Nitrate adsorption from aqueous solutions by calcined ternary Mg-Al-Fe hydrotalcite
Xiaowen Tong, Zhiquan Yang, Pan Xu, Ying Li and Xiaojun Niu

ABSTRACT

Calcined ternary hydrotalcite-like compounds had been synthesized by co-precipitation and calcined at 450°C for 6 h. It had been applied into the nitrate removal from aqueous solutions. Various factors during adsorption process, such as chemical composition of adsorbents, adsorbent dosage, initial concentration of nitrate, initial pH and co-existing anions on nitrate adsorption had been investigated. It was found that 1.5 g/L CHTlcs (Mg/Al/Fe molar ratio = 3:0.1:0.9) could achieve ideal adsorption efficiency at an initial nitrate concentration of 100 mg/L. The value of pH had little effect on nitrate adsorption. The co-existing anions had the inhibitory effect on nitrate adsorption, which was in the order of PO₄³⁻ > SO₄²⁻ > Cl⁻ > ClO₄⁻. The batch adsorption studies showed that experimental data were well described by the pseudo-second-order kinetic model and Langmuir isotherm model, and the maximum isotherm adsorption capacity was 123.305 mg/g. The adsorption of nitrate was a spontaneous exothermic process with the reduction of entropy. The proposed adsorption mechanism obtained from characterization was that CHTlcs uptake nitrate through reconstruction effect and adsorption on external surface.

Key words | adsorption, isotherm, kinetic, mechanism, Mg-Al-Fe hydrotalcite, nitrate

INTRODUCTION

Nitrate pollution has been a global water pollution problem for many years. There is increasing nitrate pollution in surface and ground waters due to overuse of fertilizer in agriculture, disposal of massive livestock excrement and release of poorly treated municipal and industrial wastewater (Hamid et al. 2016). High concentration of NO₃⁻ in water can lead to eutrophication, deleterious effect on agricultural crops and serious threat to human health (Khattee et al. 2016). Because of the high stability and solubility of nitrate, nitrate removal from water has been a challenge. Several biological and physicochemical methods such as reverse osmosis, electrodialysis and biological processes are relatively costly (Wan et al. 2012). Adsorption is regarded as an appropriate technology of nitrate removal which is less expensive and more flexible. Selection of a suitable adsorbent is the key to nitrate adsorption.

As desirable adsorbents for ionic pollutants, layered double hydroxides (LDHs), including hydrotalcite and hydrotalcite-like compounds (HTLcs) have received much attention in recent years. Hydrotalcite is one of anionic clay minerals with the structure formula of [M²⁺ₓ₋ₓM³⁺ₓ(ΟΗ)₂]ₓ₋ₓ₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋ₐ₋₋}_n·mH₂O, where M²⁺ and M³⁺ are divalent and trivalent cations, An⁻ represents interlayer charge-compensating anion (Halajnia et al. 2012). Due to its special structure, the hydrotalcite has large specific surface area and pore volume, which helps to adsorb exotic objects easily. In addition, calcined hydrotalcite-like compounds (CHTlcs) have larger surface areas and alkaline centers. They also can reconstruct the layered structure by incorporating with available ions in the solution (Chebli et al. 2016). This unique feature of memory effect of structure makes them excellent candidates for anions sorption from wastewater. Many researchers had applied them into nitrate removal and obtained satisfactory results. Xue et al. (2016) found that Mg-Al LDH (4:1) has much higher nitrate adsorption capacity (118.11 mg/g) than activated carbon from sugar beet bagasse (5.022 mg/g) and activated bamboo charcoal (5.54 mg/g). Wan et al. (2012) synthesized the calcined Mg-Al-HTlcs, which has larger nitrate adsorption capacity than chitosan hydrogel beads, modified wheat residue and acid treated C-cloth. Except for the high adsorption capacity, some hydrotalcites have high selective property.
with free secondary pollution. Ni-Fe LDH was sufficiently stable in seawater and has effective selective adsorptive properties for nitrate, which could remove NO\textsubscript{3} from sea-water effectively even though seawater consisting large amount of coexisting anions (Tezuka et al. 2004). Furthermore, hydrotalcites can be found in the natural environment and can be synthesized easily with low cost. Comparing with other conventional adsorbents, hydrotalcite is a desirable adsorbent for nitrate removal. LDHs usually contain only two kinds of metal. LDHs and their calcined compounds with different kinds of metal ions (Mg-Al, Mg-Fe, Zn-Al, Co-Fe and Ni-Fe) are widely explored to nitrate adsorption (Bhatnagar & Silanpaa 2011). With the further research, ternary or multiple LDHs with different compositions of metal, such as Ca-Al-Zn-LDH (Bakr et al. 2016), Zn-Mg-Al-LDH (Zheng et al. 2012), Zn-Mg-Ni-Al-LDH (Tiar et al. 2016), have been synthesized. They are applied to water treatment such as copper ions, phosphate, arsenate, fluoride, perchlorate, organic pollutants and so on (Halajnia et al. 2012). However, there have been limited researches on nitrate adsorption onto multiple CHTlcs. Their adsorptive properties and proposed mechanisms are not reported clearly.

