



## Research paper

# Evaluation of anion adsorption properties of nanocomposite polymer hydrogels containing layered double hydroxides



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## ABSTRACT

The feasibility of nanocomposite polymer hydrogels as anion adsorbents was explored by using agarose-layered double hydroxide (LDH) hybrids. Also, to obtain fundamental data for possible applications such as slow drug release of more complex hybrid hydrogels such as ionic polymer–LDHs, the adsorption ability of LDH highly dispersed in an uncharged polymer, agarose, was evaluated. An aqueous colloidal dispersion of LDH containing lactate was mixed with agarose and water. Then, the mixture was boiled to dissolve the agarose and cooled to form a gel. It was confirmed by SEM that LDH nanoplates were uniformly dispersed in the resulting nanocomposite hydrogels. LDH restacked from the colloidal dispersion by evaporation of water was used for comparison. Samples were treated with an acetate-buffer/NaCl solution to replace lactate anions in LDHs with  $\text{Cl}^-$  anions and to exclude contaminating carbonate anions from LDHs. Adsorption ability for  $\text{SO}_4^{2-}$  was evaluated as the amount of adsorbed anion per unit quantity of LDH by normalizing the amounts of adsorbed anion by the Al content (mol/mol). The adsorption ability of the LDH nanoplates in the hybrid gels was lower than that of the restacked LDH when the LDH contents were low. When LDH/agarose ratio was lower, agarose polymer probably covered the LDH nanoplates more, which may have hindered anion access to the LDH nanoplates. When the LDH content was increased so that the ratio of LDH to agarose approached 1:1 by weight, the adsorption ability of the LDH nanoplates was about the same as or slightly greater than that of the restacked LDH. In addition, when LDH: agarose = 1:1, anion selectivity among  $\text{SO}_4^{2-}$ ,  $\text{I}^-$  and  $\text{HPO}_4^{2-}$  was about the same between the hybrid gel and the restacked LDH.

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## 1. Introduction

Layered double hydroxides (LDHs), which can also be called hydrotalcite-like compounds, are a class of layered compounds possessing relatively high anion exchange capacities. Due to their anion exchange properties, they are expected to be promising anion adsorbents. The anion exchange properties of LDHs arise from their structure, which can be expressed by the general formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}_{x/n}; m\text{H}_2\text{O}]$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are divalent and trivalent metal cations, respectively, A is an anion, and x usually ranges between 0.20 and 0.33. The metal hydroxide sheets are positively charged as a result of replacement of  $\text{M}^{2+}$  with  $\text{M}^{3+}$ , and the positive charge is compensated by anions in the interlayer space (Cavani et al., 1991; Evans and Duan, 2006; Vaccari, 1998, 1999). Anion uptake by LDHs has already been intensively investigated, including anion selectivity, effects of competing anions, and effects of surrounding conditions (Bravo-Suárez et al., 2004; Cavani et al., 1991; Chaparadza and Hossenlopp, 2011; Chitrakar et al., 2005; Das et al., 2003; Kuzawa et al., 2006; Lv et al., 2007; Ookubo et al., 1993; Sasai et al., 2012; Torashi et al., 2002; Wang et al., 2009). Recently, wastewater regulations have

become more strict, and the maximum allowed concentrations of hazardous ions in wastewater have become lower. One result of this trend toward stricter regulation is that the removal of hazardous ions by adsorption becomes more attractive (Jorgensen and Weatherley, 2003; X. Zhao et al., 2010).

