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

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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 SO_4^{2-}, PO_4^{3-} 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].

$$Al_2O_3+2Cl^-+4Ca^{2+}+7H_2O+6OH^- \rightarrow 3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O \qquad (1)$$

Friedel's salt ($3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$) 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 CrO_4^{2-}, AsO_3^- and silicates from the waste water [14-16]. The Friedel's salt in the landfill may adsorb NO_3^- from the leachate. Thus, the migration of NO_3^- will be affected. In the landfill, the nitrogen removal mainly depends on the denitrification of NO_2^- and NO_3^- [17-21]. Our previous study demonstrated that Friedel's salt possessed a high affinity toward NO_2^- [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

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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^-, SO_4^{2-} and PO_4^{3-} were imposed to explore the impact of anion competition on the adsorption. The concentration of Cl^-, SO_4^{2-} and PO_4^{3-} 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 NO_3^- 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 (η%) were calculated according to Eqs. (2) and (3), respectively.

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

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

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).

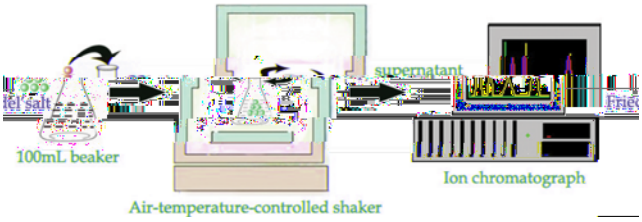
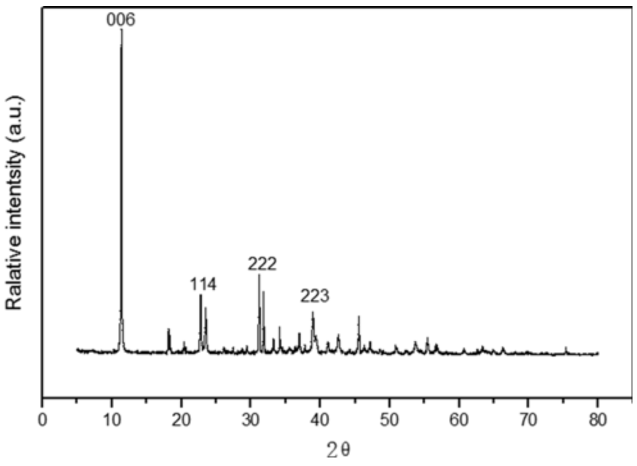


Fig. 1. Setup of the experiment.



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 CO_3^{2-}, indicating the incorporation of CO_2 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

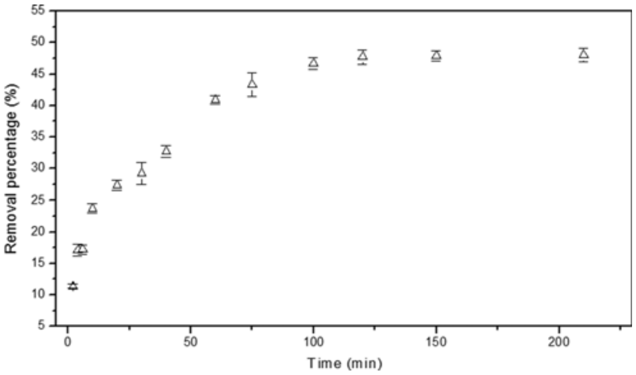


Fig. 4. Nitrate removal percentage as a function of shaking time (conditions: V=50 mL; nitrate concentration=200 mg L^{-1}; Friedel's salt dosage=2.0 g; T=298 K).

