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Novel separation medium spongy monolith for high throughput analyses

Fuminori Watanabe, Takuya Kubo*, Kunimitsu Kaya, Ken Hosoya

Graduate School of Environmental Studies, Tohoku University, Aoba 6-6-20, Aramaki, Aobaku, Sendai 9808579, Japan

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ABSTRACT

Sponge-like material was utilized as novel chromatographic media for high throughput analyses. The pore size of the sponge-like material was several dozen micrometer, and was named spongy monolith because it consists of continuous structured copolymers, which was made of poly(ethylene-co-vinyl acetate), such as monolithic materials including silica monoliths and organic polymer monoliths. The spongy monolith was packed into a stainless steel column (100 mm × 4.6 mm I.D.) and evaluated in liquid chromatography (LC) with an on-line column-switching LC concentration system. The results indicate that the packed column could be used with high flow rates and low back pressure (9.0 mL/min at 0.5 MPa). Furthermore, bisphenol A was quantitatively recovered by on-line column-switching LC concentration with the spongy monolithic column. Additionally, the adsorption capacity and physical strength of the media was enhanced via chemical modification of spongy monoliths using glycerol dimethacrylate. The results compared with original spongy monolith demonstrated that a higher adsorption capacity was achieved on a shorter column, and a stable low back pressure was obtained at high throughput elution even with a longer column.

1. Introduction

Liquid chromatographic (LC) analyses are widely utilized for quantitative analyses or preparative purifications. In order to achieve high sensitivity separations, small-sized particles and capillary-type columns have been developed for several LC systems. Recently, high throughput analyses have become very important in the fields of biochemistry, environmental chemistry, and industrial chemistry because of an increase in the demand for analytes. In most quantitative analyses, pretreatment procedures are ineluctable to remove contaminants from the environmental water samples and to concentrate objective compounds. The most serious problem associated with pretreatment using solid-phase extraction (SPE) and/or on-line column-switching liquid chromatography [1–9], is the high back pressure. If the problem could be overcome, we will achieve to handle a lot of test substance by high throughput elution.

To achieve high throughput analyses and/or preconcentration, several materials of uniform particle size [10–12] and monolithic type materials [13–15] have been employed. Especially, monolithic materials are suitable for high throughput elution because of their high porosity and domain size [16–18]. Therefore, monolithic materials, including silica-based and organic polymer-based materials, have been widely studied in chromatographic separations, sample preparation, and purification [19–23]. One of the important drawbacks of previously reported monolithic materials is the difficulty associated with controlling pore size. In particular, it is difficult to obtain a pore size of more than 10 μm, and therefore, monolithic materials cannot be utilized for high throughput analyses. Other important limitations to high throughput chromatographic separations are column packing procedures including in situ preparation (monoliths). All these procedures involve complicated handling and demonstrate low reproducibility. Thus, in order to practically achieve high throughput elution, it is necessary to develop novel materials that can be prepared using simple techniques with high reproducibility. In addition, the materials must have a large domain size (skeleton and pore), and be suitable for high throughput analyses. Furthermore, materials should possess superior formability, flexibility, and operationality for column packing.

In a previous study, we reported some advantages using spongy monoliths and provided data on its application [24]. In this paper, we present additional data derived from comparing a column using this material with a commercially used LC column in terms of factors including back pressure; we also examined the recovery of bisphenol A (BPA) on a column-switching LC concentration system. In this paper, we hope to suggest that the spongy monolithic columns are useful as pretreatment column on a column-switching LC concentration system with high throughput. Moreover, we report chemical modification of spongy monoliths that demonstrated superior adsorption capacity and physical strength using glycerol dimethacrylate (GDMA).

* Corresponding author. Tel.: +81 22 795 7410; fax: +81 22 795 7410.
E-mail address: kubo@mail.kankyo.tohoku.ac.jp (T. Kubo).

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2. Experimental

2.1. Materials

GDMA was used as purchased without further purification. Acetone, alkylbenzenes, and BPA were used as solutes; ultra pure water, HPLC-grade methanol (MeOH) and acetonitrile (MeCN) were used as chromatographic mobile phases; and 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN) was used as the radical initiator of chemical modification. All of the abovementioned chemicals were purchased from Wako Chemicals (Osaka, Japan).

2.2. Preparation of spongy monoliths

The spongy monolith was prepared as follows: polyolefin chips (consisting of polyethylene and polyvinyl acetate: EVA resin) and pore templates (water-soluble compounds: pentaerythritol) were melted at 130 °C and stirred. The resulting material was extruded as a column at 130 °C. The columnar material was immediately cooled in water to obtain the stick shaped material. After cooling, the stick shaped material was washed with water using ultrasonication to remove water-soluble compounds. At this stage water-soluble compounds functioned as pore templates. The porosity of the obtained spongy monolith was 74% and the diameter of its cross-section across its entire length was 4.7 mm.

