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Studies on Selective Adsorbents for Oxo-Anions. NO_3^- Adsorptive Properties of Ni-Fe Layered Double Hydroxide in Seawater

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Abstract. We report the selective adsorptive properties for NO_3^- in seawater of Ni-Fe layered double hydroxide (LDH (Ni-Fe)), containing Ni and Fe metal atoms in each layer. LDH (Ni-Fe) with Cl^- in the interlayers was synthesized by co-precipitation at constant pH. It showed a higher distribution coefficient (K_d) for NO_3^- than for other anions (HPO_4^{2-}, SO_4^{2-} etc.). NO_3^- adsorption on LDH (Ni-Fe) was also studied batchwise using NO_3^- enriched seawater (NO_3^- concentration: 40 μmol/dm^3). The NO_3^- uptake attained equilibrium after the adsorption for 4 h. The adsorption isotherm followed Freundlich's equation. The NO_3^- uptake reached 0.33 mmol/g when LDH (Ni-Fe) (0.10 g) was added to NO_3^- enriched seawater (1 dm^3), corresponding to the removal of 83% NO_3^- from seawater. The pH dependence of NO_3^- adsorption showed a maximum NO_3^- uptake at around pH 8 with low Ni dissolution (less than 0.6%). This adsorbent is therefore promising for the selective removal of NO_3^- from seawater for the benefit of the environment.

Keywords: selective adsorption, nitrate ion, layered double hydroxide, seawater, environment

1. Introduction

Nitrate pollution of ground and surface water has become a common concern in both industrial and developing countries. Increased nitrate uptake affects human health, and can cause methaemoglobinaemia. Enriched nitrate ions in the hydrosphere fertilize plant life, causing it to grow markedly, but the subsequent decaying process of plants consumes available oxygen in environmental water. A lack of oxygen causes life in the affected aqueous medium to migrate elsewhere or die. The problem of eutrophication is serious in closed water areas.

We are interested in the application of adsorption technology for the removal of NO_3^-, since the adsorption method can selectively recover of elements at markedly low concentrations. However, there have been few adsorbents to date suitable for the removal of NO_3^- from solutions with high salinity and high concentrations of chloride, sulfate, or carbonate ions. Most adsorbents show lower selectivity toward NO_3^- than to the other anions.

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We have studied the NO_3^--exchange properties of layered double hydroxides (LDHs) consisting of different kinds of skeletal metal atoms (Tezuka et al., 2003; Tezuka et al., 2004). Layered double hydroxide consists of positively charged metal hydroxide layers separated by counter anions and water molecules. The chemical composition can be expressed in general as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot zH_2O$, where M(II) and M(III) are divalent and trivalent cations in the octahedral interstices of the hydroxide layer and A^{n-} is the charge-balancing interlayer gallery anion. An interlayer anion can be exchanged with other anions (Cavani et al., 1991; Tsuji et al., 2002; Meyn et al., 1990; You et al., 2001; Aisawa et al., 2002; Ookubo et al., 1993; Zhang et al., 1995; Ramírez et al., 2001; Miyata, 1983). From a study of distribution coefficients (K_d) on LDHs, we were the first to find that the layered double hydroxide has a nitrate ion-sieve property depending on the basal spacing of the brucite layer (Tezuka et al., 2003, 2004). LDHs with Ni or Fe as skeletal metal atoms has a markedly high selectivity for nitrate ions. We proposed a Cl^-/NO_3^- ion exchange mechanism on the basis of chemical analysis and pH dependence studies of NO_3^- adsorption (Tezuka et al., 2004).

The present paper describes the selective adsorptive properties of LDH (Ni-Fe) for NO_3^- in raw seawater. From studies of adsorption rate, adsorption isotherm and pH dependence, we could conclude that it is a promising adsorbent for NO_3^- removal, even from solutions with highly salinity.

2. Experimental

2.1. Preparation of LDH

A mixed solution (10 cm^3) of 0.8 M (1 M = 1mol/dm^3) $NiCl_2$ and 0.2 M $FeCl_3$ with a Ni^{2+}/Fe^{3+} ratio of 4, and a 1M NaOH solution were added simultaneously with vigorous stirring at room temperature to 100 cm^3 of deionized water while maintaining the pH around 10. After the addition, the suspension was stirred for 2 h, and then autoclaved at 120°C for 1 d. The precipitates were centrifuged, washed with deionized water and dried at 50°C for 1 d (Sato et al., 1998). The sample was designated as LDH (Ni-Fe).