In this article, ternary Mg-Al-Fe CHTlcs with well performance of nitrate removal was synthesized. A variety of impact factors (chemical composition of CHTlcs, adsorbent dosage, initial nitrate concentration, pH, co-existing anions) during the adsorption process were investigated. The adsorption kinetic, isotherm and thermodynamic were analyzed to discuss the properties of nitrate adsorption. Samples were characterized to investigate its sorption mechanism.

**EXPERIMENTAL**

**Materials**

All the reagents used in this study, including Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Cu(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, NaOH, Na\textsubscript{2}CO\textsubscript{3} and KNO\textsubscript{3} were of analytical grade and purchased from chemical agents. Deionized water was used in the experiment.

**Preparation of CHTlcs**

CHTlcs in this study were synthesized via co-precipitation method by modifying a reported method (Yang et al. 2015). Typically, the Mg/Al/Fe-HTlcs was prepared by the following procedure. An aqueous solution, containing Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O and Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, was prepared in the required amounts. Meanwhile, an alkaline solution, including NaOH and Na\textsubscript{2}CO\textsubscript{3} (n(NaOH) = 2n (M\textsuperscript{2+} + M\textsuperscript{3+})) was prepared. The two solutions were added simultaneously to a 1 L beaker containing 100 mL of deionized water under vigorous stirring at a controlled pH of 9–10. The resulting slurry was aged at 60 °C for 24 h, and then filtered, washed thoroughly with deionized water until the pH of supernatant reached 7, finally dried at 100 °C for 12 h. The synthesized HTlcs were calcined at 450 °C for 6 h in a muffle furnace to form the CHTlcs. Other CHTlcs with different metal composition and metal molar ratio were prepared through similar procedures.

**Nitrate adsorption experiments**

Nitrate adsorption on Mg-Al-Fe CHTlcs was carried out in a batch system. All of the experiments, except for special note, were investigated by adding 150 mg adsorbents to 200 mL flasks containing 100 mL of 100 mg/L nitrate solution (pH 7.0), which were shaken at 250 rpm in room temperature. After 24 h, the aqueous samples were filtered and analyzed. In addition to the test of chemical composition effect, the Mg-Al-Fe-CHTlcs with the metal molar ratio of 3:1:0.9 were used in all other experiments. The adsorbent dosage effect was evaluated by various adsorbent doses (20, 50, 70, 100, 150 and 200 mg). The effect of initial solution pH on nitrate removal was monitored at pH 3, 5, 7, 9 and 11, respectively. The effect of adsorbent dosage was conducted in the systems of NO\textsubscript{3}/Cl\textsuperscript{−}, NO\textsubscript{3}/ClO\textsubscript{−}, NO\textsubscript{3}/SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}/PO\textsubscript{4}\textsuperscript{3−} with different concentration of co-existing anions. Adsorption kinetic was investigated at different contact time. Adsorption isotherm was studied at 30 °C. Adsorption thermodynamic was studied at 20, 30, 40, 50 and 60 °C by putting the samples in constant temperature shaker. Nitrate was measured by UV-spectrophotometer (UV-2100). Other inorganic anions were analyzed by Dionex ion chromatography (ICS-1000) system. All adsorption experiments were replicated three times.

**Data analysis**

Four different kinetic models containing intraparticle diffusion kinetics model, Elovich model, pseudo-first-order model, and pseudo-second-order model were used in analysis of adsorption kinetic.
Intraparticle diffusion kinetics: The linear form of the equation was as follows:

$$q_t = k_{ip} t^{1/2} + C$$  \hspace{1cm} (1)

where $k_{ip}$ is the intraparticle diffusion rate, and $C$ is a constant.

