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Continuous Treatment of Bisphenol A and Diethyl Phthalate Solutions Using Dodecylsulfate-Intercalated Mg-Al Layered Double Hydroxide Particles Packed in Column

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Dodecylsulfate ion (DS^-)-intercalated Mg-Al layered double hydroxide (DS·Mg-Al LDH) particles packed in a column has been investigated to continuously treat bisphenol A and diethyl phthalate solutions. The effluents obtained by passing bisphenol A and diethyl phthalate solutions through the column are constantly measured by using a photomultiplier detector in order to analyze residual bisphenol A and diethyl phthalate.

During the flow of bisphenol A and diethyl phthalate solutions, no absorbance was detected in the effluents for a certain amount of time. This suggests that bisphenol A and diethyl phthalate were continuously taken up by the DS·Mg-Al LDH particles in the column due to the hydrophobic interactions with intercalated DS^- until the shortage of its accommodation in the interlayer of the LDH. DS^- was rigidly fixed in the interlayers of DS·Mg-Al LDH during the flow of bisphenol A and diethyl phthalate solutions. Furthermore, the cycle of the uptake of bisphenol A from an aqueous solution and the elution of taken-up bisphenol A by ethanol was repeated by the alternately passing bisphenol A solution and ethanol through the column until the column ruptured by the swelling of the DS·Mg-Al LDH particles.
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1. Introduction

Mg-Al layered double hydroxide (Mg-Al LDH) is an inorganic compound with a layered structure and exhibits anion-exchange property.[1–3] Its basic chemical composition is expressed as $[Mg^{2+}{}_{1-x}Al^{3+}{}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, where x is the Al/(Mg + Al) mole ratio and A^{n-} indicates an anion with a valency of n. Its crystal structure consists of positively charged brucite-like octahedral hydroxide layers containing Al at Mg-sites, which are electrically neutralized by the interlayer anions, and water molecules in the hydration shell of the intercalated anions occupying the remaining interlayer space. Recently, the use of Mg-Al LDH as a scavenger to treat wastewater bearing anionic contaminants has been investigated. Mg-Al LDH is known to function as an effective anion exchanger in the removal of phosphate.[4–6] The uptake of phenols, anionic surfactants, and colored organics from aqueous solutions has also been examined.[7–11] Based on the anion exchange characteristics of Mg-Al LDH to intercalate various types of organic and inorganic anions in interlayers, we have carried out a series of experiments to develop organic-inorganic composite materials by intercalation of organic anions having functional groups in their structure into the interlayers of Mg-Al LDH.[12–15] Due to the action of the functional groups of the organic anions, the materials are expected to selectively take up and collect both inorganic and organic contaminants present at low concentrations in aqueous solutions. This method enables us to handle water-soluble or liquid materials in the form of solid particles and is expected to aid the preparation of various types of composite materials.

For example, Mg-Al LDH intercalated with ethylenediaminetetraacetate (EDTA) anions was found to rapidly and selectively take up heavy-metal ions from aqueous solutions due to the formation of an EDTA-metal complex in the interlayers.[12] Furthermore, DS·Mg-Al LDH, which has dodecylsulfate ions (DS^-) intercalated in the interlayers of Mg-Al LDH, was reported to take up bisphenol A from an aqueous solution in a batch-type operation in our previous study.[13] Bisphenol A once taken-up by DS·Mg-Al LDH was eluted by ethanol. After the ethanol treatment, DS·Mg-Al LDH showed a bisphenol A uptake behavior as well as that of fresh LDH.

It is expected that practical water cleaning processes should be able to continuously treat wastewater contaminated with hazardous organic compounds at an acceptable flow rate. This can be certainly achieved by passing wastewater through a column containing absorbents. In this study, firstly, the uptake of bisphenol A and diethyl phthalate dissolved in an aqueous solution using the DS·Mg-Al LDH particles and the elution by ethanol solution in batch-type operation have been studied. The test solution containing bisphenol A or diethyl phthalate and ethanol are alternately passed through a DS·Mg-Al LDH particle column (length = 48 mm, inner diameter = 4.6 mm) in order to examine the cycles of uptake of bisphenol A and elution of taken-up bisphenol A by ethanol.