2.2. Characterization of LDH

X-ray diffraction analysis was carried out using a Rigaku RINT 1200 X-ray diffractometer with a graphite monochromator. Thermal analysis curves of adsorbents were measured on a Rigaku Thermo plus TG 8110 at a heating rate of 10°C/min air. The chemical composition of the adsorbent was determined by conventional methods. A solid sample was dissolved in a 0.5 M HCl solution and the metal concentrations were determined with a Shimadzu AA-760 atomic absorption spectrometer.

2.3. NO_3^- Exchange Study

The NO_3^- exchange capacity was determined by mixing LDH (Ni-Fe) (0.10 g) with a 0.1 M $NaNO_3$ solution (100 cm^3) for 3 d at room temperature. The solids were separated by filtration and the NO_3^- content was determined by ion chromatography after the solid was dissolved in a concentrated H_2SO_4 solution. K_d values of oxo-anion were determined by the same method as described in our previous studies (Tezuka et al., 2003, 2004). A mixed solution of NaCl, Na_2CO_3, $NaNO_3$, NaH_2PO_4, and Na_2SO_4 (1 mM each) was used. The K_d values were calculated using the equation:

$$K_d(\mathrm{cm}^3/\mathrm{g}) = \text{anion uptake (mg/g)/equilibrium anion concentration (mg/cm}^3\text{)}$$

2.4. Adsorption of NO_3^- in Seawater

Raw seawater was obtained at Bisan Seto, Kagawa, Japan. All the adsorption studies were carried out using NO_3^--enriched seawater (NO_3^- concentration: 40 $\mu mol/dm^3$), which was prepared by adding a known amount of $NaNO_3$ to raw seawater. The adsorption studies were carried out by a batch method. LDH (Ni-Fe) was immersed in NO_3^--enriched seawater (1 dm^3). After stirring for 2 d, the solid was separated by filtration. The NO_3^- concentration of seawater was determined by colorimetric method with a Portable Colorimeter (Model DR/700), HACH Company, USA. The NO_3^- uptake was calculated from the decrease of NO_3^- concentration relative to the initial concentration. The rate of NO_3^- adsorption was determined at room temperature by sampling a small amount of solution with different time intervals. The isotherm for NO_3^- adsorption was obtained from adsorption studies with different ratios of adsorbent (0.05–0.175 g) to NO_3^--enriched seawater (1 dm^3). The effect of temperature on NO_3^-adsorption was determined from adsorption

Table 1. Chemical composition, NO_3-exchange capacity and distribution coefficients (K_d).

Chemical composition	NO_3^- exchange capacity (mmol/g)	Distribution coefficients K_d			
		SO_4^{2-}	HPO_4^{2-}	NO_3^-	CO_3^{2-}
$[Ni_{0.794}\ Fe_{0.206}\ (OH)_2]$ $[Cl_{0.200}\ (CO_3)_{0.003}\ 0.609\ H_2O]$	1.4	150	320	$>10^4$	$>10^4$

studies at different temperatures (10, 25, and 40°C). The pH dependence of NO_3^- uptake was studied by controlling the pH of NO_3^--enriched seawater with a 0.1 M HNO_3 or 0.1 M NaOH solution. After adsorption, the NO_3^- concentration and the pH value were determined. The amounts of Ni and Fe dissolved were evaluated from their concentrations after adsorption, using a Shimadzu AA-760 atomic absorption spectrometer.

3. Results and Discussion

3.1. Characterization of the Starting LDH

Chemical composition of the synthesized LDH (Ni-Fe) is shown in Table 1. Elemental chemical analysis data (Ni and Fe) indicated that the molar LDH (Ni-Fe) ratio in the synthesized sample (Ni/Fe = 3.9) was close to the value in the starting solution (Ni/Fe = 4.0). The sample contains a small amount of carbonate ions, absorbed from the atmosphere during the preparation.