Elovich model can be expressed as:

$$q_t = \beta \ln (\alpha \beta) + \beta \ln (t)$$  \hspace{1cm} (2)

where $\alpha$ is the initial adsorption rate (mg/(gh)) and $\beta$ is the adsorption rate constant.

Pseudo-first-order model and pseudo-second-order model are generally described in the following form:

Pseudo-first-order model:

$$\ln (q_e - q_t) = \ln (q_e) - k_1 t$$  \hspace{1cm} (3)

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (4)

where $q_e$ (mg/g) and $q_t$ (mg/g) are the amount of adsorbed nitrate at equilibrium, and the amount of adsorbed nitrate at time $t$ (min), respectively. $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the adsorption rate constants.

Freundlich and Langmuir models were used to analyze the adsorption isotherm. The Freundlich equation can be expressed in linear form as follows:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$  \hspace{1cm} (5)

where $q_e$ (mg/g) is the equilibrium adsorption capacity, $C_e$ (mg/L) is the equilibrium concentration; $k_f$ (L/mg) and $1/n$ are the Freundlich constant and heterogeneity factor. The Langmuir isotherm model can be expressed in linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{q_m}{q_m}$$  \hspace{1cm} (6)

where $b$ (L/mg) is the Langmuir adsorption constant, $q_m$ (mg/g) is the maximum adsorption capacity. In the model, dimensionless constant is an important parameter for further analyzing the adsorption efficient. The equation follows:

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} (7)

where $R_L$ and $C_0$ are the equilibrium parameter and initial concentration of nitrate, respectively. The value of $R_L < 1$ represents favorable adsorption (Islam & Patel 2011).

The thermodynamic parameters, including the Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy change ($\Delta S$), can be determined by using the following equations:

$$\Delta G = -RT \ln K_c$$  \hspace{1cm} (8)

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$  \hspace{1cm} (9)

where $R$, $T$ are ideal gas constant ($8.314$ J/mol K) and the temperature in Kelvin. The distribution constant $K_c = q_e/C_e$. $\Delta H$ and $\Delta S$ were obtained by using the slope and intercept of plots of $\ln K_c$ versus $1/T$.

Characterization methods

The zeta potentials were measured by using a zeta potential analyzer (Malvern, Zetasizer Nano, ZS90). Specific surface area and pore structure were determined by an automatic Brunauer–Emmett–Teller (BET) and pore size distribution analyzer (Quantachrome, NOVA4200e). Morphological analysis of the samples was performed by scanning electron microscopy (SEM) using a Carl Zeiss EVO LS10 microscope. The powder X-ray diffraction (XRD) patterns for the HTlcs were recorded using an X-ray diffractometer (Bruker D8 diffractometer, Germany) with Cu-Kα radiation and at scan speed of 0.02˚/s over the range of 5–90˚ at 40 kV and 40 mA. Fourier transfer infrared (FTIR) spectra of the materials were measured by a Bruker Vector 33 spectrophotometer (Germany). The samples recorded by the KBr pellet technique in the wave number range from 400 to 4,000 cm$^{-1}$.

RESULTS AND DISCUSSION

Effect of chemical composition of CHTlcs

Different types of metal have important influence in various anions adsorption onto LDHs and HTlcs. Iron-based LDHs are promising candidates for anions removal and incorporation of La$^{3+}$ into them can further enhance the uptake efficiency (Guo et al. 2012). Comparing with Mg-Fe-LDHs, Mg-Al-LDH has well crystallinity and better efficiency for the removal of nitrate from soil solution (Halajnia et al. 2012). Calcined Mg-Al LDHs acquire a high removal efficiency of perchlorate, while calcined Mg-Fe hydroxides have weak...
perchlorate adsorption but efficient nitrate uptake capacity (Yang et al. 2015). The divalent cations of LDHs commonly include Zn$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, and the trivalent cations usually contain with Al$^{3+}$, Fe$^{3+}$ and Cr$^{3+}$. The values of $M^{2+}/(M^{2+} + M^{3+})$ are usually changed between 0.10-0.33. In this study, various metals used usually had been chosen to synthesize different calcined ternary hydrotalcite like compounds with the $M^{2+}/(M^{2+} + M^{3+})$ molar ratio of 0.25. The nitrate removal percentages and adsorption capacities of different ternary CHTlcs are displayed in Table 1. It can be seen that the CHTlcs with metal components of Mg-Al-Fe had the highest removal percentage (84.97%) and the highest adsorption capacity (60.36 mg/g), when the value of $n$(NaCO$_3$)/$n$(M$^{3+}$) was 0.5. Other CHTlcs prepared with different metal compositions exhibited poor nitrate adsorption efficiency. With the increasing value of $n$(NaCO$_3$)/$n$(M$^{3+}$) from 0.5 to 2, nitrate adsorption efficiency of CHTlcs increased. The maximum removal efficiency of 97.69% and the highest uptake capacity of 63.62 mg/g were obtained by the Mg-Al-Fe CHTlcs with the $n$(NaCO$_3$)/$n$(M$^{3+}$) value of 2. The concentration of NaCO$_3$ might affect the symmetry and the order of CO$_3^{2-}$/CO$_2$ and H$_2$O molecules in the middle layer of HTlcs (Xu et al. 2008). It indirectly affects the refactoring structure of CHTlcs, bringing the change of nitrate adsorption efficiency. The Mg-Al-Fe CHTlcs with the $n$(NaCO$_3$)/$n$(M$^{3+}$) value of 2 were used in the further batch test.

