Regular Article

Highlighted Paper selected by Editor-in-Chief

Adsorption of Nitrite and Nitrate Ions from an Aqueous Solution by Fe–Mg-Type Hydrotalcites at Different Molar Ratios

Fumihiko Ogata,^a Noriaki Nagai,^a Yukine Kariya,^a Eri Nagahashi,^a Yuhei Kobayashi,^a Takehiro Nakamura,^a and Naohito Kawasaki^{*a,b}^aFaculty of Pharmacy, Kindai University; 3–4–1 Kowakae, Higashi-Osaka, Osaka 577–8502, Japan; and ^bAntiaging Center, Kindai University; 3–4–1 Kowakae, Higashi-Osaka, Osaka 577–8502, Japan.

Received December 27, 2017; accepted January 24, 2018

In this study, we prepared Fe–Mg-type hydrotalcites (Fe-HT3.0 and Fe-HT5.0) with different molar ratios and evaluated their adsorption capability for nitrite and nitrate ions from aqueous solution. Fe-HT is a typical hydrotalcite-like layered double hydroxide. Adsorption isotherms, as well as the effects of contact time and pH were investigated, and it was found that Fe-HT can adsorb larger amounts of nitrite and nitrate ions than Al-HT (normal-type hydrotalcite). Adsorption isotherm data were fitted to both Freundlich (correlation coefficient: 0.970–1.000) and Langmuir (correlation coefficient: 0.974–0.999) equations. Elemental analysis and binding energy of Fe-HT surface before and after adsorption indicated that the adsorption mechanism was related to the interaction between the adsorbent surface and anions. In addition, the ion exchange process is related to the adsorption mechanism. The adsorption amount increased with increasing temperature (7–25°C). The experimental data fit the pseudo-second-order model better than the pseudo-first-order model. The effect of pH on adsorption was not significant, which suggested that Fe-HT could be used over a wide pH range (4–12). These results indicate that Fe-HT is a good adsorbent for the removal of nitrite and nitrate ions from aqueous solution.

Key words Fe–Mg-type hydrotalcite; ion exchange; nitrate ion; nitrite ion

Nitrate contamination in natural water bodies has become an increasingly serious environmental problem around the world, mainly because of the extensive use of chemical fertilizers, improper treatment of wastewater from industrial and municipal sites, landfills, and animal wastes (particularly from animal farms).^{1,2} High levels of nitrite and nitrate contaminants in drinking water can cause methemoglobinemia in children³ and these contaminants are classified under the category “probably carcinogenic to humans” by the International Agency for Research on Cancer (IARC).^{4,5} Therefore, nitrites and nitrates should be effectively removed from drinking water.⁵ However, it is difficult to remove nitrites and nitrates from aqueous solution owing to their stability, high solubility, and poor adsorption ability.^{6,7}

An attractive option for contaminant removal is adsorption, which is characterized by ease of operation, simplicity of design, and cost effectiveness.^{6,7} Various adsorbents have been developed to remove nitrites and nitrates from aqueous solution.⁸ However, there are several limitations to the practical applications of these materials, such as small particle size, poor acid–alkali resistance, and poor desorption efficiency.

Hydrotalcites are layered double hydroxides with a brucite structure, in which some of the divalent cations are replaced by trivalent cations resulting in a layer charge.⁹ The chemical composition of hydrotalcites can be described by the general formula: $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation, and x is the $M^{3+}/(M^{2+}+M^{3+})$ ratio (x normally ranges from 0.17 to 0.33).¹⁰ Hydrotalcite is a good sorbent with a large anion sorption capacity because of its high surface area, phase purity, basic surface properties, and structural stability.^{9–11} Previous studies have reported the adsorptive removal of nitrite and nitrate ions by Mg–Al hydrotalcite,¹⁰ Ca/Al chloride hydrotalcite-like com-

