



Layered double hydroxide–agarose composites for water treatment: carbonate contamination during the drying process



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ABSTRACT

Layered double hydroxides (LDH) are anion exchangers and have been investigated intensively as adsorbents for removal of hazardous and toxic anionic substances in water treatment. However, LDH, which are usually synthesized in the form of a powder, are often difficult to separate from suspensions in water treatment. Incorporating LDH into composite hydrogels is a strategy to avoid this difficulty: in this study, aqueous suspensions of Cl-containing LDH of high and low crystallinity were mixed with agarose solution while heating, and the mixtures were allowed to cool to form gels. However, in wet conditions, LDH would be susceptible to carbonate contamination from atmospheric CO₂. In this context, LDH–agarose composite hydrogels were synthesized, and gels dried in three different ways (air drying, oven drying in air at 110 °C, and vacuum drying) were evaluated as anion adsorbents by using SO₄²⁻. The air-dried gels showed significant reductions in SO₄²⁻ adsorption abilities compared to those of the original undried gels: 56% reduction for air-dried gels containing the low-crystallinity LDH and 29% reduction for air-dried gels containing the high-crystallinity LDH. This result shows that carbonate contamination was extremely serious for low-crystallinity LDH in the gel. In contrast, the oven- and vacuum-dried gels retained adsorption abilities that were almost the same as those of the original undried gels, regardless of crystallinity of LDH in the gels. Powdery form of LDH showed similar results about drying. These results show how important the drying methods are, and provide fundamental information about carbonate contamination.

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1. Introduction

Layered double hydroxides (LDH), which are also termed hydrotalcite-like compounds or anionic clays, are a class of lamellar compounds with exchangeable anions in their interlayer space (Cavani et al., 1991; Vaccari, 1999). Although variations exist (e.g., the Al³⁺–Li⁺ and M²⁺–M³⁺–M⁴⁺ systems), most LDH have the general formula [M²⁺_{1-x}M³⁺_x(OH)₂]Aⁿ⁻_{x/n}·mH₂O, where M²⁺ and M³⁺ are divalent and trivalent cations, and Aⁿ⁻ represents anions. Partial substitution of M³⁺ for M²⁺ induces positive charges on the metal hydroxide layers, which are counterbalanced by interlayer anions. Because of their exchangeable anions, LDH are excellent candidates for adsorbents in water treatment for removal of hazardous or toxic anionic substances such as fluoride, boron species, selenite, selenate, arsenite, arsenate, and dichromate (Goswamee et al., 1998; You et al., 2001; Ardau et al., 2013; Theiss et al., 2013; Bagherifam et al., 2014; Habuda-Stanić et al., 2014) and for removal of phosphate and nitrate that may lead to eutrophication (Das et al., 2006; Halajnia et al., 2013; Koilraj et al., 2013; Shimamura et al., 2013). LDH are usually synthesized in the form of a powder, and separating LDH from suspensions during water treatment is often difficult. To enhance the efficiency of solid–

liquid separation, granulation, which is a particle size enlargement process, has been employed (Kawamoto et al., 2003; Kuzawa et al., 2006; Murayama et al., 2013). However, the binder that glues powders together may hinder access to adsorbent powders by covering the surface of the powders or narrowing paths into the inner core of the granulated grains (Lee et al., 2001). A more sophisticated method using LDH–magnetic substance composite particles, in which magnetic cores such as Fe₃O₄ are covered with LDH, has been reported for high separation efficiency (Li et al., 2009; Chen et al., 2011, 2012). In this method, the composite particles are collected with magnets after the target anions are removed. Another strategy involves the use of macroscopic three-dimensional (3D) bodies with macropores (some of the 3D bodies also had mesopores): in this approach, LDH are formed on the surfaces of various porous substrates (e.g. cloth, paper and cotton) by a sol–gel technique or an in situ growth method (Zhao et al., 2010; Zhang et al., 2014a, 2014b), or macroporous LDH/Al(OH)₃ monoliths are synthesized by a sol–gel method (Tokudome et al., 2013). Additionally, macroscopic 3D bodies with macropores created by sacrificial polymer beads have also been used for water treatment (Géraud et al., 2006, 2008).