The XRD pattern (Fig. 1) of the synthesized LDH (Ni-Fe) was similar to those of layered double hydroxide materials typically reported in the literature (Cavani et al., 1991). The Cl^--form LDH (Ni-Fe) shows very sharp peaks, indicating a crystalline, ordered material. The basal spacing was calculated as $d_{003} = 0.808$ nm from the main diffraction peak in Fig. 1. The distribution coefficients of LDH (Ni-Fe) show a markedly high selectivity for NO_3^-, as shown in Table 1. Since the interlayer distance (0.33 nm) of LDH (Ni-Fe) is close to the ionic size (0.33 nm) of NO_3^-, it is sterically advantageous for fixing NO_3^- in the interlayers (Tezuka et al., 2003).

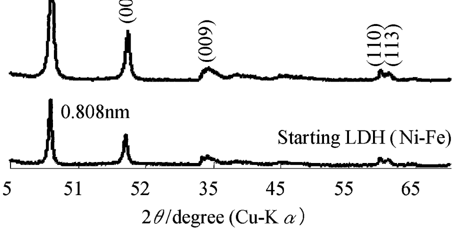

Figure 1. XRD pattern of LDH (Ni-Fe).

The NO_3^- exchange capacity was determined as 1.4 mmol/g, which is a little smaller than the theoretical anion exchange capacity (1.9 mmol/g) calculated from the Cl and CO_3 contents of LDH (Ni-Fe). The basal spacing of LDH (Ni-Fe) was reduced slightly to 0.801 nm by the NO_3^- exchange, as shown in Fig. 1. The IR spectra showed a sharp peak at 1384 cm^{-1}, due to the presence of NO_3^- in the interlayer (Aisawa et al., 2001).

3.2. Adsorption of NO_3^- in Seawater

The rate of NO_3^- removal is given in Fig. 2. The NO_3^- concentration of seawater decreased steeply with contact time and adsorption equilibrium was achieved within 4 h at room temperature. This shows that LDH (Ni-Fe) can remove NO_3^- effectively, even in seawater containing large amounts of coexisting anions (2.3 mM of carbonate ions, 14 mM of sulfate ions, 550 mM of chloride ions, etc.). The rate of NO_3^- adsorption was fast, even though the NO_3^- concentration was markedly low. The fraction of NO_3^- removal reaches 83% at the

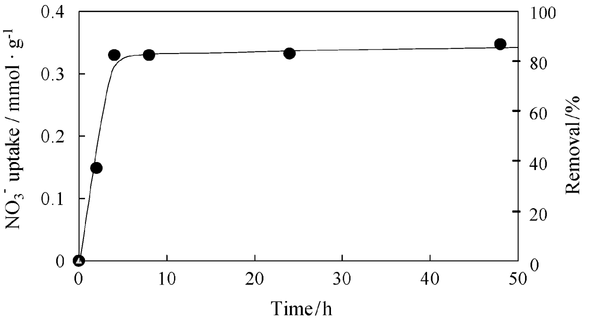

Figure 2. Rate of NO_3^- removal from NO_3^--enriched seawater. Adsorbent: 0.1 g, Solution: 1 dm^3, Initial NO_3^- concentration: 40 μ mol/dm^3.

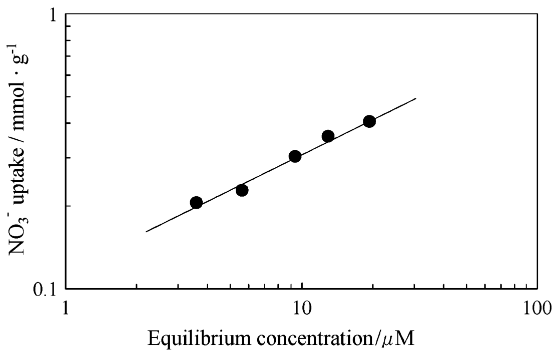

Figure 3. Isotherm for NO_3^- adsorption in seawater. Adsorbent: 0.05–0.175 g, Solution: 1 dm^3, Initial NO_3^- concentration: 40 μ mol/dm^3, Temperature: 27°C.

solid / solution ratio of 0.1 g/1 dm^3. We examined NO_3^- adsorption on other kinds of adsorbent under the same conditions. Several adsorbents including, strong-base anion exchange resin, hydrous zirconium oxide, and LDH (Mg-Al), failed to show any NO_3^- uptake, due to the influence of coexisting anions. LDH (Mg-Fe) showed NO_3^- adsorption, but with a markedly smaller uptake (0.06 mmol/g) than LDH (Ni-Fe).

