MATERIALS IN NEW ZEALAND

Complete desorption of interlayer hydrogen phosphate in Mg/Al-layered double hydroxides by means of anion exchange with 1-octanesulfonate

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Abstract Hydrogen phosphate intercalated Mg/Al-layered double hydroxides (LDH-HPO$_4$) were synthesized by a homogeneous precipitation method with urea and anion exchange. The intercalated hydrogen phosphate was removed by anion exchange with Na$_2$CO$_3$, NaOH–NaCl, and 1-octanesulfonate solutions. The phosphate removal behavior was characterized by X-ray diffraction (XRD), Fourier Transform-InfraRed (FT-IR) spectroscopy, and elemental analysis. Complete removal of interlayer hydrogen phosphate from LDH-HPO$_4$ was realized using 1-octanesulfonate solution. Two reasons are proposed to explain complete hydrogen phosphate removal from the interlayer space of LDH-HPO$_4$. Complete desorption and cyclability suggest this is a viable technique to use as an efficient adsorption/desorption system in industrial applications.

Introduction

Removal of phosphate in wastewater is a critical issue to protect water resources from pollution. Eutrophication, or

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the excessive growth of algal bloom, in riverwaters can kill aquatic life and results in red-tide in quasi-island seawaters when the riverwaters feed into oceans. Many kinds of inorganic adsorbents including paddy soil have been tested for the removal of these phosphates [1–5]. Layered double hydroxides (LDH), are a group of layered compounds with the general formula of M$_{1-x}$M$'_x$(OH)$_2$A$_n$·mH$_2$O (abbreviated as M/M$'$/A-LDH where M and M$'$ are divalent and trivalent metal cations, respectively, forming positively charged layers of double hydroxide and A is a charge compensating interlayer anion with negative charge of x/n). These materials have been used as an anion exchanger of the interlayer anion with phosphate in water, and it has been reported that some types of LDH adsorb phosphate in water by making insoluble metal phosphate salts. Ca/Al/Cl-LDH adsorbs phosphate and forms an insoluble Ca-salt of apatite or Ca$_3$(PO$_4$)$_2$ [6–8]. Radha et al. [7] have also reported that MgHPO$_4$·3H$_2$O and (NH$_4$)MgPO$_4$·H$_2$O are formed at low pH and NH$_4$MgPO$_4$·H$_2$O is formed at neutral conditions, although intercalation of phosphate occurred under basic conditions when Mg^{2+} was used as the divalent metal cation. When ZrO$_2$ is incorporated in the interlayer region of LDH, phosphate is adsorbed on the surface of nano-size ZrO$_2$ particles [9]. High phosphate loading, up to 300 mgP/gLDH, has been reported when calcined Mg/Al-LDH was used with some of the Al^{3+} replaced by Fe^{3+} [10]. The unexpectedly high loading of phosphate probably includes adsorption onto LDH particles. Early studies by Badreddine et al., Khaldi et al., and Ookubo et al. have reported that hydrogen phosphate is intercalated by means of anion exchange with interlayer chloride of the pristine Zn/Al/Cl-LDH and Mg/Al/Cl-LDH [11–13], respectively. Nomura et al. [14] reported that in Mg/Al/Cl-LDH, phosphate is intercalated by anion exchange with interlayer chloride. Shimamura et al. [15]

have reported that the crystal morphology of the pristine LDH is maintained after the intercalation of hydrogen phosphate, and $Mg_3(PO_4)_2$ has been observed in XRD patterns after heating the resulting Mg/Al/HPO$_4$-LDH at 1273 K. High selectivity for phosphate has also been reported when calcined Zn/Al/NO$_3$-LDH was used [16].