Previously, Hibino (2010) synthesized nanocomposite polymer hydrogels in which LDH nanoplates were homogeneously dispersed in agarose gel. The hybrid gels have an interesting aspect as a 3D material: it can be easily molded into different shapes (Géraud et al., 2006, 2008; Touati et al., 2012; Y. Zhao et al., 2010). A wide variety of combinations of polymers and nanoparticles have been used to create nanocomposite polymer hydrogels, especially for development of biomaterials (Scheuñailder and Schmidt, 2009). Various properties of polymer–LDH-based hybrid gels have been also investigated: swell ratio, water absorbance, mechanical properties, and suitability for enzyme immobilization or drug release applications (Hua et al., 2012; Lee and Chen, 2004a,b, 2005, 2006; Lee and Lee, 2006; Zhang et al., 2008, 2009a,b,c, 2010). Drug release applications in particular take advantage of the anion exchange properties of LDHs. Polymer–LDH-based hybrid gels are obtained by in situ polymerization of appropriate monomers in the presence of organo-modified LDHs, or by adding LDHs to aqueous anionic polymer solutions, with gel formation subsequently induced by cooling or by the addition of appropriate cross-linking reagents

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(Hua et al., 2012; Lee and Chen, 2004a, 2006; Lee and Lee, 2006; Zhang et al., 2010). In those reports, polymers had negative charges, and the addition of LDHs affects the release rates of model drugs by changing the swelling behavior and the charge of the hybrid gels.

In the present study, the feasibility of nanocomposite polymer hydrogels as anion adsorbents was explored by using agarose-LDH hybrid gels. Agarose is an essentially uncharged polysaccharide, and the quantity of the positive charge on the LDHs is not compromised within the agarose polymer matrix. Therefore, examination of the simpler interaction between the uncharged agarose polymer and the LDHs, compared with the more complex hybrid hydrogels mentioned above, can contribute fundamental data for slow drug release. Considering these aspects, the adsorption ability of agarose-LDH nanocomposites, which possess the attractive features mentioned above, was investigated and compared with that of powdered LDHs.

## 2. Materials and methods

### 2.1. Materials

All chemicals used in this study were reagent grade, and purchased from Wako Pure Chemical Industries, Ltd., including agarose (Agarose-H, setting point 37–39 °C [1.5%], gel strength  $\geq 2600$  g/cm<sup>2</sup> [1.5%], content of SO<sub>4</sub> < 0.1%, original manufacturer Nippon Gene Co., Ltd.). The chemicals were used as received. Water purified with a Millipore ultrapurification system was used for all experiments.

### 2.2. Synthesis of LDHs

LDH containing lactate was synthesized in a similar way to that reported previously (Hibino, 2011; Jaubertie et al., 2006). First, 250 mL each of two aqueous solutions were prepared: Solution A, which contained Mg(C<sub>3</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Al(C<sub>3</sub>H<sub>5</sub>O<sub>3</sub>)<sub>3</sub> ([Mg] + [Al] = 0.1 M; Mg:Al = 3:1), and Solution B, which contained D,L-lactic acid. The amount of lactate in each solution was the same. Solution A and Solution B were mixed, and then 2 M NaOH aqueous solution was added to the mixture dropwise at a flow rate of 100 mL/h until the pH of the mixture reached 10. Subsequently, the pH was kept at 10 for 30 min by occasional addition of more 2 M NaOH aqueous solution. The resulting precipitate of lactate-containing LDH was washed with water, and then the wet LDH was dispersed in water. The LDH concentration was measured by drying and weighing a small portion of the dispersion, and it was adjusted at about 35 g/L by adding an appropriate amount of water. This procedure was repeated until the necessary amount of LDH dispersion for the experiments was obtained. The aqueous LDH dispersion was transformed into an almost transparent colloidal dispersion within several days by delamination. This aqueous colloidal dispersion was mainly used for synthesis of nanocomposite hydrogels, but some was used for preparation of a reference sample. To prepare the reference sample, the colloidal dispersion was heated at about 50 °C with stirring to evaporate water until it became a paste. Then, it was dried completely in an oven at 50 °C overnight and crushed into powder. This restacked LDH is denoted as Rstck-LDH(LCT) (Table 1).

**Table 1**  
Feed weight ratios of LDH to agarose.

Sample	Weight ratios of added components	
	LDH <sup>a</sup>	Agarose
LDH/AG-25/100(LCT)	25	100
LDH/AG-50/100(LCT)	50	100
LDH/AG-75/100(LCT)	75	100
LDH/AG-100/100(LCT)	100	100
LDH/AG-200/100(LCT)	200	100
Rstck-LDH(LCT)	100	0

<sup>a</sup> At this stage, the LDH contained lactate.

