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Anionic surfactant enhanced phosphate desorption from Mg/Al-layered double hydroxides by micelle formation

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ABSTRACT

Desorption of interlayer hydrogen phosphate (HPO_4) from hydrogen phosphate intercalated Mg/Al-layered double hydroxide (LDH–HPO_4) by anion exchange with surfactant anions has been investigated under controlled conditions. Three types of surfactant, Dodecylbenzenesulphonate (DBS), Dodecylsulphate (DS) and 1-Octanesulphonate (OS), anions were used for intercalation experiments over a range of concentrations, and for all solutions, it was shown that the desorption of hydrogen phosphate is enhanced at concentrations close to the critical micelle concentration (CMC). Intercalation of the surfactant anions into LDH–HPO_4 was confirmed by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning electron microscopy (SEM). More than 90% removal of the hydrogen phosphate was achieved at CMC. Repeat adsorption tests to investigate recyclability showed that desorption with 0.005 M DBS improved subsequent phosphate re-adsorption, allowing around 90% of the original adsorption over three cycles. This is much higher than when desorption was conducted using either Na_2CO_3 or NaCl–NaOH solutions, even at much higher concentrations. This study suggests potential economic and environmental advantages in using these surfactants in improving the cycling performance of LDH materials as absorbents for clean-up of water systems.

1. Introduction

Mg/Al-Layered double hydroxides (LDH) are a hydrotalcite-like compound [1], with a general composition of $Mg_{1-x}Al_x(OH)_2A_{x/n}$·$mH_2O$. The material forms positively charged layers of double hydroxide where A is a charge compensating interlayer anion with negative charge of x/n. This interlayer anion can be exchanged with anions in solution, and the anion exchange capacity of LDH is high (2–3 meq/g) and comparable to those of anion exchange resins [2]. Furthermore, LDH is found to have potential as a cost-effective adsorbent for the removal of anions from solution [3]. LDH materials have been studied for environmental applications because of their potential as absorbents for environmentally harmful species, such as arsenate, selenate, chromate and phosphate [4–7]. In particular, LDH have been studied as an adsorbent for phosphate by several researchers [8–12] since phosphate is as an essential nutrient for the growth of organisms in ecosystems and is often found in municipal and some industrial wastewaters [3]. Excess amounts of phosphate in water cause eutrophication and subsequent deterioration of water quality.

One advantage of using LDH materials compared with other absorbents is the potential for recycling by anion exchange. However, although considerable research has been reported on phosphate adsorption with LDH, few studies have addressed the desorption of phosphates by anion exchange. Carbonate, chloride and hydroxyl anions have been investigated as potential counter anions to exchange interlayer phosphate [10,13]. High concentration NaCl–NaOH or Na_2CO_3 solutions have been shown to be efficient eluting solutions for removing absorbed phosphate from LDH materials [14]. However, in order to remove the interlayer phosphate efficiently, these solutions need to be in high concentration because of the affinity between the phosphate and the LDH layer. Our previous research reported that a 1.0 M Na_2CO_3 solution and NaOH(0.5 M)–NaCl (1.0 M) solution removed 46.4% and 58.8% of the interlayer hydrogen phosphate from hydrogen phosphate intercalated LDH [15]. In contrast, repeated anion exchange with 1-Octanesulphonate (OS) succeeded in completely removing the interlayer hydrogen phosphate in Mg/Al-LDH. It was concluded that the high removal of interlayer phosphate was due to the relatively high concentration of OS and that increasing the interlayer spacing after intercalating with OS anions allows the hydrogen phosphate in the interlayer space to more easily move through the interlayer and be eliminated. However, this still required a relatively high concentration of OS solution (0.1 M). From the point of

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view of environmental burden and economics, it would be advantageous to use lower concentrations.

Surfactant anions are known to intercalate into the interlayer region of LDH materials and the intercalation results in an expansion of the interlayer spacing [16–21]. The most studied surfactant anions for intercalation into LDH are Dodecylbenzenesulphonate (DBS) and dodecylsulphate (DS) [22,23]. The interlayer spacing after intercalation of the surfactant increases to almost the same size as the surfactant chain length. One possible arrangement of the surfactant anion within the LDH interlayer region is the formation of a monolayer where the long chain axes lie perpendicular to the LDHs [24]. It is also known that the surfactants form micelles or aggregates above a certain concentration known as the Critical Micelle Concentration (CMC). The CMC is different depending on the type of surfactant, and it has been reported that the CMC of DBS and DS are independent of pH in solution between pH 7 and pH 9.

Pavan et al. reported surfactant adsorption on the surface of carbonate intercalated LDH and showed that the adsorption behaviour is divided into three or four different stages due to the multicomponent nature of the surfactant adsorptive system [25]. The first stage was characterised by non-aggregative adsorption; in other words, only unimer (i.e. surfactant monomer) ions are present at this stage. The second stage was characterised by the beginning of aggregate formation of unimers at concentrations close to the CMC. The transition between the first and the second stages occurs when the surfactant aggregates are formed more quickly. Therefore, stage 2 is characterised by a rapid increase in adsorption with concentration. The third stage was characterised by a surfactant bilayer with a consequent saturation of the surface of LDH at concentrations close to the CMC. Thus, it is expected that the aggregation of surfactant monomers results in a strong interaction between the surface of the LDH material and the surfactant anion. However, the intercalation behaviour of surfactant anion desorption depending on surfactant concentration has not been reported. In particular, DBS has a lower CMC than that of DS and OS, and so it may be that DBS has a stronger interaction with LDH at lower concentrations. Furthermore, DBS is a Linear Alkylbenzene Sulphonate (LAS) recognised for its low risk, low cost and biodegradability. Since the LDH is a potentially recyclable absorbent, methods that enhance this recyclability can improve the performance of LDH as an absorbent for water treatment applications.