Recently, it has been recognized that phosphate is a natural resource steadily being exhausted and effective methods of capture and recycling of phosphate are sought [17]. For this purpose, adsorbed phosphate should be released by desorption into water. LDH is a candidate material as an anion exchanger for adsorption/desorption of inorganic phosphate in water. Das et al. [17] have reported that a maximum desorption of 63% was achieved when an aqueous solution containing 0.1 M NaOH and 4 M NaCl was used in anion exchange of the interlayer phosphate. Care should be taken not to overestimate the amount of desorbed phosphate in spectrophotometric measurements since fine LDH particles pass through the membrane filter used in the separation of sample solutions containing desorbed phosphate from the particles, and are dissolved in the solution when the solution is acidified. On the other hand, intercalation of anionic surfactants as interlayer anions of LDH has been reviewed and a linear dependency of the basal spacing on the alkyl chain length of the surfactants has been reported [18]. Among the anionic surfactants, 1-octanesulfonate ($C_8H_{17}O_3S^-$; OS) has rarely been used in the intercalation of LDH probably because the basal spacing of the intercalated LDH is smaller than that of the other aliphatic surfactants such as DS and DBS [19, 20].

In this study, the interlayer hydrogen phosphate of synthetic Mg/Al/HPO$_4$-LDH was eliminated by anion exchange with chloride, carbonate, and OS. Among the three types of exchanging anion, OS was the most effective and the interlayer phosphate was completely eliminated following two treatment steps with an aqueous solution of OS.

Experimental

Synthesis of LDH-HPO$_4$

The synthesis of LDH-HPO$_4$ has been published previously [15]. The synthesis was carried out in a two-neck flask equipped with a reflux condenser. In a typical procedure, MgCl$_2$·6H$_2$O (20.6 mM), AlCl$_3$·6H$_2$O (9.46 mM), and urea (300 mM) were dissolved in deionized water and the solution was refluxed at 97 °C with stirring for 2 days. The resulting white solid, Mg/Al/CO$_3$-LDH was filtered, washed with deionized water twice, and finally dried under reduced pressure for 12 h. A portion (0.1 g) of the dried solid was suspended in an aqueous solution containing NaCl (1.5 M) and HCl (5 mM) to expel interlayer carbonate ions [21].

The suspension was stirred for 24 h at room temperature, filtered, and then washed twice with deionized water. The mixture of white slurry and KH$_2$PO$_4$ aqueous solution (100 mM) at pH 9.80 was stirred for 12 h at 35 °C, filtered, and then washed with deionized water. The resultant white product was dried at room temperature, and its composition, determined by ICP-AES measurement. The material, hereafter LDH-HPO$_4$, had a composition of Mg$_{0.66}$Al$_{0.34}$(OH)$_2$ HPO$_{0.17}$·1.07H$_2$O with a loading of 57.3 mgP/gLDH.

HPO$_4$ desorption method

Desorption of the interlayer HPO$_4^{2-}$ from LDH-HPO$_4$ was carried out by treating the LDH with aqueous solutions of Na$_2$CO$_3$ (1.0 M), NaOH (0.5 M) + NaCl (1.0 M), or sodium 1-octanesulfonate (OS; 0.3 M) separately. The treatment of the LDH in the aqueous solution of OS was repeated twice. LDH-HPO$_4$ (10 mg) was suspended in one of the aqueous solutions (40 mL) and the suspension was stirred at 35 °C between 0.5 and 96 h and then filtered. The resulting precipitate was washed with deionized/purified water (Milli-Q) and was dried in air before experimental measurements. The filtrate was collected to determine the amount of desorbed phosphate from the solid sample. These precipitates after treatment with aqueous solutions of Na$_2$CO$_3$ and NaOH + NaCl are hereafter referred to as LDH (Na$_2$CO$_3$) and LDH (NaOH–NaCl), respectively. The precipitate treated with OS solution both once and twice are referred to as LDH (OS-1) and LDH (OS-2), respectively. The desorption ratio (D) was calculated using the equation below, where (P/Al)$_{before}$ and (P/Al)$_{after}$ represent the atomic ratio of P/Al in the LDH before and after the anion exchange with the counter anions, respectively.