2. Experimental

2.1 Materials

All the reagents used were of the chemical reagent grade (Wako Pure Chemical Industries, Ltd., Japan). DS·Mg-Al LDH was prepared by the coprecipitation reaction described in our previous paper.[13] The prepared DS·Mg-Al LDH contained 13.6 mass% of Mg, 5.1 mass% of Al, and

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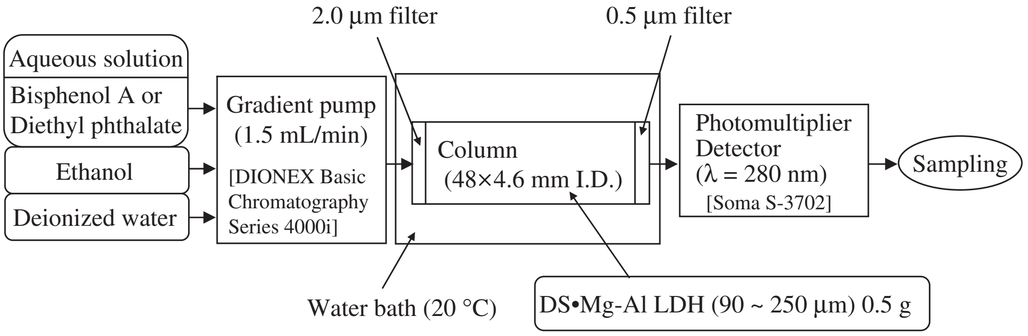

Fig. 1 General flow of experimental operation.

47.8 mass% of DS. The calculated Mg/Al and DS/Al mole ratios were 3.0 and 1.0, respectively. These indicate that the prepared Mg-Al LDH had the designed composition and the positive charge of the host lattice was neutralized by the intercalation of the DS^- ion into the interlayers. DS·Mg-Al LDH was then sieved to obtain a fraction of particles with diameter of 90–250 μm.

2.2 Treatment of bisphenol A and diethyl phthalate by DS·Mg-Al LDH particles in batch-type operation

In order to examine the uptake of bisphenol A and diethyl phthalate in an aqueous solution by the DS·Mg-Al LDH particles, 0.1 g of DS·Mg-Al LDH was added to 20 mL of 100 mg/L bisphenol A or diethyl phthalate solution and shaken at 20 °C for holding times ranging from 10 to 180 min. For the elution of bisphenol A or diethyl phthalate, 0.1 g of the DS·Mg-Al LDH loaded in advance with bisphenol A or diethyl phthalate was suspended in 5 mL of 0–99.5 vol% ethanol solutions at 20 °C for 5 min. Furthermore, DS·Mg-Al LDH treated with 99.5 vol% ethanol solution was suspended again in the solution of the bisphenol A or diethyl phthalate. The resulting suspensions were filtered, and the filtrates were analyzed for the residual bisphenol A and diethyl phthalate spectrometrically at the wavelengths of 225 and 275 nm, respectively.

2.3 Continuous treatment of bisphenol A and diethyl phthalate solutions by DS·Mg-Al LDH particles packed in column

The test solution was passed through the column containing DS·Mg-Al LDH particles in order to investigate the cycles of uptake of organic contaminant by the particles, elution of the taken-up contaminants by ethanol, and washing of the column content with deionized water. Figure 1 gives the general flow of the experimental operation. The test solution containing bisphenol A or diethyl phthalate, ethanol, or deionized water was passed through the column at a rate of 1.5 mL/min at 80 psi using a gradient pump according to the designed pattern of flow. The column packed with fine particles of the adsorbent produced a high pressure drop and a high operation pressure was applied to maintain designed flow rates. The volume of the column was 0.8 mL, and the space velocity was calculated to be 112.5 h^{-1} under the conditions in this study. The column was filled with 0.5 g of the DS·Mg-Al LDH particles and maintained at 20 °C using a water bath. Metal filters with pore diameters of 2.0 and 0.5 μm were placed at top and bottom of the column to hold the particles. Residual bisphenol A or diethyl phthalate in the effluent from the column was continuously monitored at a wavelength of 280 nm using the photomultiplier detector. The effluent was also sampled at each stage. The pH of the sample solution was measured, and dissolved Mg^{2+} was analyzed by the inductively coupled plasma-atomic emission spectrometry (ICP-AES). Furthermore, before and 300 min after the flow of bisphenol A and diethyl phthalate solutions the DS·Mg-Al LDH particles were subjected to an X-ray diffraction (XRD) analysis by CuKα radiation in order to investigate the change in the particles taking place during the repeated cycles of the operation.