Binary Mg-Fe hydrotalcite with 3:1 Mg-Fe molar ratio is thought to have high adsorption efficiency during nitrate adsorption process (Yang et al. 2015). In order to investigate the effect of Mg-Al-Fe molar ratio on nitrate adsorption, some ternary CHTlcs with various molar ratio of Mg-Al-Fe (3:1.0, 3:0.7:0.3, 3:0.3:0.7, 3:0.1:0.9, and 3:0:1) were used in uptake experiments. The results are presented in Figure 1. The CHTlcs with Mg-Al-Fe molar ratio of 3:0.1:0.9 exhibited maximum nitrate removal percentage of 92.7% and the highest adsorption capacity of 63.62 mg/g. The appropriate replacement of Al$^{3+}$ by Fe$^{3+}$ in LDH increased the positive surface charge of the mixed metal hydroxide layers, leading to the higher adsorption efficiency (Triantafyllidis et al. 2010). It also can be found that Mg-Al-Fe-CHTlcs acquired higher removal efficiency than the CHTlcs with two kinds of metal. The Mg-Al-Fe CHTlcs (3:0.1:0.9) were used in the next batch studies.

**Effect of adsorbent dose**

The effect of the dosage of Mg-Al-Fe CHTlcs on nitrate adsorption with initial concentration of 100 mg/L was investigated (Figure 2). It can be seen that the removal efficiency of nitrate increased sharply with increasing dose of adsorbent from 20 mg to 150 mg. A further increase of adsorbent...
dosage did not improve the nitrate removal efficiency significantly. The equilibrium removal efficiency of nitrate was more than 99%. However, the higher adsorbent dose led to a lower uptake capacity when the adsorbent dose was over 50 mg. Because the surface sites of CHTIcs particles are heterogeneous, the adsorption capacity closely relates to surface active sites. At low adsorbent dosage, all active sites were entirely exposed and the adsorption on the surface was saturated quickly, showing a high uptake capacity (Wu et al. 2010). While the CHTIcs particles were conglomerated at high dose. The available high energy sites decreased with the increase of adsorbent, and the effective surface area were not increased significantly, resulting in a low uptake capacity and stable adsorption efficiency. According to the two facts of percentage removal and adsorption capacity, 150 mg CHTIcs was regarded as optimum dose.

**Effect of initial nitrate concentration**

Figure 3 gives the influence of variation of initial nitrate concentration. The uptake capacity of Mg-Al-Fe CHTIcs increased from 12.6 to 107.18 mg/g with the increase of initial nitrate concentration. It also could be seen that the percentage removal of nitrate increased to 96.6% as the initial nitrate concentration rose from 20 to 40 mg/L. With further increase of nitrate concentration up to 200 mg/L, the removal efficiency decreased to 80.39%. It was indicated that the adsorption of CHTIcs was saturated when the initial concentration of nitrate was high enough, resulting in a decrease of removal rate. 100 mg/L initial nitrate concentration was considered as optimum concentration during the adsorption process with the CHTIcs dose of 1.5 g/L.