$$D\,(\%) = \frac{(P/Al)_{before} - (P/Al)_{after}}{(P/Al)_{before}} \times 100\,(\%)$$

Characterization

XRD patterns of powder solids were recorded on a Rigaku Rint 1200 diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 0.1541$ nm) with a graphite monochromator operating at 30 kV and 100 mA. Data were collected over a 2θ range of 2°–65° with a step angle of 0.02° and a scanning speed of 2° min^{-1}. FT-IR spectra were obtained using a Bio-Rad FTS-3000MX FT-IR spectrometer in the range of 500–4000 cm^{-1} using the KBr pellet method. Differential thermal analysis/thermogravimetry (DTA/TG) was carried out using a Shimadzu DTA-50 instrument under N$_2$ flow with a heating rate of 1 K min^{-1} from room temperature to 1273 K and with α-Al$_2$O$_3$ as a reference material. Elemental analysis for Mg, Al, P, and S was conducted by ICP-AES spectrometry.

Result and discussion

Figure 1 shows the HPO_4^{2-} desorption ratio versus reaction time with the aqueous solution of OS (0.3 M). The ratio increased rapidly until around 15 h and then increased more gradually up to 48 h. Since the desorption ratio did not change for reaction times longer than 48 h, the HPO_4 desorption was considered to have reached equilibrium at this time, with an equilibrium desorption ratio of 92.0 ± 1.8%, and all further experiments were carried out for this length of time. When the HPO_4^{2-} desorption with OS was conducted a second time, the desorption ratio went to 100% and no phosphate was detected in the analysis of the anion-exchanged solid. In the current experiments it was not possible to measure the phosphate concentration in the solid phase since the mass of the LDH is changeable due to the interlayer and surface water, and drying under air. Other methods for phosphate desorption from the LDH interlayer have been reported by several researchers. The effective elution of the interlayer hydrogen phosphate has been reported when an aqueous solution of Na_2CO_3 (1.0 M) was used [22]. An NaCl–NaOH mixed solution has also been reported as another effective anion-exchanging solution to remove HPO_4 from LDH [23]. In this study, these two aqueous solutions were tested and the results are listed in Table 1 together with the result of anion exchange when using OS solution. Aqueous solutions of Na_2CO_3 (0.1 M) and NaCl
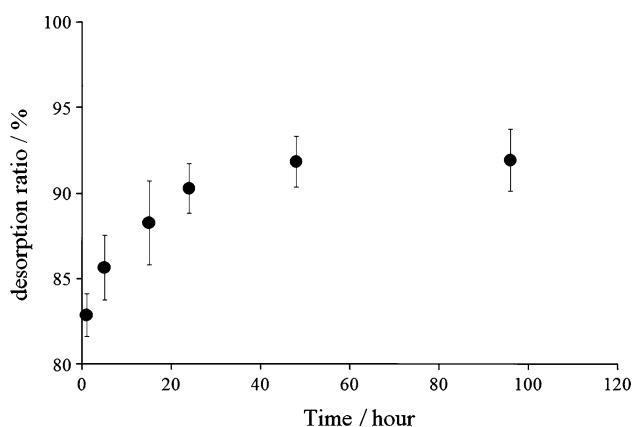

Fig. 1 Time dependence of HPO_4^{2-} desorption from LDH-HPO$_4$ with OS. The data points represent the mean of three repeat experiments with the spread in data given by the *error bars*

(5 w/v%) + NaOH (3 w/v%) were used for the elution. The Mg, Al, phosphate, and OS amounts were measured by ICP-AES and the chemical species of phosphate was determined depending on the pH of the solution. The amount of water was calculated from the mass remaining after subtraction of the above measured species. The desorption ratio D, when using OS was much higher than for the other two solutions, which removed only around 59 and 46% of the phosphate, respectively. The low D values observed for the LDH (Na_2CO_3) and LDH (NaCl + NaOH) did not increase when the reaction time was increased to 96 h.