3. Results and Discussion

3.1 Treatment of bisphenol A and diethyl phthalate by DS·Mg-Al LDH particles in batch-type operation

We have already confirmed the uptake of bisphenol A dissolved in an aqueous solution by the DS·Mg-Al LDH particles in a batch-type operation.[13] The interaction of diethyl phthalate dissolved in an aqueous solution with DS·Mg-Al LDH in a batch-type operation has been examined for the first time in this study. The results are summarized as follows. Figure 2 shows the variation in the concentrations of bisphenol A and diethyl phthalate with time when the DS·Mg-Al LDH particles are suspended in the solutions. The concentration of bisphenol A decreases very rapidly from 100 to 10 mg/L in the first 30 min, after which it is almost constant until 180 min. The concentration of diethyl phthalate also decreases very rapidly from 100 to 20 mg/L in the first 30 min, after which it continues to decrease gradually. It has been proved that DS·Mg-Al LDH can take up hazardous organic compounds such as bisphenol A and diethyl phthalate dissolved in an aqueous solution. Mg-Al LDH intercalated with CO_3^{2-}, whose interlayer is not intercalated with organic acid anions, is known to have considerably less activity for the uptake of hazardous organic compounds.[13] Therefore, the uptake of bisphenol A and diethyl phthalate by the DS·Mg-Al LDH particles in the column is attributed to the hydrophobic interactions between intercalated DS^- and the hazardous organic compounds originally dissolved in the aqueous solution. This indicates that DS^- effectively functions as an organic material even when intercalated in the interlayers of Mg-Al LDH. At 180 min, the uptake of bisphenol A and diethyl phthalate in Mg-Al LDH reaches 18

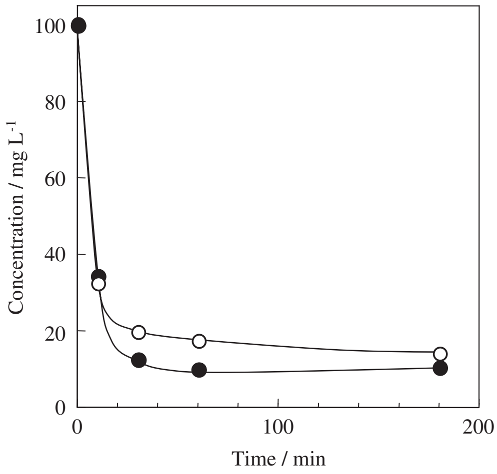

Fig. 2 Variation in concentrations of bisphenol A (●) and diethyl phthalate (○) with time when DS·Mg-Al LDH particles are suspended in solutions.

Table 1 Effect of ethanol concentration on elution of bisphenol A taken up by DS·Mg-Al LDH.

Ethanol concentration (vol%)	Elution (%)
0	5
25	32
50	87
99.5	97

Table 2 Comparison of uptake capacity of DS·Mg-Al LDH and ethanol-treated DS·Mg-Al LDH for bisphenol A and diethyl phthalate dissolved in aqueous solution.

(mg/L)

	Bisphenol A	Diethyl phthalate
DS·Mg-Al LDH	10.2	13.9
Ethanol-treated DS·Mg-Al LDH	10.1	10.3

Initial concentration 100 mg/L, 180 min

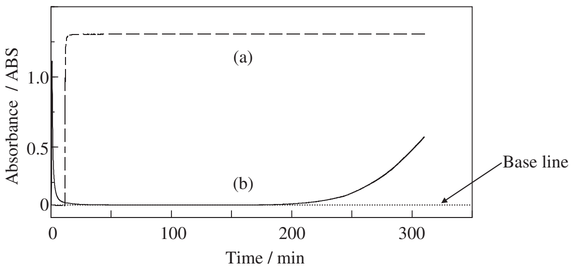

Fig. 3 Variation in absorbance ($\lambda = 280$ nm) observed using photomultiplier detector for (a) flow of 100 mg/L bisphenol A solution without column and (b) effluent from column containing DS·Mg-Al LDH particles. Initial pH = 5.2