pounds,⁹ and Mg–Cu–Al-layered double hydroxide.¹²

Recently, we demonstrated the adsorption capability of anions (phosphate or tungsten anion) using Fe–Mg-type hydrotalcite at different molar ratios.^{13,14} These materials showed efficient adsorption capability for anions from aqueous solution. Therefore, we expect the novel Fe–Mg-type hydrotalcite to be a potential adsorbent for the removal of nitrite and nitrate ions. Thus, if efficient nitrite and nitrate ion adsorption methods using Fe–Mg-type hydrotalcite are developed, the applications of this material will be widespread. However, there are no reports on the adsorption of nitrite and nitrate ions by Fe–Mg-type hydrotalcite with different Mg^{2+}/Fe^{3+} ratios. Therefore, the objectives of this study are to prepare a novel Fe–Mg-type hydrotalcite with different Mg^{2+}/Fe^{3+} ratios, investigate the adsorption behavior for nitrite and nitrate ions, and elucidate the adsorption mechanism.

Experimental

Materials The Al–Mg/Fe–Mg-type hydrotalcite with different molar ratios was obtained from Tomita Pharmaceutical Co., Ltd., Japan (Al-HT3.0: $Mg^{2+}/Al^{3+}=3.0$, Al-HT5.0: $Mg^{2+}/Al^{3+}=5.0$, Fe-HT3.0: $Mg^{2+}/Fe^{3+}=3.0$, Fe-HT5.0: $Mg^{2+}/Fe^{3+}=5.0$). Standard nitrite/nitrate ion solutions were prepared using potassium nitrite/potassium nitrate obtained from Wako Pure Chemical Industries, Ltd., Japan.

Adsorbent characteristics were previously reported by Ogata *et al.*¹⁴ Briefly, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were performed using JSM-5200 (Yuasa, Japan) and Mini Flex II (Rigaku, Japan) systems, respectively. Elemental analysis was carried out using an electron microanalyzer (EPMA, JXA-8530F, JEOL, Japan), at an accelerating voltage of 30 kV and a beam diameter of 5 μm . Electron spectroscopy for chemical analysis was

* To whom correspondence should be addressed. e-mail: kawasaki@phar.kindai.ac.jp

Fig. 1. Adsorption Isotherms of Nitrite and Nitrate Ion

●: Fe-HT3.0, ◆: Fe-HT5.0, ○: Al-HT3.0, ◇: Al-HT5.0.

carried out using an X-ray photoelectron spectroscopy system (AXIS-NOVA, Shimadzu Co., Ltd., Japan).

Adsorption Isotherms The adsorbent (0.05 g) was added to a nitrite and/or nitrate ion solution at different initial concentrations (initial concentration: 10–50 mg/L) in single or binary solution systems. The suspension was shaken at 100 rpm for 24 h at 7, 15, and 25°C. The sample was then filtered through a 0.45- μ m membrane filter (Toyo Roshi Kaisha, Ltd., Japan), and the filtrate was analyzed by ion chromatography (DIONEX ICS-900, Thermo Fisher Scientific Inc., Japan). The measurements were performed using the IonPac AS12A system (4 $\times$ 200 mm, Thermo Fisher Scientific Inc., Japan). The mobile phase and regenerant comprised 2.7 mmol/L Na_2CO_3 + 0.3 mmol/L NaHCO_3 and 12.5 mmol/L H_2SO_4 , respectively. The flow rate was 1.0 mL/min at ambient temperatures. The micro membrane suppressor was an AMMS 300 system (4 mm, Thermo Fisher Scientific Inc., Japan), and the sample volume was 10 μ L. The amount of nitrite/nitrate ions adsorbed onto the adsorbent was calculated using Eq. (1):

$$q = (C_0 - C_e)V/W \quad (1)$$

where q is the amount of adsorbed nitrite/nitrate ions (mg/g), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solvent volume (L), and W is the weight of the adsorbent (g).