Fixing LDH particles in polymer hydrogels is another simple and effective method to avoid difficulty in solid–liquid separation. Hibino found that even when the LDH:agarose ratio in an LDH–agarose composite gel was 1:1 by mass, the LDH nanoplates dispersed in the agarose gel matrix exhibited an anion adsorption ability per unit weight of LDH

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equivalent to that of the powder form of LDH (Hibino, 2014a), despite the fact that such a high content of agarose was used as a binder, compared with the fact that the amount of binder was not more than 10% of the total mass in previous reports (Kawamoto et al., 2003; Kuzawa et al., 2006; Murayama et al., 2013). This result implies that agarose gel is a good binder. This high content of agarose ensured that LDH nanoplates were firmly retained inside the gels. However, hydrogels are inconvenient for storage and transportation because of their high water content. Indeed, polymer hydrogels and related materials (hydrogels with inorganic particles other than LDH) used as adsorbents for dyes or metal ions were reported, and most of them were used in the dried form (Kaşgöz and Durmus, 2008; Yi et al., 2008; Chen and Wang, 2009; Dalaran et al., 2011; Li et al., 2011; Ramírez et al., 2011; Taleb et al., 2012; Hui et al., 2014; Pandi and Viswanathan, 2015).

In the present study, dried LDH–agarose composite hydrogels were tested as a prototype of dried LDH–polymer hydrogel composites. To simplify synthesis procedures, aqueous suspensions of Cl-containing LDH were used, instead of an aqueous dispersion of delaminated LDH, which was used previously (Hibino, 2014a). Uniform dispersion of LDH particles in composite hydrogels was confirmed. After that, the LDH–agarose hybrid hydrogels were dried, and their adsorption abilities were evaluated. It is expected that polymer hydrogels such as agarose gel will swell to some extent by soaking in water even after complete drying and that adsorbates in water will penetrate into the swollen bodies. However, drying methods should be investigated for LDH. In wet conditions, contamination of LDH by CO_3^{2-} ions from atmospheric CO_2 should be considered (Iyi et al., 2008, 2011; Troutier-Thuilliez et al., 2009; Crosby et al., 2014). LDHs in composite hydrogels are in the wet condition and would be vulnerable to contamination with CO_3^{2-} ions during drying in air. Because LDH have a high affinity for CO_3^{2-} ions, it is difficult to exchange other ions for CO_3^{2-} ions. Therefore, carbonate contamination will result in a decrease of the adsorption ability of the LDH. It is uncertain how much the adsorption ability would be damaged during drying in air, and to the best of my knowledge, evaluation of carbonate contamination has not been yet evaluated systematically. Thus, various drying methods were investigated, and their effect on prevention of carbonate contamination was evaluated in this study: drying under vacuum (to exclude CO_2) and drying in air at high temperature (over the boiling temperature; to prevent dissolution of CO_2 in water) were tested, compared with air drying. In this context, the present study evaluates a new type of dried LDH–agarose composite hydrogel as an anion adsorbent and presents fundamental information about carbonate contamination; preventing carbonate contamination is important for various applications of LDH.

2. Materials and methods

2.1. Materials

All chemicals used in this study were purchased from Wako Pure Chemical Industries and were used as received. Ultrapure water produced with a Yamato Scientific Co. Autopure WR600G and an ELGA Lab Water PureLab Flex-3 was used for synthesis and all procedures.

2.2. Synthesis of suspensions of LDH

Two types of LDH aqueous suspensions, in which the LDH differed in crystallinity and size, were synthesized. For the first type, Cl-containing LDH was synthesized by a coprecipitation method. First, 3.812 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 1.509 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ($[\text{Mg}]:[\text{Al}] = 3:1$), and 3.287 g of NaCl were dissolved in water, and the total solution was made to 50 mL. This solution was added dropwise to 350 mL of stirred water at a rate of 50 mL/h, while a 2 M NaOH aqueous solution was simultaneously added dropwise to keep the pH of the mixture at 10. Subsequently, the mixture was stirred for 30 min and then allowed to stand overnight. The resulting precipitate (LDH) was vacuum filtered and

