ and organic matter could restrict the adsorption, while the presence of Cl⁻ could enhance the adsorption. According to the profile of the variation of leachate characteristics, the low pH was commonly observed at the acidogenic stage, while the pH 9.0 was usually observed at the mature stage. The temperature of the landfill started to rise at the acidogenic stage due to the fermentation of the refuse and showed a decrease at the mature stage. Besides, the level of SO₄²⁻, PO₄³⁻ and organic matter at the mature stage was lower than the acidogenic stage. The concentration of Cl⁻ was slightly higher at the acidogenic stage. At the mature stage of the landfill, the low pH, temperature, concentration of SO₄²⁻, PO₄³⁻ and organic matter are favorable to the adsorption of the nitrate on Friedel's salt. However, the low concentration of Cl⁻ is disadvantageous for the adsorption. Similar situation was also found at the initial, acidogenic and methane production stages of the landfill. Therefore, it is still difficult to determine the effect of alternation of the landfill stage on the adsorption. Further research, such as column study or pilot study, is needed to figure out the comprehensive effect of the variation of landfill circumstance on the adsorption. Combining the results of the present and our previous study [22], it seems that Friedel's salt could affect the migration of NO₂⁻ and NO₃⁻ in the landfill. As the nitrogen removal mainly depends on the denitrification of NO₂⁻ and NO₃⁻, Friedel's salt may play an important role in the nitrogen pollution control in the landfill.

CONCLUSIONS

The adsorption capacity of nitrate on Friedel's salt was 2.494 mg g⁻¹. The adsorption was exothermic and could be well described by the pseudo-second-order kinetics and Langmuir-Freundlich model. The adsorption was affected by the variation of the landfill circumstance. The optimum pH for the adsorption was 9.0. Cl⁻ could enhance the adsorption by increasing the anion exchange capacity of Friedel's salt. However, SO₄²⁻, PO₄³⁻ and organic matter could restrict the adsorption process. These results suggest that Friedel's salt could affect the nitrate migration in the landfill, which was related to the landfill circumstance. According to the variation of landfill characteristics, it is still difficult to determine the comprehensive effect of alternation of the landfill stage on the adsorption. Future research, such as column study or pilot study, is required to explore this comprehensive effect.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

Adsorption properties of Friedel's salt for the nitrate in the landfill

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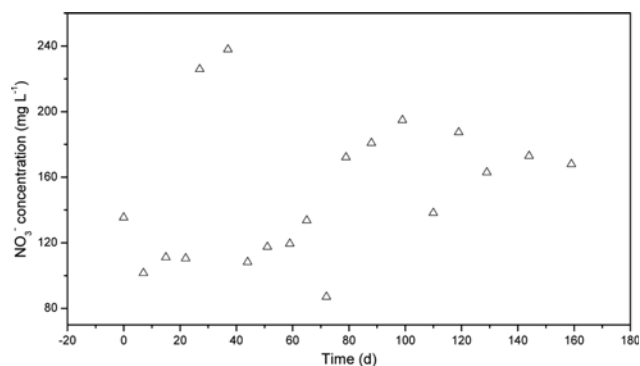


Fig. S1. Variation of NO₃⁻ in landfill leachate.

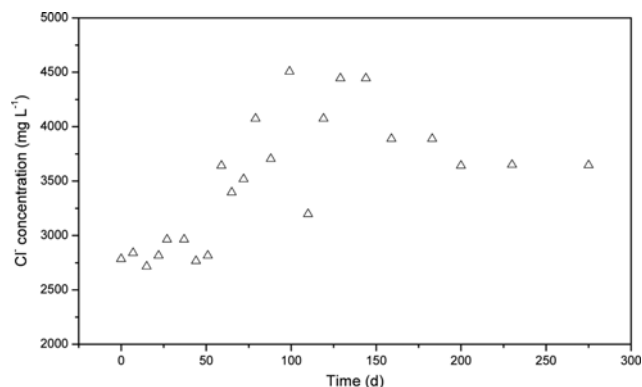


Fig. S3. Variation of Cl⁻ in landfill leachate.