Effect of Contact Time and pH on the Adsorption of Nitrite and Nitrate Ions The adsorbent (0.05 g) was added to a nitrite/nitrate solution (50 mL aliquot of 50 mg/L). The suspension was shaken at 100 rpm for different time intervals (1, 3, 6, 12, 15, 20, and 24 h) at 25°C.

To examine the effect of pH, the adsorption experiments were performed with 0.05 g of the adsorbent and a nitrite/nitrate ion solution (50 mL aliquot of 50 mg/L) at different pH values (pH: 4, 6, 8, 10, and 12). The solution pH was adjusted by either 0.01 or 0.1 mol/L hydrochloric acid or sodium hydroxide solution. The adsorption amount was calculated by the aforementioned techniques.

Results and Discussion

Properties of Adsorbent The characteristics of the adsorbents were previously reported.¹⁴⁾ Al-HT and Fe-HT have a rounded morphology that lacks a perfect crystal boundary.

This reflects a poor degree of crystallinity and is typical for hydrotalcite-like layered double hydroxides formed by co-precipitation methods. In addition, the XRD patterns of the adsorbents showed several diffraction peaks that could be indexed to the crystal structure of the hydrotalcite (data not shown).^{11,15–17)}

Adsorption Capability of Nitrite and Nitrate Ions onto Al-HT or Fe-HT The adsorption isotherms of the nitrite and nitrate ions are shown in Fig. 1. The amount of nitrite/nitrate ions adsorbed onto Fe-HT is greater than that adsorbed onto Al-HT, which indicates that Fe-HT is effective in removing nitrite and nitrate ions from aqueous solution. The structure of hydrotalcites can be derived from the layered mineral, brucite ($\text{Mg}(\text{OH})_2$), where a fraction of the divalent cation Mg^{2+} is located at the center of an edge-sharing octahedral and surrounded by hydroxyl groups. Isomorphous substitution of divalent cations by trivalent cations (e.g. Al^{3+} or Fe^{3+}) generates positive charges on the layers, forming positively charged sheets.¹⁰⁾ Previous studies have reported that both the interlayer spacing and electrical properties of hydrotalcite compounds are affected by the $\text{M}^{2+}/\text{M}^{3+}$ ratio (M^{2+} and M^{3+} are divalent and trivalent cations, respectively).^{18–20)} Interlayer spacing and electrical properties are crucial characteristics that affect anion adsorption. This study focuses on the more suitable Fe^{3+} (trivalent cation) than Al^{3+} (trivalent cation) for the removal of nitrite and nitrate ions. Moreover, as the Mg/Fe ratio increases from 3.0 to 5.0, the electric charge density between the layers becomes weaker. Therefore, Fe-HT3.0 is more effective than Fe-HT5.0 for the removal of nitrite and nitrate ions from aqueous solution.

The experimental data were applied to the Langmuir and Freundlich isotherm equations. The Langmuir isotherm equation is given by

$$C_e/q_e = 1/W_s K_L + C_e/W_s \quad (2)$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount adsorbed at equilibrium (mg/g); and W_s and K_L are Langmuir constants related to monolayer adsorption capacity and energy of sorption, respectively. The Freundlich adsorption equation as follows:

$$\log q_e = \log k + (1/n) \log C_e \quad (3)$$

where q_e and C_e are the amount of adsorbed (mg/g) and the

Fig. 2. Elemental Analysis of Fe-HT Surface before and after Adsorption of Nitrate Ion

Table 1. Freundlich and Langmuir Constants for the Adsorption of Nitrite and Nitrate Ions