and 16 mg/g LDH, respectively. In the next series of experiment, DS·Mg-Al LDH loaded with bisphenol A and diethyl phthalate is suspended in ethanol solutions of different concentrations. Table 1 presents the effect of ethanol concentration on the elution of bisphenol A taken up by DS·Mg-Al LDH. The degree of elution increases with the ethanol concentration and is as high as 97% in 99.5 vol% ethanol solution. In the case of diethyl phthalate, the degree of elution is 87% in 99.5 vol% ethanol solution. These observations demonstrate that bisphenol A and diethyl phthalate taken up by DS·Mg-Al LDH are easily eluted by ethanol solution of concentration exceeding 50 vol%. DS·Mg-Al LDH treated with 99.5 vol% ethanol solution is suspended again in bisphenol A and diethyl phthalate solutions to examine its activity. Table 2 shows the comparison of the uptake capacity of DS·Mg-Al LDH and ethanol-treated DS·Mg-Al LDH for bisphenol A and diethyl phthalate dissolved in the aqueous solution. The concentrations of residual bisphenol A and diethyl phthalate in ethanol-treated DS·Mg-Al LDH are low and at almost similar level as compared to the results with fresh DS·Mg-Al LDH. This indicates that the activity of DS$^-$ intercalated in the LDH stays unchanged during the cycles of uptake and ethanol elution of bisphenol A and diethyl phthalate.

3.2 Continuous uptake of bisphenol A and diethyl phthalate from aqueous solution by DS·Mg-Al LDH particles packed in column

The next series of experiments are conducted to examine the rate of the uptake and ethanol elution of the hazardous organic compounds with the DS·Mg-Al LDH particles packed in the column. In the column experiment, the progress of uptake and ethanol elution is observed continuously using a photometric method. In this study, the contact between intercalated DS$^-$ and the hazardous organic compounds dissolved in the aqueous solution is limited to the interlayer space at the particle surface. The geometrical limitations are considered to have significant effect on the uptake of the hazardous organic compounds into the interlayer, i.e., the organic layer of Mg-Al LDH. One of the objectives of the column experiment is to understand the above mentioned effect, i.e., to determine how quickly the organic contaminants can be eliminated from the aqueous solution and eluted by ethanol solution at the contact sites between two phases.

The baseline for this column test system was recorded using deionized water. Deionized water was passed through the column for 10 min to clean the column and to monitor the system. Then, bisphenol A and diethyl phthalate solutions were fed to the column. Figure 3 presents the variation in the absorbance ($\lambda = 280$ nm) observed using the photomultiplier detector for the flow of 100 mg/L bisphenol A solution without the column and that for the effluent from the column containing DS·Mg-Al LDH particles. In the absence of the column (Fig. 3(a)), no absorbance was detected during the first 10 min of deionized water flow. The line until 10 min shown in Fig. 3(a) is hereafter referred as the baseline. Immediately after the flow of bisphenol A solution, the absorbance quickly increases to a value corresponding to the concentration of bisphenol A and remains constant. This proves that the bisphenol A in aqueous solution is continuously monitored with a high sensitivity at the detector. On passing deionized water through the column containing DS·Mg-Al LDH particles (Fig. 3(b)) for 10 min, the absorbance rapidly increases and immediately decreases down to the base line. The rapid increase in the absorbance may be

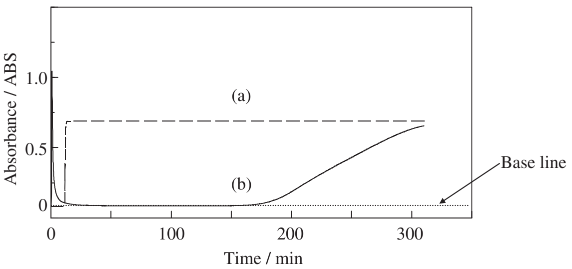

Fig. 4 Variation in absorbance ($\lambda = 280\,\mathrm{nm}$) observed using photomultiplier detector for (a) flow of 100 mg/L diethyl phthalate solution without column and (b) effluent from column containing DS·Mg-Al LDH particles. Initial pH = 5.6