**Effect of initial pH**

The pH value of the solution can affect the uptake efficiency by affecting the surface charge of the adsorbent and the ionization of adsorbate in solution. The effect of initial pH on nitrate adsorption was examined by adding HCl or NaOH to adjust the pH at the range of 3–11. The zeta potential of CHTlc was also evaluated to explain the results. As shown in Figure 4, the pH value had no enormous impact on the adsorption of nitrate onto Mg-Al-Fe CHTIcs, and the removal ratios of the adsorbent all exceeded 80%, which was in accordance with the zeta potential result. The positive zeta potential of CHTlc in various pH was in favor of nitrate adsorption. The result agreed with the nitrate adsorption onto Mg-Al-CHTIcs and Mg-Fe CHTIcs (Halajnia et al. 2012). The percentage removal and uptake capacity of nitrate
increased as the pH value rose from 3 to 7, and then decreased at higher pH value. The maximum percentage removal and the highest adsorption capacity were 97.8% and 72.87 mg/g, respectively. Due to the deprotonation effect, the zeta potential of CHTlcs was decreased rapidly when pH > 9, causing the unfavorable effect for nitrate adsorption. In addition, the OH⁻ competed with NO₃⁻ at alkaline environment, which prevented the nitrate from cutting into layers of CHTlcs. Although the zeta potential was more positive at low pH, the adsorption efficiency of nitrate decreased for the possible collapse or dissolution of hydroxide talcite (Tyner et al. 2004).

**Effect of co-existing anions**

Since there are various competitive anions, such as the PO₄³⁻, SO₄²⁻, Cl⁻, ClO₄⁻ existing in the solution containing nitrate, the adsorption of nitrate by CHTlcs was investigated in the presence of other anions in solution. Figure 5 shows the effect of competing anions (PO₄³⁻, SO₄²⁻, Cl⁻, ClO₄⁻) on nitrate adsorption by Mg-Al-Fe CHTlcs. The percentage removal of nitrate was at the range of 93%–97% in the absence of other anions. It can be found that these anions affected the nitrate uptake in some extent. And the higher concentration of these anions resulted more reduction of nitrate removal percentage. Co-existing anions below 50 mg/L concentration had less effect on nitrate adsorption. When the concentration of co-anions were up to 200 mg/L, removal percentages of nitrate in these system (NO₃⁻/PO₄³⁻, NO₃⁻/SO₄²⁻, NO₃⁻/Cl⁻, and NO₃⁻/ClO₄⁻) were 16.2%, 26%, 45.7% and 86%, respectively. The impact on nitrate removal rate varied from different anions, and they followed the order of PO₄³⁻ > SO₄²⁻ > Cl⁻ > ClO₄⁻. The order agreed with several previous studies for oxyanion adsorption by calcined and uncalcined HTlcs (Wu et al. 2010; Halajnia et al. 2012). LDHs generally have a greater affinity toward anions with a higher ionic charge density (Guo et al. 2012). The effect of ClO₄⁻ on nitrate adsorption was the minimum one mainly for the relative weak interfering effect between ClO₄⁻ and the layer boards of LDH. Comparing with the anions of monovalent valence, high valence are more easily going into the layers of LDHs, resulting in a better competitive ability.

**Adsorption kinetic**

The adsorption kinetic of nitrate onto CHTlcs was further investigated. In general, the adsorption transformation processes always depend on time. Figure S1 (available with the online version of this paper) depicted the removal of nitrate from solution at a different contact time. The percentage removal and adsorption capacity increased fast at the beginning, and then remarkably slowed down and gradually proceeded to the equilibrium after 9 h.

In order to further determine the adsorption rate and find out the interaction mechanism, four different kinetic models containing intraparticle diffusion kinetics model, Elovich, pseudo-first-order model and pseudo-second-order model were used to fit the experimental data. According to their linear Equations (1)–(4), the predicted curves were depicted and shown in Figure S2 (available with the online version of this paper). Their kinetic parameters were listed in Table 2.

From predicted curves of intraparticle diffusion kinetics model (Figure S2(a)), it can be found that the adsorption

![Figure 5](https://iwaponline.com/wst/article-pdf/75/9/2194/453628/wst075092194.pdf)

**Figure 5** Effect of competitive anions on nitrate adsorption.
process can be divided into two stages: rapid phase and stable phase. The immediate adsorption in rapid phase was ascribed to external mass transfer, and the second phase was attributed to the slow intraparticle diffusion within the microspores of the adsorbent (Li et al. 2008). It also can be seen that the line was not through the origin, which indicated that the intraparticle diffusion was not the only limiting step. Other control steps such as chemisorption or boundary layer effect might exist in the adsorption process. Elovich equation is suitable for a system with heterogeneous adsorbing surfaces (Wu et al. 2009). The high correlation indicated that the existence of nitrate chemisorption onto the heterogeneous materials. Comparing with the value of correlation coefficient for the four kinetic models, the pseudo-second-order models ($R^2 = 0.8783$) exhibited the best fit for nitrate adsorption onto CHTlcs, suggesting that the chemical adsorption was the rate-limiting step of nitrate adsorption. The adsorption capacity at equilibrium by the pseudo-second-order model was about 78.55 mg/g.