Adsorbent	Sample	Langmuir constants			Freundlich constants		
		W_s (mg/g)	K_L (L/mol)	r^2	$\log k$	$1/n$	r^2
Fe-HT3.0	Nitrate ion	39.7	3.7×10^4	0.974	1.12	0.5	0.970
	Nitrite ion	46.3	5.1×10^3	0.998	0.77	0.6	0.980
Fe-HT5.0	Nitrate ion	46.7	1.4×10^4	0.999	1.05	0.6	0.985
	Nitrite ion	N.D.	N.D.	N.D.	0.00	1.0	1.000
Al-HT3.0	Nitrate ion	5.20	-1.2×10^3	0.014	-1.95	1.0	0.244
	Nitrite ion	8.07	-5.5×10^3	0.046	-0.76	0.7	0.736
Al-HT5.0	Nitrate ion	0.10	1.2×10^4	0.532	-1.17	0.8	0.293
	Nitrite ion	-0.83	-1.8×10^2	0.989	-2.18	1.7	0.931

equilibrium concentration (mg/L), respectively, $\log k$ and $1/n$ are the Freundlich constants related to the adsorption of the adsorbent and intensity of adsorption, respectively.^{21,22)}

The calculated parameters are summarized in Table 1. The correlation coefficient indicates that both the Freundlich (0.970–1.000) and Langmuir (0.974–0.999) isotherm equations are good fits for the data corresponding to nitrite and nitrate ion adsorption on Fe-HT when compared with Al-HT. Nitrite and nitrate ions were easily adsorbed onto the Fe-HT surface when $1/n$ was in the range 0.1–0.5 but not when $1/n > 2$. These findings are also consistent with previous reports, according to which nitrite and nitrate ion adsorption readily occurred when $1/n < 2$ (0.5–1.0, when compared with Al-HT).²³⁾ Therefore, the adsorption of nitrite and nitrate ion onto Fe-HT is attributed to monolayer adsorption in this study.

As mentioned earlier, the adsorption of nitrite and nitrate ions is related to the Fe-HT surface. Therefore, we carried out the elemental analysis of Fe-HT surface before and after adsorption of the nitrate ions (initial concentration is 50 mg/L, Fig. 2). After adsorption, the amount of nitrogen atoms increased while iron and magnesium atoms decreased, suggesting that the nitrate ions were adsorbed onto the Fe-HT

surface. The values (intensity) of nitrogen before and after adsorption onto Fe-HT3.0 or Fe-HT5.0 were 2–19 and 2–16, respectively. Next, we investigated the binding energy before and after the adsorption of nitrite and nitrate ions (initial concentration is 50 mg/L, Fig. 3). $\text{NO}_2\text{-N}$ (ca. 403 eV) and $\text{NO}_3\text{-N}$ (ca. 407 eV) peaks, which were not detected before adsorption, were clearly detected after nitrite and nitrate ion adsorption. These results indicate that the adsorbent surface is one of the most important factors for the removal of nitrite and nitrate ions. Moreover, the degree of anion replacement in the hydrotalcites depends on the structural characteristics, such as the nature of the interlayer anion (chloride ion in this study) and crystallinity. Then, the amount of anions (chloride ion) released from Fe-HT was measured before and after adsorption (Fig. 4). A positive correlation between the amount of chloride ions released and the amount of nitrite and nitrate ions adsorbed (correlation coefficient: 0.981–0.998) was established, suggesting that the adsorption of nitrite and nitrate ions is also related to ion exchange with the chloride in the interlayer spaces of Fe-HT. In addition, more chloride ions were released from Fe-HT in nitrite ions adsorption compared to nitrate ions adsorption in this study. This phenomenon is attributed to the

Fig. 3. Binding Energy of Fe-HT Surface before and after Adsorption of Nitrite and Nitrate Ions

--- Before adsorption — After adsorption of nitrite ion — After adsorption of nitrate ion.

Fig. 4. Relationship between Amount of Nitrite or Nitrate Ions Adsorbed and Amount of Chloride Ion Released

●: Fe-HT3.0 (nitrite ion), ◆: Fe-HT5.0 (nitrite ion), ○: Fe-HT3.0 (nitrate ion), ◇: Fe-HT5.0 (nitrate ion).

differences of adsorption contribution in the ion exchange process and the interaction between the adsorbent surface and the anions (nitrite and nitrate ions). That is to say, the size of nitrite ion is smaller than that of nitrate ion, suggesting that nitrite ion easily exchanges with the chloride ions in Fe-HT.