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]:

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

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 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]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where k_2 is the rate constant of the pseudo-second-order adsorption (g mg^{-1} 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]:

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

where c is the intercept (mg g^{-1}) and k_{id} is the intra-particle diffusion rate constant (mg g^{-1} 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:

$$q_e = \frac{b q^0 C_e}{1 + b C_e} \tag{7}$$

$$q_e = K_F C_e^{1/n} \tag{8}$$

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

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

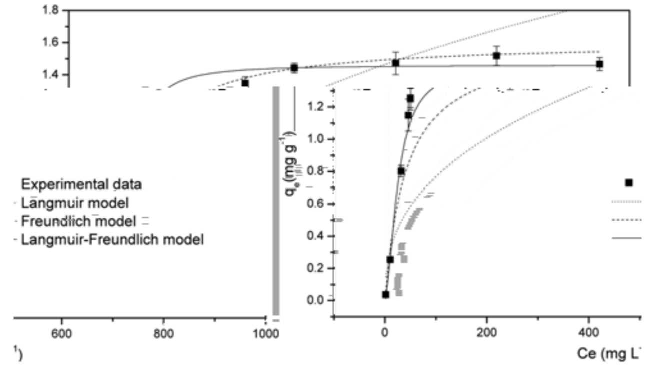


Fig. 5. Isotherm for adsorption of nitrate on Friedel's salt (conditions: V=50 mL; Friedel's salt dosage=2.0 g; T=298 K).

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 change (ΔG^o) was studied for a better understanding of the effect of temperature on the adsorption. The results showed ΔG^o 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.

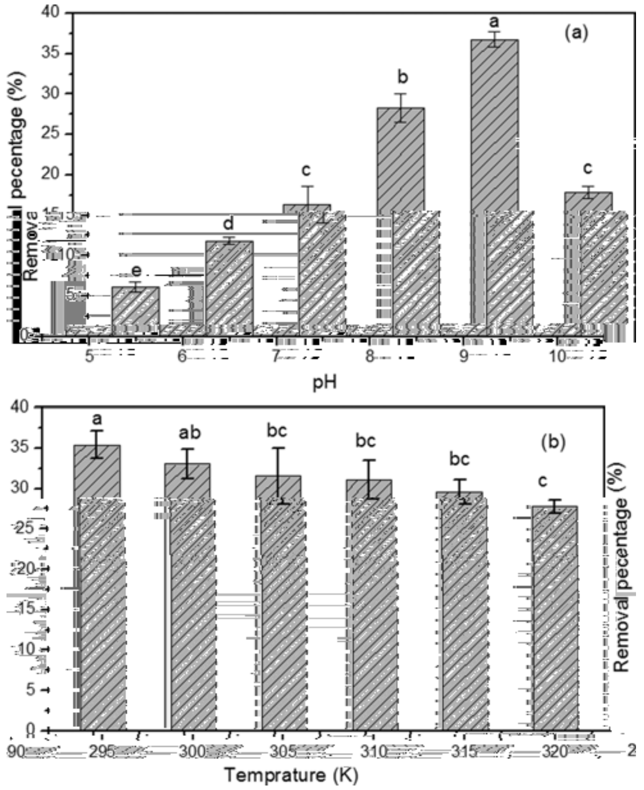


Fig. 6. Effect of pH (a) and temperature (b) on the adsorption of nitrate on Friedel's salt.

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 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 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 (L mg^{-1})	n	R^2	q^o (mg g^{-1})	b (L mg^{-1})	R^2	q^o (mg g^{-1})	K_{lf} (L mg^{-1})$^{1/\nu}$	v	R^2
0.417	3.512	0.776	2.811	0.0185	0.937	2.494	0.0214	2.450	0.985

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, SO_4^{2-}, PO_4^{3-} 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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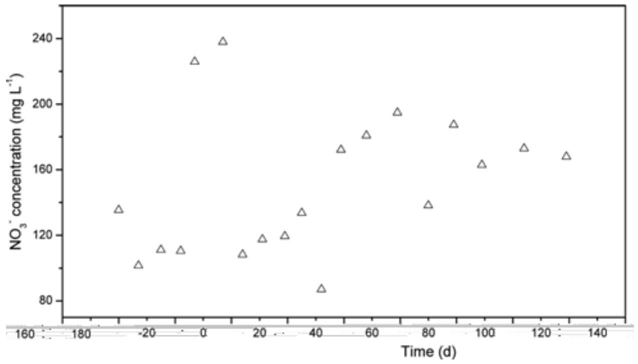

Fig. S1. Variation of NO_3^- in landfill leachate.