In this study, the de-intercalation behaviour of interlayer hydrogen phosphate with surfactants below and above the CMC was investigated. Three types of surfactant solution were used as the counter anion to displace the interlayer hydrogen phosphate. The reported CMCs of dodecylbenzenesulphonate (DBS), dodecylsulphate (DS) and sodium octylsulphate (OS) are 0.003 M, 0.009 M and 0.1 M, respectively [26]. Surfactant intercalation was studied by Powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM).

2. Experimental

The hydrogen phosphate intercalated Mg/Al-LDH(LDH–HPO_4) was synthesised as described previously [27]. The chemical formula of LDH–HPO_4 was $Mg_{0.66}Al_{0.34}(OH)_2HPO_{0.17}$ $1.07H_2O$ with a loading of 57.3 mgP/gLDH. The desorption of hydrogen phosphate from the layered double hydroxides was carried out using a batch method. Dodecylbenzene sulphonate (DBS), Dodecylsulphate (DS) and 1-octylsulphonate (OS) were used as the counter anions in the eluting solution. A portion of LDH–HPO_4 (0.1 g) was mixed with 150 mL of the eluting solutions at 298 K. The initial concentrations of DBS, DS and OS were 0.01 M, 0.01 M and 0.02 M, respectively. The suspensions were shaken for up to 96 h. The phosphate concentration of the supernatant solution was determined by the molybdenum blue method using UV–vis spectrometry [11]. The desorption ratio of hydrogen phosphate was also investigated after 48 h at 298 K for different concentrations of the solutions from 0.0001 M to 0.4 M, and the pH of the eluting solutions was adjusted to 9.0 ± 0.2 with diluted NH_3 solution. The concentrations of anionic surfactants in the eluting solutions were determined by spectrophotometric methods using methylene blue [15]. The amount of desorbed phosphate in the elute solutions was calculated from the phosphate concentration of the eluting solution, and the desorption ratios were calculated from the following equation:

$$\mathrm{Des}(\%) = \frac{\text{amount of phosphate in elute solution/mol}}{\text{amount of phosphate in 10 mg LDH—HPO}_4\text{/mol}} \times 100$$

The potential for recyclability was assessed by measurements of phosphate adsorption following the desorption experiments with the DBS solution (0.005 M) and also using both NaCl–NaOH (1.0–0.1 M) and $NaCO_3$ (1.0 M). The HPO_4 intercalated LDH for these experiments were obtained by mixing a chloride intercalated Mg/Al-LDH with HPO_4 solution (200 mg(P)L^{-1}) at pH 9.2 ± 0.2 for 24 h. For the experiments using DBS as the elute solution, 10 mg of this phosphate intercalated LDH was mixed with 40 mL of DBS solution, and the precipitate was separated by centrifuge. Since it has been reported that the intercalated DBS in LDH was not exchanged with other anions [20,28], the intercalated DBS was removed using a cationic surfactant (e.g. N-cetyl-N,N,Ntrimethylammonium bromide, CTAB), and the LDH then ion exchanged with chloride anions. 1.0 mL of CTAB solution (0.1 M), 3 mL of NaCl solution (1.0 M) and 3 mL of chloroform were added to the precipitate, which was then shaken for 0.5 h. The precipitate was separated by centrifuge and washed with acetone. In the case of using NaCl–NaOH mixed solution or Na_2CO_3 solution as the elute solutions, 10 mg of the LDH–HPO_4 was dispersed into 40 mL of either NaCl (1.0 M)–NaOH (0.1 M) or Na_2CO_3 (1.0 M) solution for 36 h. The precipitate was separated by centrifuge and washed with deionised water.

In all cases, 10 mL of KH_2PO_4 adjusted to a pH of 9.0 was added to the precipitate and shaken for 24 h. The amount of absorbed phosphate was calculated by subtracting the phosphate concentration following the reaction from the initial concentration. The recyclability experiments were carried out three times, and the adsorption at each stage was compared with the amount of phosphate in the initial LDH–HPO_4 using the following equation in each cycle.

$$\mathrm{Ads}\ (\%) = \frac{\text{adsorbed phosphate in each cycle/mol}}{\text{amount of phosphate in 10 mg LDH—HPO}_4\text{/mol}} \times 100$$

2.1. Characterization

XRD patterns of powder solids were recorded on a Rigaku MiniFlex diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 0.1541$ nm) with a graphite monochromator operating at 30 kV and 15 mA. XRD measurement was conducted for powder samples under atmosphere at room temperature. Data were collected over a 2θ range of 2–65° with a step angle of 0.02° and a scanning speed of 2°/min. FT-IR spectra were obtained using a PerkinElmer Spectrum 100 FT-IR spectrometer in the range of 500–4000 cm^{-1} with ATR (8 line Attenuated Total Reflection) detector. SEM images were obtained using a Hitachi S-4700 scanning electron microscope with an accelerating voltage of 10 kV. Samples were attached to a glass slide and lightly coated with platinum to reduce surface charging. Chemical formulas of samples were determined by EDX and UV–vis spectroscopy.