attributed to the dissociation of molecular sodium dodecyl sulfate (SDS) dissolved in the intercalated DS^- medium in DS·Mg-Al LDH due to the hydrophobic interactions. As a result, the DS·Mg-Al LDH particles in the column is required to be washed initially with water in order to remove SDS from the LDH. After the first 10 min (Fig. 3(b)), when bisphenol A is passed through the column, the measured absorbance stays on the base line for 200 min, i.e., the concentration of bisphenol A in the effluent is less than the detection limit of the detector used in this study (0.1 mg/L). This elimination of bisphenol A was observed for the effluent of volume of 356 times that of the column. This suggests that bisphenol A has been taken up by the DS·Mg-Al LDH particles during its flow through the column. However, the absorbance gradually increases after 200 min, indicating the presence of bisphenol A in the effluent. This is considered to reflect the gradual decrease in the accommodation space for bisphenol A in the interlayers of DS·Mg-Al LDH with time, approaching a break through point, 260 min, at which the concentration reaches to 10 mg/L. After all, the column is possible to be used for the treatment of bisphenol A solution for 260 min under the conditions in this study. In Fig. 4, the variation in the absorbance ($\lambda = 280\,\mathrm{nm}$) of effluent obtained by the flow of 100 mg/L diethyl phthalate solution through the column containing the DS·Mg-Al LDH particles is compared with that for the flow of deionized water for the first 10 min followed by the phthalate solution without the column. Similarly to the case of the flow of bisphenol A solution, the absorbance is equal to the baseline until 170 min for the column effluent (Fig. 4(b)), indicating that the concentration of diethyl phthalate in the effluent is less than the detection limit (0.1 mg/L) for the effluent of volume of 300 times that of the column. The diethyl phthalate has been almost completely taken up by the LDH particle. However, the absorbance gradually increases after 170 min, reaching to a break through point (10 mg/L) in 195 min. This implies that the column is used for the treatment of diethyl phthalate solution for 195 min under the conditions in this study.

For the experiment in the batch-type operation shown in Fig. 2, 0.1 g of the DS·Mg-Al LDH, which was determined to hold 47.8 mg (1.8×10^{-4} mol) of DS^- in the interlayer, was able to take up 7.9×10^{-6} mol of bisphenol A and 7.2×10^{-6} mol of diethyl phthalate when DS·Mg-Al LDH was suspended for 180 min. The mole ratios of intercalated DS^- to taken-up bisphenol A and diethyl phthalate were calculated to be 23 and 25, respectively, indicating that a large excess amount of DS^- was required to remove bisphenol A and diethyl phthalate dissolved in the aqueous solution. In the column experiment, bisphenol A and diethyl phthalate were continuously taken up from the aqueous solution for approximately 190 and 160 min, respectively. In this case, 5.7 mg, i.e., 2.5×10^{-5} mol, of bisphenol A and 4.8 mg, i.e., 2.2×10^{-5} mol, of diethyl phthalate were taken up by 0.1 g of DS·Mg-Al LDH. The mole ratios of intercalated DS^- to taken-up bisphenol A and diethyl phthalate were calculated to be 7 and 8, respectively, which were considerably smaller than 23 and 25 obtained in the batch-type operation. The LDH with intercalated DS^- in the column-type operation performed larger accommodation for bisphenol A and diethyl phthalate as compared to in the batch-type operation. As compared to the batch-type operation, in the column-type operation the unsaturated LDH could work continuously with fresh solution of bisphenol A and diethyl phthalate flowing through the column at a rate of 1.5 mL/min. In the microscopic scale, the uptake of the hazardous organic compounds dissolved in the aqueous solution by intercalated DS^- in the interlayers was considered to take place at the interlayer space extruded to the surface of the DS·Mg-Al LDH particles. This transfer was more effective in the column-type operation than in the batch-type operation. Inside the column, the particles near the top of the column were in contact with a fresh solution and the concentration of the target organic material decreased toward the bottom of the column. In other words, a mass transfer zone was formed at the region where the uptake of the target material took place, and this zone shifted toward the bottom of the column with time. As a result of this process, the organic layers of Mg-Al LDH were free from the geometrical limitations, which negatively affected the uptake of hazardous organic compounds into the interlayer in the batch-type operation. Hence, the column-type operation was comparatively more effective than the batch-type operation for the treatment of bisphenol A and diethyl phthalate solutions.