Hence, it can be surmised that the nitrite and nitrate ion adsorption mechanism involves an ion exchange process and interaction between the adsorbent surface and the anions (electrostatic attraction or surface inner-sphere complex formation between the anions and hydroxide ions ($-\text{OH}$ or $-\text{OH}_2^+$)). Similar trends in the adsorption mechanism were reported in previous studies.^{24,25)}

Figure 5 shows the adsorption isotherms of nitrite and nitrate ions in single- or binary-solution systems. The nitrite and nitrate ion adsorption capacity decreased significantly when both the anions were present, which indicated that both types of ions compete for the cations. The obtained results were similar to those reported previously.^{10,26)} Hence, future studies will focus on the effect of co-existing anions for the removal

of nitrite and nitrate ions in complex solution systems.

Effect of Temperature on the Adsorption of Nitrite and Nitrate Ions onto Fe-HT The effect of temperature on the adsorption of nitrite and nitrate ions onto Fe-HT was investigated (Fig. 6). The amount of nitrite and nitrate ions adsorbed onto Fe-HT3.0 and Fe-HT5.0 increased with an increase in temperature from 7 to 25°C, which suggests that the adsorption of those ions is related to chemisorption (indicates the endothermic nature of the process). The calculation of thermodynamic parameters further supported the results obtained. The change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of adsorption was calculated using the following equations.^{9,27,28)}

$$\Delta G = -RT \ln K \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

$$\ln K = \Delta S/R - \Delta H/RT \quad (6)$$

where R (8.134 J/mol K) is the gas constant, T (K) is the absolute temperature, and K is the standard thermodynamic equilibrium constant defined by q_e/C_e . In the plot of $\ln K$ versus $1/T$, ΔH and ΔS can be estimated from the slopes and intercept, respectively. Using the K values determined from the adsorption isotherms, the corresponding values of ΔG of adsorption can be determined at different experimental temperatures.

Thermodynamic parameters for the adsorption of nitrite and nitrate ions onto Fe-HT3.0 and Fe-HT5.0 are shown in Table 2. A decrease in ΔG with an increase in temperature (Fe-HT3.0: from 1.7 to -1.5 kJ/mol and from 2.3 to -2.9 kJ/mol for nitrite and nitrate ions, Fe-HT5.0: from 2.3 to -0.7 kJ/mol and from 7.8 to -2.6 kJ/mol for nitrite and nitrate ions) suggests more adsorption of nitrite and nitrate ions at higher temperatures. The positive value of ΔS (Fe-HT3.0: 176.8 and 294.2 J/mol K for nitrite and nitrate ions, Fe-HT5.0: 171.5 and 1045.8 J/mol K for nitrite and nitrate ions) indicated an increase in the randomness of the system. During adsorption, the chloride ions (which are displaced by the nitrite and nitrate ions) gain entropy that is lost by the adsorbent species.²⁶⁾ Moreover, in this study, a positive value of ΔH indicated that the adsorption

Fig. 5. Adsorption Isotherms of Nitrite and Nitrate Ion in Single or Binary Solution

●: Fe-HT3.0 (single), ◆: Fe-HT5.0 (single), ○: Fe-HT3.0 (binary), ◇: Fe-HT5.0 (binary)

Fig. 6. Adsorption Isotherms of Nitrite and Nitrate Ion at Different Temperatures

▲: 25°C, ■: 15°C, ●: 7°C

Table 2. Thermodynamic Parameters for the Adsorption of Nitrite and Nitrate Ion

Adsorbent	Sample	Temperature (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)
Fe-HT3.0	Nitrite ion	7	1.7	51.3	176.8
		15	0.6		
		25	-1.5		
	Nitrate ion	7	2.3	8.6	294.2
		15	3.0		
		25	-2.9		
Fe-HT5.0	Nitrite ion	7	2.3	50.5	171.5
		15	1.5		
		25	-0.7		
	Nitrate ion	7	N.D.	0.3	1045.8
		15	7.8		
		25	-2.6