The adsorption isotherm for NO_3^- with LDH (Ni-Fe) follows Freundlich's equation, as is shown in Fig. 3. Usually, adsorption of ion (uranium, lithium, molybdenum, or vanadium ions) with low concentration follows empirical Freundlich equation from seawater. The NO_3^- uptake increased with increasing equilibrium concentration and reached 0.4 mmol/g at an equilibrium concentration of 20 μmol/dm^3.

The temperature dependence of NO_3^-uptake is shown in Fig. 4. The NO_3^- uptake increased with an increase in adsorption temperature, showing an apparent endothermic reaction for NO_3^- adsorption on LDH (Ni-Fe). Since the basal spacing is nearly equal independent of adsorption temperature, the dehydration of NO_3^- at the adsorption may be caused by the apparent endothermic reaction.

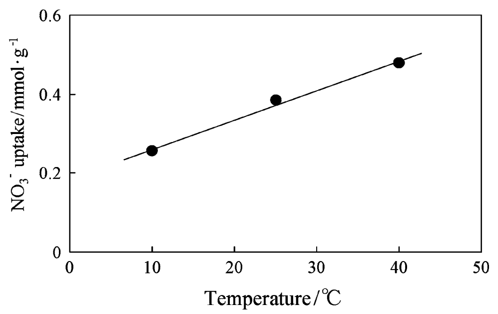

Figure 4. Effect of temperature on NO_3^- adsorption in seawater. Adsorbent: 0.05 g, Solution: 1 dm^3, Initial NO_3^- concentration: 40 μ mol/dm^3.

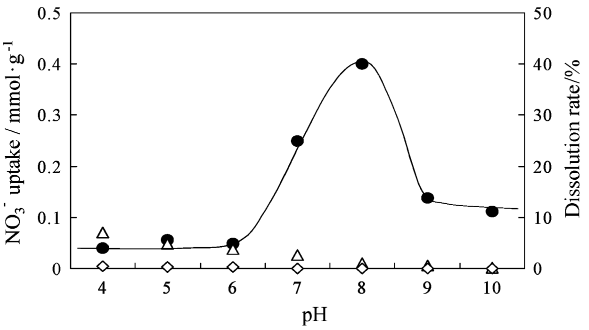

Figure 5. The pH dependence of NO_3^- adsorption in seawater. Dissolution rate: Ni; Δ, Fe; , Adsorbent: 0.05 g, Solution: 1 dm^3, Initial NO_3^- concentration: 40μ mol/dm^3.

The pH dependence of NO_3^- uptake from seawater is shown in Fig. 5. The NO_3^- uptake by LDH (Ni-Fe) showd a maximum of 0.4 mmol/g at pH 8. Dissolutions of Ni and Fe from LDH (Ni-Fe) were studied by analysis of Ni and Fe concentrations after adsorption. Dissolution was less than 0.6% for Ni and less than 0.1% for Fe at pH 8, indicating that LDH (Ni-Fe) was sufficiently stable in seawater. In the regions above pH 9 and below pH6, LDH (Ni-Fe) showed markedly small NO_3^- uptakes of less than 0.2 mmol/g. The pH dependence in seawater differs from that in a 0.1 M $NaNO_3$ solution, due to low NO_3^- concentration. Our previous study on NO_3^- uptake in the latter solution showed a nearly constant NO_3^- exchange capacity (around 1 mmol/g) in the region $4.5 < pH < 10$ (Tezuka et al., 2004). The decrease of NO_3^- uptake in the region of $pH > 9$ can be explained by the influence of OH^-; the OH^-/Cl^- exchange reaction dominates that of NO_3^-/Cl^- due to the increase of OH^- concentration. However, it is not clear why LDH (Ni-Fe) shows a markedly small NO_3^- uptake at $pH < 6$ in spite of its large NO_3^- exchange capacity in this region. A possible explanation is that the NO_3^- selective sites of LDH (Ni-Fe) are closely related to the Ni atoms of the layers, and therefore a small amount of Ni dissolution results in the destruction of NO_3^- specific ion exchange sites.

4. Conclusion

LDH (Ni-Fe) had a high selectivity for NO_3^- due to optimal interlayer spacing for NO_3^-, and could remove

NO_3^- effectively from raw seawater while maintaining high chemical stability.

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