### 2.3. Synthesis of nanocomposite hydrogels

The concentration of LDH in the colloidal dispersion described in Section 2.2, which was measured by air-drying a small portion of the dispersion, was 34.3 g/L. Agarose, the LDH colloidal dispersion, and water were mixed in appropriate calculated amounts, and the mixture was boiled for 10 min to dissolve the agarose. The approximate amount of water that was lost by evaporation during boiling was quickly added to adjust the agarose content to 1% of the total mass of the aqueous mixture. The mixture was again stirred well while still hot, and then poured into polystyrene cases, used as molds to obtain gels with a thickness of about 3 mm. When the aqueous mixture cooled to room temperature, it formed a gel. The hydrogels were stored immersed in water in sealed containers. The LDH to agarose ratios of the hydrogels used in this study are listed in Table 1. The LDHs in these nanocomposite hydrogels contained lactate anions, and the nanocomposite hydrogels are denoted as LDH/AG-X/100(LCT), where LCT is lactate, AG is agarose, and X/100 is the ratio of LDH to agarose by weight (i.e., the ratio in the original mixture).

### 2.4. Adsorption experiments

The 3-mm-thick nanocomposite hydrogels, including pristine agarose gel (agarose without LDH), were cut into cubes about 3 mm to a side with a lattice of razor blades. Before the adsorption tests, the cubed hydrogels and the restacked LDH powder were treated with acetate-buffer/NaCl solution, as described by Iyi and Sasaki (2008), for two purposes: to replace the anions in the restacked LDH and in the LDHs in the nanocomposite hydrogels with chloride anions, and for decarbonation, that is, to exclude from the LDHs any carbonate anions with which they might have become contaminated during synthesis and storage. Carbonate anion has extremely high affinity for LDHs. Therefore, decarbonation treatment is necessary for adsorption of other anions. In this treatment, the equilibrium concentrations of sodium acetate, acetic acid, and sodium chloride were adjusted to 0.085, 0.015, and 1 M, respectively, taking into account the water content of the hydrogels. The volume of the solutions was set at a ratio of 10 mL per 0.015 g of LDH. The treatment was conducted at 25 °C for 24 h. After the treatment, the samples were washed with water. In the case of the hydrogels, the gels were immersed in water for at least 30 min and then the water was replaced. The ratio of water to gel (w/w) was 7:1. Before the water was replaced, the water in the spaces among the gel cubes was removed by blotting, which was done through the mesh of a sieve to prevent direct contact of the cubes with the blotting paper. This procedure was repeated five times. The nanocomposite hydrogels after acetate-buffer/NaCl treatment (abCL) are denoted as LDH/AG-X/100(abCL), and the restacked LDH after the treatment is denoted as Rstck-LDH(abCL).

A batch experiment was used to investigate the anion adsorption behavior of the gels and the restacked LDH. The adsorption tests on gels were carried out immediately after the acetate-buffer/NaCl treatment. The gels were weighed as soon as the water in which they had been stored or washed was removed by blotting in the same way as mentioned earlier. In the experiment, specific aliquots of adsorbents (i.e., gels or restacked LDH powder) were contacted with aqueous salt solutions of Na<sub>2</sub>SO<sub>4</sub>, NaI or Na<sub>2</sub>HPO<sub>4</sub> in capped bottles at 25 °C, with occasional shaking. After specific periods of time, the mixtures were filtered through syringe filters (pore size = 0.2 μm), and the anion concentrations in the filtrates were measured with a Dionex ICS-1500 ion chromatography (IC) system. Solutions containing high concentrations of salt were diluted before the IC measurement. Anion uptakes were calculated from the decreases in the anion concentrations compared with those of the initial solutions. In the case of gels, the amount of water was also taken into account: the water content of the gels was measured by the weight difference before and after the gels were air-dried.

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