The variations in the pH and Mg^{2+} concentrations of the effluents from the column containing DS·Mg-Al LDH particles for bisphenol A and diethyl phthalate solutions are shown in Figs. 5 and 6. In both cases, the Mg^{2+} concentration is low at each stage. The pH values increase immediately after the start of flow, from the initial values of 5.2 and 5.6 to a value close to 7.0, and then remain distributed between 6.0 and 8.0. These results indicate the dissolution of Mg^{2+} from the brucite-like octahedral host layers containing Al in DS·Mg-Al LDH during the flow of deionized water, bisphenol A solution, and diethyl phthalate solution. The effluents are acceptable in the water quality standard in Japan ($5 < \mathrm{pH} < 9$; Mg^{2+} is not listed there), while the LDH particles will be chemically attacked in the aqueous solution of pH around 5.5, only slightly. The XRD patterns of DS·Mg-Al LDH before and after the flow of bisphenol A or diethyl phthalate solution for 300 min are compared in Fig. 7. Since the XRD peaks of Mg-Al LDH are generally indexed on the basis of a hexagonal unit cell, the basal spacing of Mg-Al LDH is equivalent to $1/n$ of the c parameter, where n is the number of layers in the unit cell.[16] The basal spacing is the

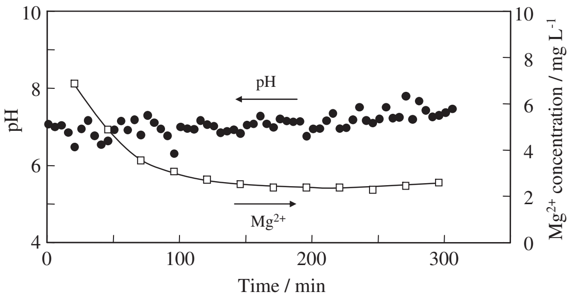

Fig. 5 Variation in pH and Mg^{2+} concentration of effluent from column containing DS·Mg-Al LDH particles for bisphenol A solution. Bisphenol A concentration = 100 mg/L, Initial pH = 5.2

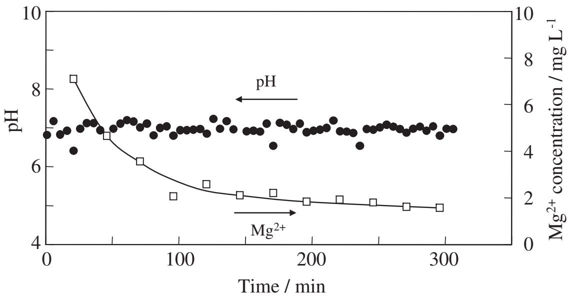

Fig. 6 Variation in pH and Mg^{2+} concentration of effluent from column containing DS·Mg-Al LDH particles for diethyl phthalate solution. Diethyl phthalate concentration = 100 mg/L, Initial pH = 5.6

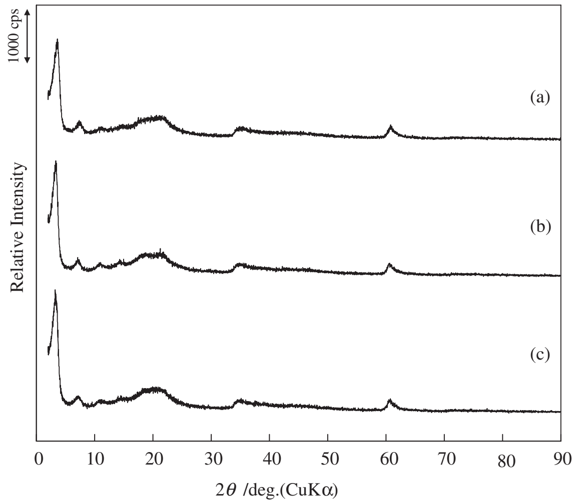

Fig. 7 XRD patterns for DS·Mg-Al LDH (a) before and after 300 min of flow of (b) bisphenol A and (c) diethyl phthalate solutions.