Fig. 7. Effect of Contact Time on the Adsorption of Nitrite and Nitrate Ion

●: Fe-HT3.0, ○: Fe-HT5.0

Fig. 8. Effect of pH on the Adsorption of Nitrite and Nitrate Ion

●: Fe-HT3.0, ○: Fe-HT5.0

Table 3. Kinetic Parameters for the Adsorption of Nitrite and Nitrate Ion

Adsorbent	Sample	$q_{e,exp}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
			$q_{e,cal}$ (mg/g)	k_1 (1/h)	r	$q_{e,cal}$ (mg/g)	k_2 (g/mg/h)	r
Fe-HT3.0	Nitrite ion	30.1	18.1	0.07	0.955	32.1	9.7×10^{-4}	0.968
	Nitrate ion	28.0	20.1	0.09	0.964	30.1	1.1×10^{-3}	0.982
Fe-HT5.0	Nitrite ion	37.6	34.4	0.13	0.953	40.0	6.3×10^{-4}	0.994
	Nitrate ion	37.6	23.2	0.17	0.948	41.3	5.9×10^{-4}	0.990

was endothermic and irreversible.

Effect of Contact Time on the Adsorption of Nitrite and Nitrate Ion onto Fe-HT The adsorption of nitrite and nitrate ions increased with elapsed time (Fig. 7). The adsorption was rapid in the first 6 h and was slow thereafter. Finally, the equilibrium was attained at 24 h. The adsorption kinetics were used to explain the adsorption mechanism and adsorption characteristics of Fe-HT. The pseudo-first-order (Eq. 7) and second-order (Eq. 8) kinetics equations are expressed in linear form, as follows^{13,29}:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (8)$$

where q_e and q_t are the amounts of nitrite and nitrate ions

adsorbed at equilibrium and at time t (mg/g), respectively; k_1 is the rate constant of the pseudo-first-order model adsorption (1/h); and k_2 is the rate constant of the pseudo-second-order model adsorption (g/mg/h).

Table 3 shows the kinetic parameters for the adsorption of nitrite and nitrate ions. It was found that the nitrite and nitrate ion adsorption could be better described by the pseudo-second-order kinetic model (0.968–0.994) since its correlation coefficient was higher than that of the pseudo-first-order kinetic model (0.948–0.964). The pseudo-second-order kinetic model based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate.³⁰ In addition, the value of $q_{e,exp}$ was closer to that of $q_{e,cal}$ in the pseudo-second-order kinetic model than that in

Table 4. Comparison of the Nitrate and Nitrite Ion Adsorption Capacities of the Various Adsorbent

Adsorbent	Adsorption capacity (mg/g)		References
	Nitrate ion	Nitrite ion	
Layer double hydroxide (Mg–Al–CO ₃)	2.2	—	Islam & Patel 2011
Layer double hydroxide (Ca–Al–Cl)	13.0	—	Islam & Patel 2011
MCM-48-NH ₃ ⁺	43.7	—	Saad <i>et al.</i> 2007
CHT4	122.7	—	Wan <i>et al.</i> 2012
Acid treated C-cloth	—	46.7	Afkhami <i>et al.</i> 2007
Sepiolite	—	0.7	Neşe & Ennil 2008
Powder activated carbon	—	1.2	Neşe & Ennil 2008
Fe-HT3.0	30.1	37.6	This study
Fe-HT5.0	28.0	37.2	This study

the pseudo-first-order model.^{14,25)} The high correlation coefficient suggests that the adsorption of both nitrite and nitrate ions is controlled by chemical sorption.^{10,31)}