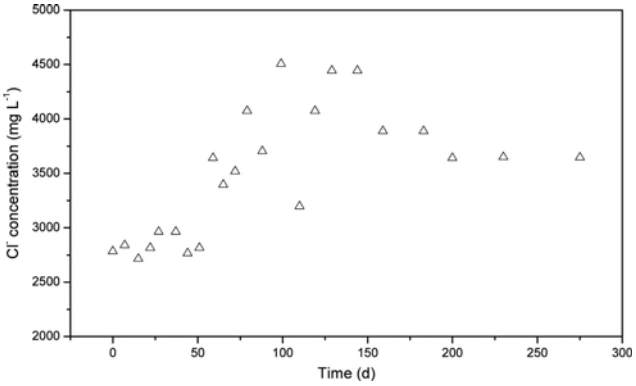

Fig. S3. Variation of Cl^- in landfill leachate.

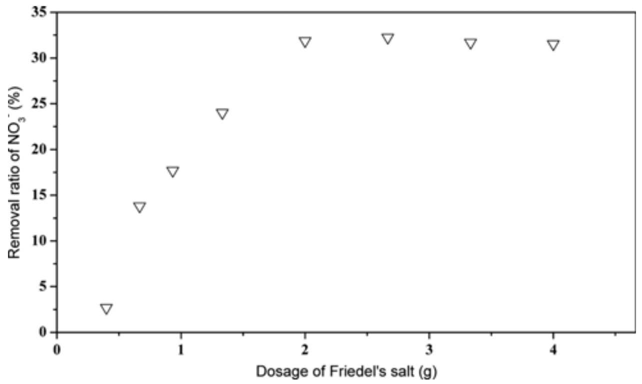

Fig. S2. Effect of Friedel's salt dosage on the removal percentage of nitrate (conditions: V=50 mL; nitrite concentration=200 mg L^{-1}; T=298 K).

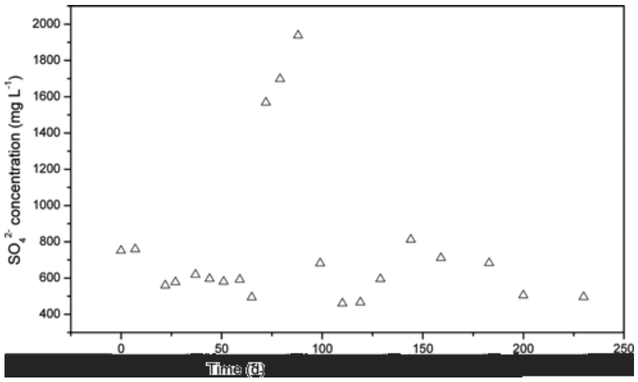

Fig. S4. Variation of SO_4^{2-} in landfill leachate.

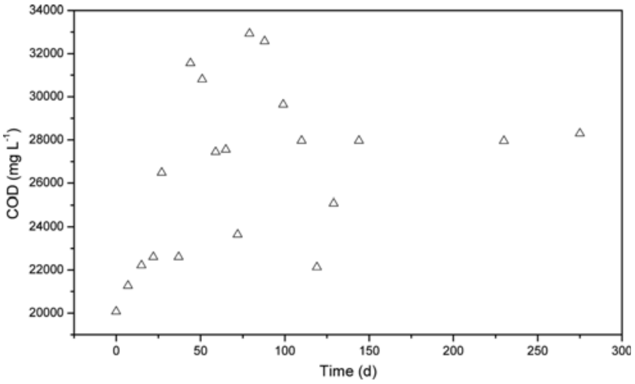

Fig. S5. Variation of COD in landfill leachate.

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

Temprature (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

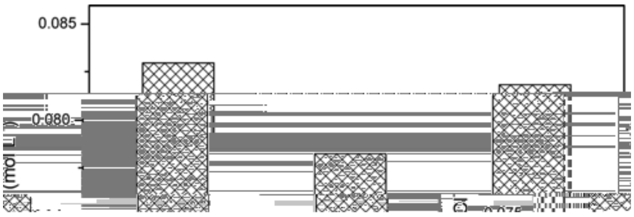

Fig. S6. Effect of pH on the Cl$^-$ release from Friedel's salt.