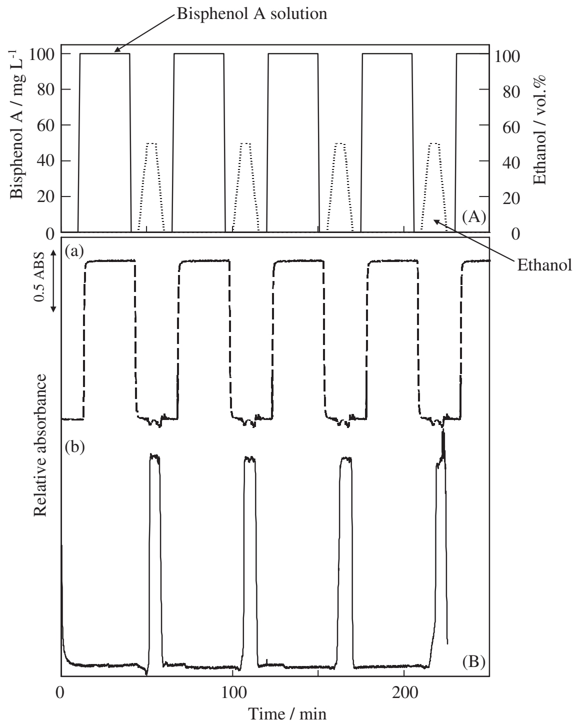

Fig. 8 (A) Designed pattern for alternate flow of bisphenol A solution and ethanol with flow rate of 1.5 mL/min.
(B) Variation in absorbance (λ = 280 nm) of effluent obtained by alternate flow of bisphenol A solution and ethanol (a) without column and (b) through column containing DS·Mg-Al LDH particles.

sum of the thickness of the brucite-like octahedral layer containing Al and the interlayer spacing depending on the size and orientation of the interlayer anions. In the XRD patterns of untreated DS·Mg-Al LDH presented in Fig. 7(a), the diffraction peak for the 2θ value of around 3.5° represents the basal spacing of Mg-Al LDH, demonstrating that DS^- with long alkyl chains is intercalated in the interlayers of Mg-Al LDH.[13] The other two XRD patterns presented in the figure are almost similar to those for untreated DS·Mg-Al LDH; no significant shift in the diffraction peak for the 2θ value of around 3.5° is observed before and after the flow of bisphenol A and diethyl phthalate solutions. This suggests that the configuration of intercalated DS^- is not detectably affected by bisphenol A and diethyl phthalate which are taken up from the solution, i.e., DS^- is rigidly fixed in the interlayers of DS·Mg-Al LDH; consequently, the interlayer spacing remains unchanged even after the introduction of the second organic materials. Thus, the stability of DS·Mg-Al LDH has been found to be high for bisphenol A and diethyl phthalate solutions, although small amounts of Mg^{2+} have been dissolved from LDH in this study.

3.3 Continuous treatment of bisphenol A solution by DS·Mg-Al LDH particles packed in column

Bisphenol A solution and ethanol were alternately passed through the column containing DS·Mg-Al LDH particles in order to investigate the possibility of continuous treatment, consisting of the cycle of uptake of bisphenol A from the aqueous solution and ethanol elution of taken-up bisphenol A.

The designed pattern of the alternate flow of bisphenol A solution and ethanol is presented in Fig. 8(A). This figure represents a series of the flow of deionized water for 0–10 min, 100 mg/L bisphenol A solution for 10–40 min, and deionized water for 40–45 min, and ethanol solution for 45–60 min to elute bisphenol A from the DS^- layer. The maximum ethanol concentration has been set at 50 vol% because bisphenol A taken up by DS·Mg-Al LDH is easily eluted with a solution of ethanol of concentration above 50 vol% in the batch-type operation, as shown in Table 1. In the ethanol elution stage, the ethanol concentration increases toward 50 vol% at 10 vol%/min during the first 5 min and is maintained constant at 50 vol% for the following 5 min. Then, for the last 5 min the concentration decreases to 0 vol% at a constant rate of 10 vol%/min. After the flow of deionized water for 60–65 min, 100 mg/L bisphenol A solution is passed through the column again, and this cycle is repeated. Figure 8(B) presents the variation in the absorbance ($\lambda = 280$ nm) for the effluent from the column by the alternate flow of bisphenol A and ethanol solutions and the corresponding curve for the system without the column. For the system without the column (Fig. 8(B)(a)), a constant absorbance is obtained for the flow of bisphenol A solution, while no absorbance is detected for the flow of deionized water and ethanol. The variation in the absorbance corresponds well to the flow conditions presented in Fig. 8(A). For the system with a column containing DS·Mg-Al LDH particles (Fig. 8(B)(b)), no absorbance is detected over the period of the flow of bisphenol A solution through the column, indicating that bisphenol A has been almost completely eliminated by the DS·Mg-Al LDH particles. On the contrary, the absorbance increases with the flow of ethanol solution, showing that bisphenol A taken-up by the DS·Mg-Al LDH particles has been eluted by ethanol. The maximum concentration of bisphenol A in the ethanol was 130 mg/L, which was higher than the concentration (100 mg/L) of bisphenol A solution, indicating that the bisphenol A was concentrated to 130% under the conditions in this study. These results show that bisphenol A could be continuously eliminated by DS·Mg-Al LDH, which can be regenerated through ethanol elution. This suggests that the uptake of bisphenol A from the aqueous phase and its elution from DS^- layer in the LDH are qualitative and fairly quick processes. The absorbance measurement is performed over 224 min of the flow, as presented in Fig. 8(B)(b), and ceases due to the increase in the pressure inside the column. Such a pressure increase in the column has not been observed in the runs presented in Figs. 3 and 4, where only deionized water and the aqueous solution have been passed through the column. Then, this may be attributed to the swelling of the DS·Mg-Al LDH particles caused by the incorporation of ethanol in the interlayers of the LDH. This is confirmed by the fact that the pressure inside the column increases with the flow of ethanol, while the increase in the pressure is gradual with the flow of bisphenol A solution and deionized water, as shown in Fig. 9. These phenomena should be taken into account for the development of this type of materials; however, these phenomena have not been further investigated in this study. In practical use of the column packed with DS·Mg-Al LDH particles, the DS·Mg-Al LDH particles should be supported by materials with the size order of mm and cm in order to keep the space of solution flow. This method makes the column operation under low operational pressure possible. A series of experiments are now designed to extend the study for the development of appropriate supporting materials.