Figure 2 shows XRD patterns of LDH-HPO$_4$, LDH (Na_2CO_3), LDH (NaCl–NaOH), LDH (OS-2), and LDH (OS-2) following heating to 1273 K. The XRD pattern of LDH-HPO$_4$ was similar to that which has been previously reported [15]. In the XRD patterns of LDH (Na_2CO_3) and LDH (NaCl–NaOH), in addition to the LDH-HPO$_4$ phase, other peaks assigned to Mg/Al/CO^3-LDH were also observed [24]. Therefore, it is concluded that both LDH (Na_2CO_3) and LDH (NaCl-NaOH) are mixtures of the pristine LDH and Mg/Al/CO$_3$-LDH. This is not due to insufficient reaction time, since increasing the time to 96 h in the desorption experiments did not increase the D value. On the other hand, the XRD pattern of LDH (OS-2) is the same as that reported previously for Cu/Al-LDH with interlayer 1-octanesulfonate [18]. All peaks in the XRD pattern of LDH (OS-2) are indexed as a single phase having a hexagonal unit cell with the $R3m$ structure of hydrotalcite and following the $-h + k + l \neq 3n$ rule. The parameters for this phase were determined as $c_0 = 6.19$ nm and $a_0 = 0.31$ nm. Table 2 shows the indexing of both LDH-HPO$_4$ and LDH (OS-2). The basal spacing calculated from the (003) diffraction peak of LDH (OS-2) was 2.05 nm, whereas that of LDH-HPO$_4$ was 1.06 nm. Thus, the interlayer spacing is increased by the intercalation of the larger OS anion. Metal phosphates were not detected in the XRD pattern of LDH (OS-2) heated at 1273 K indicating clearly that the phosphate was completely removed from the interlayer space of LDH (OS-2) due to the anion exchange of HPO_4^{2-} with 1-octanesulfonate.

Figure 3 shows FT-IR spectra of sodium 1-octanesulfonate (NaOS), LDH (OS-2), and LDH-HPO$_4$. The spectrum of NaOS shows strong absorption bands at 2957, 2920, 2873, and 2852 cm^{-1} all of which are assigned to the

Table 1 Desorption ratio of hydrogen phosphate from LDH-HPO$_4$ using different solutions

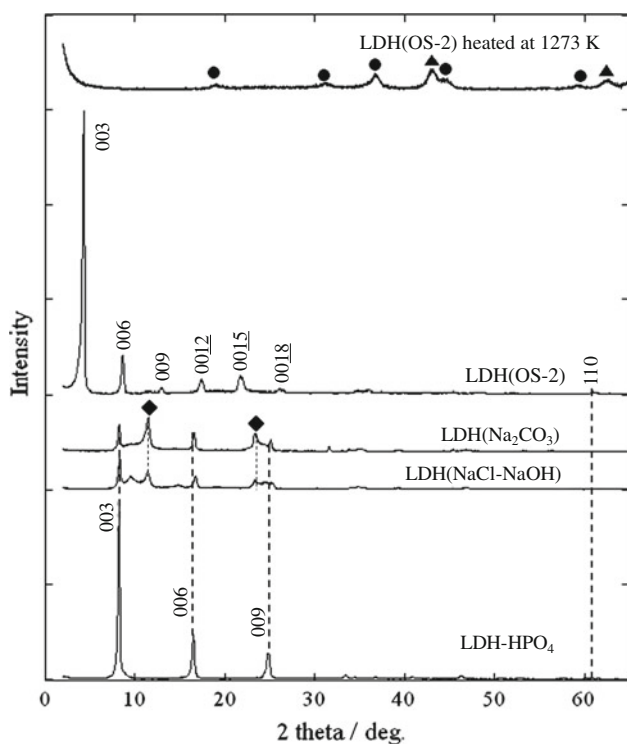| Name	D (%)	pH[a]	Chemical formula
LDH (OS-1)	93.3	9.2	$Mg_{0.65}Al_{0.35}(OH)_{2.01}(HPO_4)_{0.01}(CH_3(CH_2)_7SO_3^-)_{0.31}0.35H_2O$
LDH (OS-2)	100	9.2	$Mg_{0.65}Al_{0.35}(OH)_{2.02}(CH_3(CH_2)_7SO_3^-)_{0.33}0.29H_2O$
LDH (Na_2CO_3)	58.8	11.6	$Mg_{0.67}Al_{0.33}(OH)_{2.0}(HPO_4)_{0.04}(PO_4)_{0.03}(CO_3)_{0.12}0.68H_2O$
LDH (NaCl–NaOH)	46.4	13.4	–