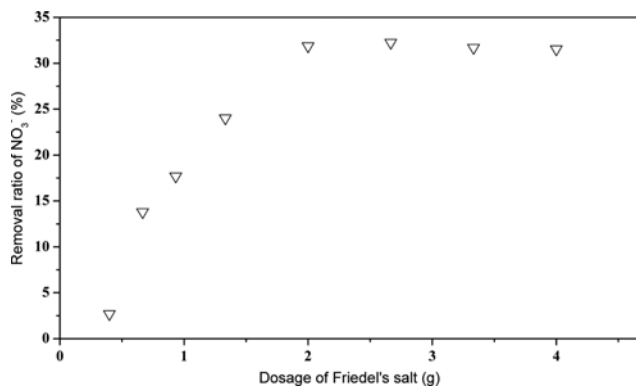


Fig. S2. Effect of Friedel's salt dosage on the removal percentage of nitrate (conditions: V=50 mL; nitrite concentration=200 mg L⁻¹; T=298 K).

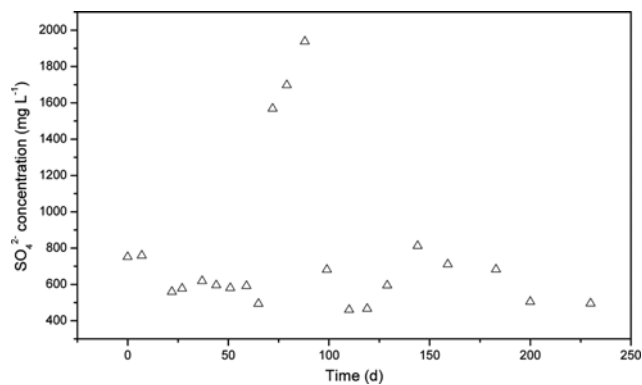


Fig. S4. Variation of SO₄²⁻ in landfill leachate.

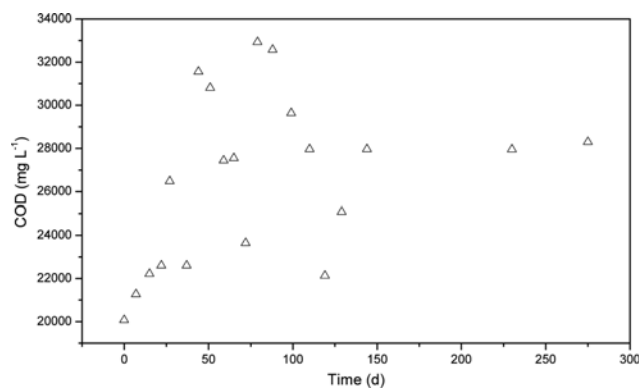


Fig. S5. Variation of COD in landfill leachate.

Table S1. Gibbs free energy for the adsorption of nitrate on Friedel's salt

Temperature (K)	Gibbs free energy (kJ mol ⁻¹)
293	10.45
298	10.89
303	11.25
308	11.49
313	11.86
318	12.28

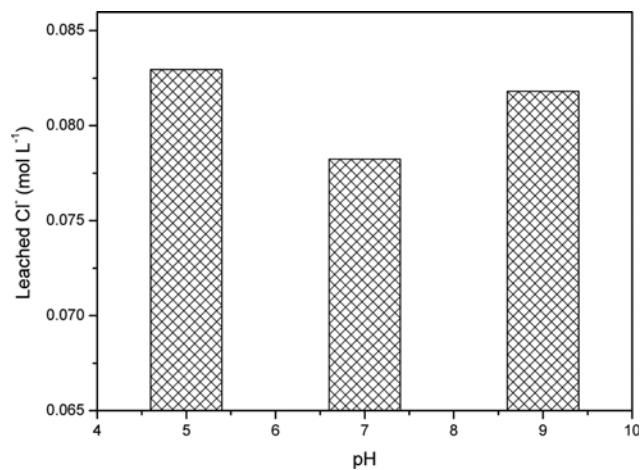


Fig. S6. Effect of pH on the Cl⁻ release from Friedel's salt.