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Preparation of a composite material for the uptake of bisphenol A from aqueous solutions, the dodecylsulfate ion-intercalated Mg–Al layer-structured double hydroxide particles

T. Kameda*, M. Saito, Y. Umetsu

Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 1-1 Katahira, 2-Chome, Aoba-ku, Sendai 980-8577, Japan

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Abstract

The preparation of Mg–Al layer-structured double hydroxide (Mg–Al LDH) particles equipped with the function of an organic acid has been attempted by modifying the interlayer with dodecylsulfate ion (DS^-). Mg–Al LDH, which had DS^- intercalated in the interlayer, was synthesized by the dropwise addition of a solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ to an aqueous solution of sodium dodecylsulfate at a constant pH of 10.0. The DS^--modified Mg–Al LDH particle was found to have an uptake capacity for bisphenol A in an aqueous solution. This indicates that the function of DS^- as an organic material was adequately maintained in the interlayer of the Mg–Al LDH. The uptake capacity increased with the increasing content of DS^- intercalated in the interlayer. The bisphenol A uptaken by the DS^--intercalated Mg–Al LDH was confirmed to be extracted with ethanol. The DS^--intercalated Mg–Al LDH treated by the ethanol had a bisphenol A uptake capacity comparable to that of fresh LDH. These results indicate that DS^--intercalated Mg–Al LDH retains its activity during repeated cycles of the uptake and ethanol extraction of bisphenol A.

Keywords: Mg–Al layer-structured double hydroxide; Dodecylsulfate ion; Modification; Uptake; Bisphenol A

1. Introduction

Recently, the contamination of effluents and water in our environment with hazardous organic materials has become more serious and a great deal of effort has been made to develop water-cleaning technology and materials usable for this purpose. It is generally known that the toxic organic contaminants including PCB (polychlorinated biphenyls), dioxin, fran and other so-called endocrine disruptors and organic halides have low solubility in water. For effective elimination of toxic organic materials from aqueous environments, the development of an adsorbent or absorbent for these materials at fairly low concentration is an urgent requisite. Some types of oils are candidates for the role of scavengers. The sufficiently frequent contact of the contaminants with these oils will require an energy intensive process, the dispersion of the oil droplets of adequately small size, which is coupled with the oil–water phase separation. In order to overcome this problem, the primary objective of this series of studies is to investigate the use of solid particles modified with organic materials that perform the function of picking up the target organic contaminant. Solids of this type are expected to enable us to handle the solid particles housing the oily and viscous organic materials and even the water-soluble materials in their structure.

The first attempt was the formation of layer-structured hydroxide particles holding an organic substance with the desired functions in their interlayers. Hydrotalcite, Mg–Al layer-structured double hydroxide (Mg–Al LDH) is well-known as having intercalation ability for anionic entities to neutralize the excess positive electric charge due to

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* Corresponding author. Tel.: +81 22 217 5148; fax: +81 22 217 5148.
E-mail address: kameda@tagen.tohoku.ac.jp (T. Kameda).

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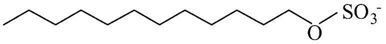
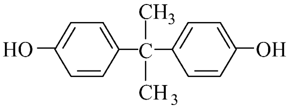
Table 1
Chemical formulas and structures of dodecylsulfate ion and bisphenol A

	Chemical formula	Structure
(a) Dodecylsulfate ion	$C_{12}H_{25}O_4S^-$	
(b) Bisphenol A	$C_{15}H_{16}O_2$	

replacement of some Mg^{2+} with Al^{3+} in their $Mg(OH)_2$-type host lattice [1–3]. The absorptions of the anions, $AsO_4{}^{3-}$, Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$, F^-, $BO_3{}^{3-}$, $CO_3{}^{2-}$, phosphate, phenols and some anionic surfactants with moderately calcined hydrotalcite-like Mg–Al compounds have been investigated [4–14]. When anionic organic acid species are intercalated into the interlayers of the double hydroxide, they remain functional; the chemically modified hydroxide can be an effective scavenger for the organic contaminants in the aqueous effluents.