[a] pH after reaction for 48 h

Fig. 2 XRD patterns of LDH-HPO₄, LDH (NaCl–NaOH), LDH (Na₂CO₃), LDH (OS-2), and LDH (OS-2) heated at 1273 K. *Circle* MgAl₂O₄, *triangle* MgO, and *diamond* carbonate intercalated Mg/Al-LDH

C–H stretching vibrations of the alkyl chains in OS [25]. The strong absorptions at 1179 and 1052 cm^{-1} are also assigned as S–O stretching vibration band in the –SO₃ group of OS [26]. These absorption bands are also detected in the spectrum of LDH (OS-2), together with some characteristic bands due to Mg/Al double hydroxide around 3340 cm^{-1} for an O–H stretching vibration and around 1650 cm^{-1} for an H–O–H bending vibration of the interlayer water molecule. In the spectrum of LDH-HPO₄, absorption bands due to the double hydroxide are observed together with both symmetrical and asymmetric absorption bands assigned as v_{as}(P–O), v_s(P–O), v_{as}(P–OH), and v_{as}(O–P–O) at 1093, 960, 844, and 563 cm^{-1}, respectively, all due to the interlayer hydrogen phosphate [27]. The spectrum indicates that the phosphate is in a similar environment to HPO_4^{2} in solution [28]. These bands of interlayer HPO_4^{2-} were not observed in the spectrum of LDH (OS-2), indicating again that the interlayer hydrogen phosphate was fully exchanged with OS. All of the absorption bands observed in the FT-IR spectra are indexed in Table 3.

It has been pointed out that anion exchange proceeds more readily when an anion with large anionic charge is used. From this point of view, divalent anions such as carbonate, phosphate and sulfonate are preferable as the

Table 2 Indexing of the XRD patterns with lattice constants of LDH-HPO₄ and LDH (OS-2)

Obs.	Calc.	
d (nm)	*hkl*	*d* (nm)
LDH-HPO₄		
1.06	0 0 3	–
0.530	0 0 6	0.527
0.356	0 0 9	0.352
0.266	0 0 12	0.265
0.259	0 1 2	0.260
0.244	0 1 5	0.244
0.221	0 1 8	0.219
0.195	0 1 11	0.194
0.180	1 0 13	0.170
0.173	0 1 14	0.172
0.160	1 0 16	0.158
0.152	1 1 0	–
0.151	1 1 3	0.151
0.147	1 1 6	0.146
a_0 (nm)	0.31	
c_0 (nm)	3.18	
LDH (OS-2)		
2.05	0 0 3	–
1.03	0 0 6	1.03
0.697	0 0 9	0.69
0.515	0 0 12	0.52
0.411	0 0 15	0.413
0.343	0 0 18	0.344
0.260	0 1 2	0.262
0.153	1 1 0	–
a_0 (nm)	0.31	
c_0 (nm)	6.19	