**Adsorption isotherm**

Freundlich and Langmuir are common models to analyze the adsorption isotherm. In this study, the two models were applied to fit the experimental data at 30 °C. By using the Equations (5) and (6), the constants calculated are listed in Table 3. It can be seen that the data were better described by Langmuir model ($R^2 = 0.982$) than by Freundlich model ($R^2 = 0.853$), which was due to the effective monolayer chemisorption of nitrate onto CHTlcs. The maximum adsorption capacity of nitrate calculated by Langmuir model for Mg-Al-Fe CHTls was 123.305 mg/g. Furthermore, the value of dimensionless constant ($R_f$) calculated by Equation (7) was 0.056, which indicated that the nitrate uptake process of Mg-Al-Fe CHTlcs was a favorable system.

**Adsorption thermodynamic**

The fluctuation of temperature has influence on nitrate adsorption equilibrium of adsorbent. The thermodynamic parameters calculated by Equations (8) and (9) were displayed in Table 4. The value of $\Delta G$ is negative, suggesting the adsorption process was spontaneous in nature. With the increase of temperature, the values of $\Delta G$ become less negative, which indicated that nitrate adsorption onto CHTlcs was unfavorable at high temperature. The negative enthalpy change ($\Delta H = -113.0041$ kJ/mol/K) demonstrated that the exothermic nature of nitrate adsorption by the CHTlcs. The negative value of $\Delta S$ implied that the decreased randomness at the solid/solution interface during the adsorption process.

**Proposed adsorption mechanisms**

Understanding the mechanism of nitrate adsorption onto Mg-Al-Fe-CHTlcs is essential for effective removal of nitrate from wastewater. Samples were characterized to further investigate its sorption mechanisms.

One of the adsorption mechanisms suggested was the reconstruction of the CHTlcs to LDH by incorporating nitrate in the solution, which is the so-called ‘memory effect’. As can be seen in XRD patterns (Figure 6), the calcined hydrotalcite had no characteristic peaks of HTlcs. The peaks at 43 °C and 62 °C were assigned to the lattice of metal oxides (Wan et al. 2012). These illustrated that the layer board structure of HTlcs was destroyed after calcination at 450 °C for 6 h. After nitrate adsorption, the sharp and symmetric peaks at lower 2θ (003, 006, 009) appeared, suggesting that the nitrate was adsorbed onto the positive layer and formed the negative layer (Kentjono et al. 2010). The calcined hydrotalcite-like compounds recovered their original layered structure after nitrate adsorption. FTIR spectra of samples were shown in Figure 7. It can be seen that the band at around 1,400 cm$^{-1}$ became stronger and
sharper after the uptake of nitrate, which was ascribed to rehydration and structural reconstruction of the calcined products in the presence of nitrate (Yang et al. 2013). The peaks at 1,500 and 1,104 cm\(^{-1}\) appeared after nitrate adsorption, which indicated the adsorption of nitrate onto the CHTlcs (Islam & Patel 2014). The SEM images (Figure 8) showed that the morphology of CHTlcs before and after nitrate adsorption was significantly different. There were no typical big flakiness structures in CHTlcs before adsorption. A lot of irregular small particles and platelet aggregates appeared, and their surfaces were rough, implying destroyed original hydroxide structures following calcinations (Sun et al. 2013). After nitrate adsorption, regular and ordered, petal-like flakiness structures appeared. Furthermore, the entropy change of the adsorption process was negative. It can be well explained that CHTlcs restored the layered structure by taking up nitrate from aqueous solution with less desorption of other molecular or ions, which decreased the randomness of the system. These results confirmed that the calcined hydrotalcite-like compounds adsorbed nitrate via the mechanism of reconstruction effect.