Effect of pH on the Adsorption of Nitrite and Nitrate Ions onto Fe-HT The effect of pH on the adsorption of nitrite and nitrate ions onto Fe-HT is shown in Fig. 8. There are no significant changes in nitrite and nitrate ion removal with pH increase, which indicates that Fe-HT3.0 and Fe-HT5.0 can remove nitrite and nitrate ions from aqueous solution over a wide pH range (except for nitrite ions adsorption in pH 4.0 condition). The initial concentration of nitrite ion at pH 4.0 was adjusted using 0.1 mol/L hydrochloric acid solution. The nitrous acid formation slightly changed from nitrite ion to nitrate ion. This phenomenon was caused by decreasing the initial concentration of nitrite ion at pH 4.0, suggesting that the amount of nitrite ion adsorbed is smaller at pH 4.0 when compared to other pH conditions.

Usually, pH influences the anion exchange reaction *via* competition between the hydroxyl ion and anions. However, adsorption of the nitrite and nitrate ions onto Fe-HT is due to both ion exchange and interaction between the adsorbent surface and the anions. Therefore in this study, the effect of pH on the adsorption of nitrite and nitrate ions onto Fe-HT is considered insignificant.

Comparison of Adsorption Capacities A comparison of the nitrite and nitrate ion adsorption capacities of various adsorbents from previous studies with the Fe-HT3.0 and Fe-HT5.0 adsorbents from this study is given in Table 4.^{9,10,32–34)} The nitrite and nitrate ion adsorption capability of Fe-HT was greater than or similar to that of the reported adsorbents (except for MCM-48-NH₃⁺, CHT4, and acid-treated C-cloth). These comparisons show that Fe-HT can be employed in commercial processes for the adsorption of nitrite and nitrate ions from contaminated aqueous solutions.

Conclusion

Two samples of a novel Fe–Mg-type hydrotalcite (Fe-HT3.0 and Fe-HT5.0) were prepared, and their adsorption capability for nitrite and nitrate ions was evaluated in this study. Fe-HT possesses a rounded, smooth morphology that lacks a perfect crystal boundary. The XRD pattern of Fe-HT could be indexed to the crystal structure of hydrotalcite. The batch

adsorption isotherms of Fe-HT for nitrite and nitrate ions were well fitted by both the Freundlich and Langmuir equations. We elucidated the interaction between the adsorbent surface and anions by elemental analysis and binding energy measurements. Thermodynamic studies indicated that the adsorption was an endothermic process, which was propelled by enthalpy. Batch kinetic studies indicated that the pseudo-second-order equation for the adsorption kinetic curve of nitrite and nitrate ions is a good fit. Moreover, the solution pH had no significant effect on the nitrite and nitrate ion adsorption within the experimental pH range (4–12). Collectively, the results suggest that Fe-HT could be useful for the removal of nitrite and nitrate ions from aqueous solution. Furthermore, we elucidated the mechanism underlying the adsorption of nitrite and nitrate ions by Fe-HT.

Acknowledgments The Ministry of Education, Culture, Sports, Science and Technology (MEXT)-supported Program for the Strategic Research Foundation at Private Universities, 2014–2018 (S1411037).

Conflict of Interest The authors declare no conflict of interest.