Underline values mean indexing number

exchanging anion in solution. This was not the case in the present study, however, since the interlayer anion used in the desorption experiment is divalent HPO_4^{2-} and the exchanging 1-octanesulfonate is a monovalent anion. The high desorption ratio when using OS may be due to the large concentration (0.3 M) of the exchanging OS in the solution. However, the basal spacing of the LDH-OS was also larger than that of LDH-HPO₄, whereas carbonate intercalated Mg/Al-LDH had a smaller basal spacing than that of the LDH-HPO₄. It is thought that increasing the interlayer spacing decreases the interaction between the interlayer phosphate and the LDH layers and enhances phosphate desorption. Thus, the ease of desorption is not necessarily dictated by the type of anion species used for the exchange, but rather the strength of the bonding between the original intercalated species and the LDH layer.
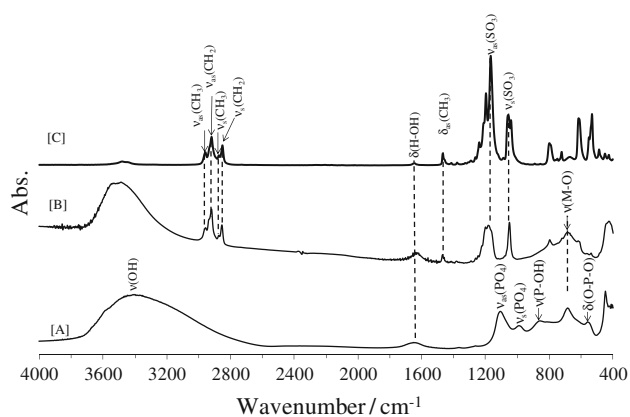
Fig. 3 FT-IR spectra of LDH-HPO$_4$ (*A*), LDH (OS-2) (*B*), and sodium 1-octanesulfonate (*C*)

Table 3 Indexing of IR absorption bands, in cm^{-1}, for LDH (OS-2), LDH-HPO$_4$, and sodium 1-octanesulfonate (Na-OS)

Na-OS	LDH-OS 2nd	LDH-HPO$_4$	Assignment
3483	3484	3400	ν(OH)
2957	2954		ν_{as}(CH$_3$)
2920	2917		ν_{as}(CH$_2$)
2873	2872		ν_s(CH$_3$)
2852	2852		ν_s(CH$_2$)
1654	1650	1650	δ(H–OH)
1470	1467		δ_{as}(CH$_3$)
1179	1180		ν_{as}(SO$_3$)
		1097	ν_{as}(PO$_4$)
1052	1048		ν_s(SO$_3$)
		975	ν_s(PO$_4$)
		840	ν_{as}(OPO)
	685	680	ν(M–O)

The high desorption efficiency observed in this work when using OS is thought then to be related to the two factors; the OS concentration and the resultant interlayer spacing when intercalating the species into the interlayer gallery. The former factor is advantageous for increasing the concentration difference of 1-octanesulfonate between the interlayer space and the aqueous solution surrounding the LDH crystalline particles, and thus increasing the driving force to intercalate OS into the interlayer space of LDH. The latter assists in propping open the interlayer spacing and thus is favorable for the exchanged hydrogen phosphate to move within the interlayer space and be eliminated from the LDH crystallite into the surrounding solution.

Conclusions

Interlayer HPO$_4$ has been completely removed from the interlayer space of LDH-HPO$_4$ by repeated anion exchange

with OS in aqueous solution at room temperature. To the author's knowledge, this is the first time that complete removal of interlayer HPO$_4$ from LDH by simple anion exchange has been observed. The anion exchange with 1-octanesulfonate is a much more efficient method to remove the interlayer hydrogen phosphate when the results are compared with existing methods using Na$_2$CO$_3$ or NaOH–NaCl solutions.

It is thought that the high removal of interlayer phosphate is due to the relatively high concentration of OS and to the fact that the interlayer spacing after intercalating with OS anions is large. This provides a driving force for the intercalation of OS and allows the hydrogen phosphate in the interlayer space to more easily move through the interlayer and be eliminated. Further investigations are needed to fully understand the mechanism of anion exchange in LDH solids using anionic surfactants.

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