washed on a membrane filter (pore size: 0.2 μm) with water several times. The washed LDH was dispersed in water without drying. The LDH concentration was measured by drying a fixed small portion of the suspension and then weighing; then the concentration was adjusted to 20 g/L by adding a calculated amount of water (Sus-A). To ensure dispersion of the LDH, the suspensions were subjected to 5-min ultrasonic treatment twice with an ultrasonic cleaner (Iuchi VS-100, 100 W). The suspensions were stored in lidded vessels. After adjustment, the LDH concentration was remeasured by vacuum drying a fixed volume of the suspension and then weighing. The second type of LDH suspension was synthesized in the same way as described for the first type until the precipitation procedure. However, in this case, the precipitate slurry and part of supernatant (total weight 100 g) were placed in a Teflon container in a stainless steel jacketed vessel. The vessel was tightly sealed and placed in an oven at 140 °C for 24 h. After cooling to room temperature, the product was washed with water and then dispersed in water; the LDH concentration was adjusted to 20 g/L in the same way as described above, including the ultrasonic treatment (Sus-B).

2.3. Synthesis of LDH–agarose composite hydrogels

First, agarose (Agarose-H, setting point 37–39 °C [1.5%], gel strength $\geq 2600 \text{ g/cm}^2$ [1.5%], content of $\text{SO}_4 < 0.1\%$; Nippon Gene Co., Ltd.) was dissolved in water by boiling for 5 min. The amount of water required at this stage was calculated backwards from the amount of water, including water in the LDH suspension, necessary to adjust the agarose concentration to 1 wt.% at the final stage. The beaker containing the agarose solution was placed in a water bath at 70 °C, a calculated amount of LDH suspension was added, and the mixture was stirred well. The concentrations of LDH and agarose were adjusted to 1 wt.% each of the total mass. After the beaker containing the mixture was removed from the water bath, the approximate amount of water that was lost during heating was quickly added. The mixture was stirred well and then poured into a polystyrene case or a glass vessel to mold the gel: the polystyrene case was used to make about 3 mm thick gel, and the glass vessel was used to make about 20 mm thick gel. The mixture was allowed to stand and cool to room temperature, and was left overnight with the lids of the containers on. After cooling, the mixture formed a hydrogel. When Sus-A was used as the LDH suspension, the composite hydrogel was denoted as Gel-A; when Sus-B was used as the LDH suspension, the composite hydrogel was denoted as Gel-B. Agarose gel (without LDH) was prepared in a similar way.

2.4. SO_4^{2-} adsorption

The 3-mm-thick composite gels and agarose gel were cut into 3-mm cubes with a lattice of razor blades. Cut gel pieces were immersed in water for about 1 h; then the pieces were removed from the water and blotted through a 1-mm-mesh sieve to prevent direct contact of the gel pieces with the blotting paper. Some odds and ends of gels obtained during cutting were also used. When undried gels were used for adsorption tests, 1.0 g portions of the cut gel pieces were each stored in a capped bottles. To prepare dried gels, 0.6 or 1.0 g portions of the cut gels were each placed in a Teflon beaker and then dried in three ways: air drying, vacuum drying, and oven drying. For vacuum drying, the beakers containing the gel pieces were placed in a vacuum desiccators at 21–28 °C; desiccator conditions were maintained at 20 hPa by using a system consisting of a vacuum controller (Tokyo Rikakikai Co., Ltd., NVC-2000), a diaphragm vacuum pump (ULVAC Kiko Inc., DTC-21), and a cold trap (Tokyo Rikakikai Co., Ltd., UT-1000). For oven drying, the cut gel pieces in the beakers were dried in an oven at 110 °C (in air). Group of Gel-A and dried gels obtained from Gel-A were denoted as series A, and group of Gel-B and dried gels obtained from Gel-B were denoted as series B. LDH powders were prepared from Sus-A and Sus-B. Suspensions were diluted with water to 1 wt.% of LDH (equivalent to the LDH concentration in the composite hydrogels) and

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