This paper will present the results of our first attempt to build up the absorbent, using dodecylsulfate ion (Table 1(a)) as an organic acid anion to be intercalated, for bisphenol A (Table 1(b)), representing a series of phenols, with an emphasis on the following aspects:

1. how can the anionic organic acid be intercalated into the interlayers of Mg–Al LDH (Mg/Al mole ratio = 3)?
2. how well can the organic acids be maintained functional?
3. how does this chemically modified double-hydroxide particles pick up the organic contaminants?

2. Experimental

All the reagents used were of chemical reagent grade (Wako Pure Chemical Industries, Ltd., Japan).

2.1. Synthesis

DS·Mg–Al LDHs ($Mg_{0.75}Al_{0.25}(OH)_2(CH_3(CH_2)_{11}OSO_3)_{0.25}$) were prepared by dropwise addition of a Mg–Al solution to an SDS solution at a constant pH of 10.0. The co-precipitation reaction can be expressed by Eq. (1), where a stoichiometry of 0.25 for $CH_3(CH_2)_{11}OSO_3{}^-$, DS^-, to be intercalated is calculated based on the neutralization of the excess electric charge of the host lattice due to the replacement of Mg^{2+} with Al^{3+} at the Mg/Al mole ratio of 3.

$$0.75Mg^{2+} + 0.25Al^{3+} + 2OH^- + 0.25CH_3(CH_2)_{11}OSO_3{}^- \rightarrow Mg_{0.75}Al_{0.25}(OH)_2(CH_3(CH_2)_{11}OSO_3)_{0.25} \quad (1)$$

The Mg–Al solution (0.15 M $Mg(NO_3)_2$ + 0.05 M $Al(NO_3)_3$) with the Mg/Al mole ratio of 3.0 was prepared by dissolving $Mg(NO_3)_2 \cdot 6H_2O$ (37.5 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (12.5 mmol) together in 250 ml of deionized water. The SDS solutions were also prepared by dissolving the required amount of sodium dodecylsulfate (SDS, $CH_3(CH_2)_{11}OSO_3Na$) in 250 ml of deionized water.

The Mg–Al solution was dropwise added to the SDS solution at a rate of 10 ml/min at 30 °C under mild agitation. The solution pH was adjusted to 10.0 by addition of 0.5 M NaOH solution using a pH-stat. After the addition of the Mg–Al solution, the resultant suspension was kept standing at 30 °C for 1 h. DS·Mg–Al LDH particles were prepared by filtering the resultant suspension and washing the particles repeatedly with deionized water and then drying at 80 °C for 40 h. Nitrogen (N_2) was bubbled into the solution throughout the operation to minimize the error caused by CO_2 in the air.

2.2. Property of DS·Mg–Al LDH particles

2.2.1. Uptake of bisphenol A from an aqueous solution

In order to confirm the properties of the prepared DS·Mg–Al LDH particles, the uptake of bisphenol A from an aqueous solution by the LDH has been investigated. One hundred milligrams of DS·Mg–Al LDH was added to 20 ml of 100 mg/l bisphenol A solution and shaken at 20 °C for 10–360 min. The resulting suspension was filtered, and the filtrate was analyzed for bisphenol A. The $CO_3{}^{2-}$-intercalated Mg–Al LDH (CO_3·Mg–Al LDH) with Mg/Al mole ratio 3.0 was also used in this experiment as a reference material to demonstrate the effect of the interlayer anion.

2.2.2. Ethanol extraction of bisphenol A uptaken by DS·Mg–Al LDH

One hundred milligrams of the bisphenol A-loaded DS·Mg–Al LDH was suspended in 5 ml of 0–99.5% ethanol solution at 20 °C for 5 min, and the extraction of bisphenol A by ethanol solution was determined. Furthermore, DS·Mg–Al LDH treated with 99.5% ethanol solution was investigated for the uptake capacity of bisphenol A from an aqueous solution by suspension in 20 ml of a 100 mg/l bisphenol A solution at 20 °C for 180 min.

2.3. Characterization methods

DS·Mg–Al LDHs, the bisphenol A-loaded DS·Mg–Al LDH, the ethanol-treated DS·Mg–Al LDH and CO_3·Mg–Al LDH were submitted to X-ray diffraction (XRD) analysis by Cu Kα radiation. In order to investigate the formation of the