References

- Ghafari S., Hasan M., Aroua M. K., *Bioresour. Technol.*, **99**, 3965–3974 (2008).
- Hu Q., Chen N., Feng C., Hu W., Liu H., *RSC Adv.*, **6**, 61944–61954 (2016).
- Yousefi N., Fatehizadeh A., Ghadiri K., Mirzaei N., Ashrafi S. D., Mahvi A. H., *Desalination Water Treat.*, **57**, 11782–11788 (2016).
- Grosse Y., Baan R., Straif K., Secretan B., El Ghissassi F., Coglianov V.; WHO International Agency for Research on Cancer Monograph Working Group, *Lancet Oncol.*, **7**, 628–629 (2006).
- Ghadiri S. K., Nasser A., Nabizadeh R., Khoobi M., Nazmara S., Mahvi A. H., *J. Mol. Liq.*, **242**, 1111–1117 (2017).
- Hu Q., Chen N., Feng C., Hu W., Zhang J., Liu H., He Q., *J. Taiwan Inst. Chem. Eng.*, **63**, 216–225 (2016).
- Loganathan P., Vigneswaran S., Kandasamy S., *J. Environ. Manage.*, **131**, 363–374 (2013).
- Katal R., Baei M. S., Rahmati H. T., Esfandian H., *J. Ind. Eng. Chem.*, **18**, 295–302 (2012).
- Islam M., Patel R., *J. Hazard. Mater.*, **190**, 659–668 (2011).
- Wan D., Liu H., Liu R., Qu J., Li S., Zhang J., *Chem. Eng. J.*, **195–196**, 241–247 (2012).
- Alvarez-Ayuso E., Nugteren H. W., *Water Res.*, **39**, 2535–2542 (2005).
- Tatjana J., Bošković C., *Acta Periodica Technologica*, **41**, 131–139 (2010).
- Ogata F., Kawasaki N., *Chem. Pharm. Bull.*, **63**, 1040–1046 (2015).
- Ogata F., Nakamura T., Ueta E., Nagahashi E., Kobayashi Y., Kawasaki N., *J. Environ. Chem. Eng.*, **5**, 3083–3090 (2017).
- Grover K., Komarneni S., Katsuki H., *Water Res.*, **43**, 3884–3890 (2009).
- Liu R., Frost R. L., Martens W. N., *Water Res.*, **43**, 1323–1329 (2009).
- Türk T., Alp İ., *J. Ind. Eng. Chem.*, **20**, 732–738 (2014).
- Vaccari A., *Catal. Today*, **41**, 53–71 (1998).
- Sideris P. J., Nielsen U. G., Gan Z., Grey C. P., *Science*, **321**, 113–117 (2008).
- Wan D., Liu H., Zhao X., Qu J., Xiao S., Hou Y., *J. Colloid Interface Sci.*, **332**, 151–157 (2009).
- Ennil Köse T., Kivanç B., *Chem. Eng. J.*, **178**, 34–39 (2011).
- Ogata F., Imai D., Toda M., Otani M., Kawasaki N., *J. Ind. Eng.*

- Chem.*, **34**, 172–179 (2016).
- 23) Abe I., Hayashi M., Kitagawa M., *J. Jap. Oil Chem. Soc.*, **25**, 145–150 (1976).
- 24) Yang K., Yan L. G., Yang Y. M., Yu S. J., Shan R. R., Yu H. Q., Zhu B. C., Du B., *Separ. Purif. Tech.*, **124**, 36–42 (2014).
- 25) Li R., Wang J. J., Zhou B., Awasthi M. K., Ali A., Zhang Z., Gaston L. A., Lahori A. H., Mahar A., *Sci. Total Environ.*, **559**, 121–129 (2016).
- 26) Wu Y., Wang Y., Wang J., Xu S., Yu L., Philippe C., Wintgens T., *J. Taiwan Inst. Chem. Eng.*, **66**, 191–199 (2016).
- 27) Islam M., Patel R. K., *J. Hazard. Mater.*, **143**, 303–310 (2007).
- 28) Islam M., Patel R. K., *J. Hazard. Mater.*, **156**, 509–520 (2008).
- 29) Bulut E., Özacar M., Şengil İ. A., *J. Hazard. Mater.*, **154**, 613–622 (2008).
- 30) Ho Y. S., McKay G., *Process Biochem.*, **34**, 451–465 (1999).
- 31) Lv L., He J., Wei M., Evans D. G., Duan X., *Water Res.*, **40**, 735–743 (2006).
- 32) Afkhami A., Madrakian T., Karimi Z., *J. Hazard. Mater.*, **144**, 427–431 (2007).
- 33) Saad R., Belkacemi K., Hamoudi S., *J. Colloid Interface Sci.*, **311**, 375–381 (2007).
- 34) Neşe Ö., Ennil K. T., *Desalination*, **223**, 174–179 (2008).