Nitrate can also be adsorbed by the mechanism of external surface adsorption on hydrotalcite to increase adsorption capacity. Zeta potential, as an important index for electrostatic adsorption processes had been mentioned above. The results of zeta potential (Figure 4(b)) concluded that the Mg-Al-Fe CHTlcs had a surface residual positive charge in suspension in various pH, and could take nitrate onto its positive surface in different media. Moreover, the results of adsorption isotherm illustrated that the experiment data were better described by Langmuir model. As a monolayer surface adsorption, electrostatic adsorption was the main external surface adsorption.
Generally, the adsorption capacity of adsorbents was evidently influenced by their specific surface area and pore volume. As the SEM images showed above, Mg-Al-Fe CHTIcs was composed of small particles and platelet aggregates, which had large enough specific surface area to uptake nitrate. Nitrogen adsorption–desorption isotherm and corresponding pore size distribution were further investigated (Figure 9). According to the IUPAC classification, the isotherm of the sample is classified as type IV adsorption isotherm, indicating that the CHTIcs is a mesoporous material (Lei et al. 2017). From the pore size distribution curves, the main pore diameter (2–3 nm) and average pore diameter (12.909 nm) of the material fitted the size range of mesoporous material (2–50 nm). Because of the presence of mesoporous material the initial adsorption process of nitrate was rapid. The adsorption rate slowed down with the decrease of mesoporous sites. The result was in agreement with the description of intraparticle diffusion kinetics model. The porous structure parameters are list in Table S1 (available with the online version of this paper). The specific surface area of Mg-Al-Fe CHTIcs was 141.636 m$^2$/g which was higher than that of other hydrotalcites such as Mg-Fe LDH (3:1) (70 m$^2$/g) (Sasai et al. 2012), Mg-Al LDH (4:1) (64.4 m$^2$/g) (Halajnia et al. 2013), and Mg-Al CLDH (131.7 m$^2$/g) (Chebli et al. 2016). Although specific surface area might be not a determining factor, a larger surface can offer more adsorption active sites, which might induce a higher nitrate adsorption capacity.

According to the adsorption specialty and the characterization of samples before and after adsorption, the main mechanism might include the intercalation by reconstruction of CHTIcs and adsorption on external surface. The external adsorption relied on electrostatic adsorption. The mesoporous structures and high surface area of the adsorbent can facilitate the nitrate adsorption.

**CONCLUSIONS**

The results obtained in this study suggest that ternary Mg-Al-Fe CHTIcs is a kind of efficient sorbent for nitrate. The ternary hydrotalcites with different metal compositions can be prepared following a simple and economic method: calcining the precursors of HTLcs from co-precipitation method without expensive raw materials. The metal composition and the content of NaCO$_3$ in preparation process had great impact on the removal of nitrate. A relatively higher value of n(NaCO$_3$)/n(M$^{3+}$) was more beneficial to the adsorption of nitrate. CHTIcs with Mg-Al-Fe molar ratio of 3:0.1:0.9 (n(NaCO$_3$)/n (M$^{3+}$) = 2) was selected as the best adsorbent for nitrate uptake. As for 100 mg/L concentration of nitrate, 1.5 g/L CHTIcs was sufficient to approach to adsorption equilibrium, which was more economic than higher absorbent doses. And 100 mg/L was optimum initial nitrate concentration during the adsorption process with the CHTIcs dose of 1.5 g/L. The pH value had no enormous impact on the nitrate adsorption process. The removal efficiency was kept in high level (>80%) with various initial pH. Co-existing anions tests illustrated that anions have a deleterious effect on nitrate adsorption. The anions of higher valence had a more significant effect on nitrate adsorption than the monovalent anions. Adsorption kinetic, isotherm, thermodynamic revealed the properties of nitrate adsorption. The adsorption of nitrate was a spontaneous exothermic process with the reduction of entropy. The adsorption process can be well-described by pseudo-second-order kinetics, suggesting that chemical adsorption was the rate-limiting step. The experimental data agreed well with the Langmuir model, and the value of $R_L < 1$ represented favorable adsorption for nitrate uptake onto Mg-Al-Fe CHTIcs. The characterization of samples proved that Mg-Al-Fe CHTIcs have ‘memory effect’, positive charges on surface, high specific surface area and appropriate pore volume, which contributed to the good adsorption performance of nitrate.

**ACKNOWLEDGEMENTS**

This work was supported by the Fundamental Research Funds for the Central Universities, Science and Technology Program of Guangzhou, China.
REFERENCES


First received 22 July 2016; accepted in revised form 31 January 2017. Available online 22 February 2017.