Consequently, the DS·Mg-Al LDH particles packed in a column were found to continuously take up bisphenol A and diethyl phthalate from the aqueous solution. Furthermore, they were found to be regenerated by the elution of the taken-up bisphenol A by ethanol. The column containing DS·Mg-Al LDH particles is expected to be applicable for the treatment of wastewater containing organic substances.

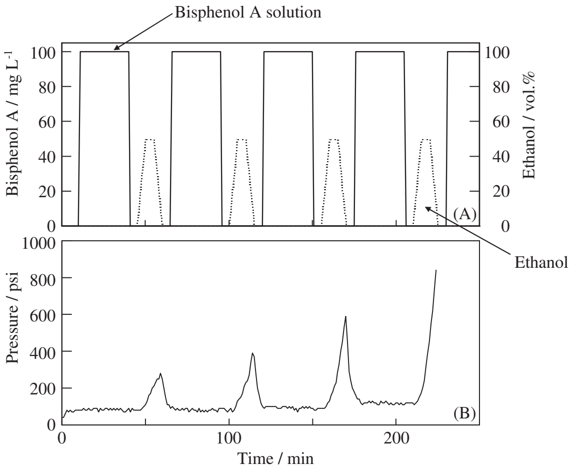

Fig. 9 (A) Designed pattern for alternate flow of bisphenol A solution and ethanol with flow rate of 1.5 mL/min.
(B) Variation in pressure with alternate flow of bisphenol A solution and ethanol through column containing DS·Mg-Al LDH particles.

According to the results of this study, the composite materials coupling hydrotalcite-like layer-structured double hydroxide with organic anions are expected to be effective absorbents for organic as well as inorganic contaminants in aqueous solution. By such a technique, water-soluble or intrinsically liquid material can be applied to water cleaning processes based on column-style operations.

4. Conclusions

(1) The uptake of bisphenol A and diethyl phthalate with DS^--intercalated Mg-Al LDH was investigated by batch-type and column tests. When 100 mg/L bisphenol A and diethyl phthalate solutions were passed through a column containing 0.5 g of the DS·Mg-Al LDH particles at a space velocity of $112.5\,h^{-1}$, bisphenol A and diethyl phthalate were continuously taken up from the solution, respectively.

(2) By the flow of bisphenol A and diethyl phthalate solutions through the column, the pH of the effluent increased immediately from the initial values of 5.2 and 5.6 to a value close to 7.0, and then remained distributed between 6.0 and 8.0. The Mg^{2+} concentrations were very low at each stage. These results are acceptable in the water quality standard in Japan ($5 < pH < 9$; Mg^{2+} is not listed there).

(3) From the XRD analysis, it can be deduced that the configuration of the intercalated DS^- in DS·Mg-Al LDH was not affected by the flow of bisphenol A and diethyl phthalate solutions.

(4) Bisphenol A was observed to be taken up from the aqueous solution and eluted from the DS·Mg-Al LDH fairly quickly.

(5) The contact of the Mg-Al LDH with DS^- in the interlayer with ethanol is considered to cause the swelling of the particles, resulting in an increase in the inside pressure of the column.

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