For packing spongy monoliths in a stainless steel column, we utilized an empty column with an internal diameter of 4.6 mm. The diameter of the spongy monolithic column (4.7 mm) was greater than the internal diameter of the empty column (4.6 mm). Nevertheless, the elasticity of the spongy monolith material facilitated the packing. The procedure for packing was as follows: One end of the spongy monolith was compressed with a thermal shrinkage tube at 120 °C. After cooling, the shrinkage tube was removed; and the diameter of the compressed end of the spongy monolith was now less than 4.6 mm. After macerating the spongy monolith into water, the shrunk portion of the spongy monolith was inserted into the empty column and pulled from the other end, until the non-shrunk portion completely filled the column. Finally, the excess portion of the spongy monolith was cut and the column-end module was connected. At this point, the shrunken end of the spongy monolith was completely cut and only the portion of the material with the initial diameter (4.7 mm) was packed into the column.

2.3. Chromatographic measurements

High-performance LC (HPLC) measurements were carried out with an LC-VP HPLC system from Shimadzu (Kyoto, Japan) consisting of a LC-10Avp, solvent delivery pump; a CTO-10Avp, column oven; FCV-12AH, a two-position flow changeover valve; FCV-13AL, a six-port flow selection valve SIL-10Avp, an automatic injector; SCL-10A, a system controller; and SPD-M10A, a photodiode array detector. Acetone and alkylbenzenes were utilized for fundamental evaluations of the column. Furthermore, in order to understand the adsorption capacity of the spongy monolithic column, frontal analyses were carried out using a certain concentration of BPA solution on each column. Each spongy monolithic column (column length; 30, 50, 100 mm) was evaluated with continuous flow of BPA solution (flow rate; 0.5 mL/min, temperature; 40 °C), which concentration of BPA was 500 mg/L in 5% aqueous methanol, and the adsorption capacities for BPA on each column including ODS-particle, ODS-monolith, and spongy monolith were determined by 1.0% breakthrough.

To examine the preconcentration of BPA using the prepared spongy monolithic column, the column-switching LC concentration system was utilized. The concept of the column-switching system is shown in Fig. 1. The pump delivered 50–100 mL of a

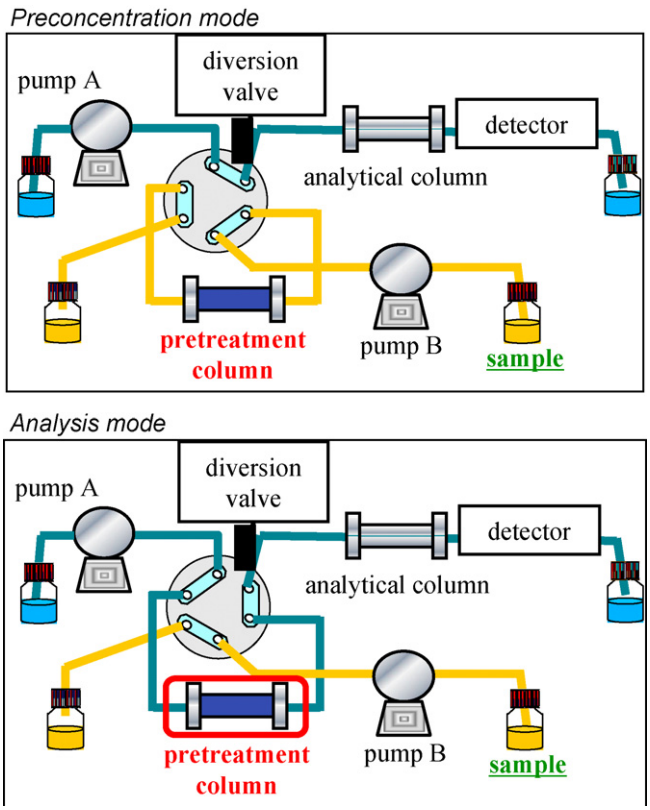

Fig. 1. Schematic images of the column switching chromatographic system.

standard solution of BPA or environmental water samples, and the BPA was concentrated on the pretreatment column. Subsequently, the mobile phase was delivered via a six-port switching valve and the concentrated BPA was directed to the analytical column and identified by the detector after separation on the column. In this study, a BPA aqueous solution at a concentration of 1.0 μg/L to 0.50 mg/L was used in evaluations at a flow rate of 1.0–9.9 mL/min at 40 °C. Additionally, we also evaluated the preconcentration of BPA using environmental water samples. BPA was spiked in river water (Hirose River, Sendai City, Miyagi Prefecture, Japan) with a 1.0 mg/L solution. First, we examined the free concentration of BPA in the original river water by commonly used SPE cartridges. As a result, we could not detect BPA from the river water sample. Then, pseudo environmental water was evaluated using the abovementioned column switching system containing the spongy monolithic column as a pretreatment column.

2.4. Chemical modification of spongy monoliths

To improve the adsorption capacity and physical strength of spongy monoliths, we chemically modified spongy monoliths using a crosslinking agent, GDMA. The modification procedure was as follows: spongy monoliths were immersed in a monomer solution consisting of 1.0 mL of GDMA, 1.0 mL of MeOH, and 100 mg of ADVN (as a radical polymerization initiator) for 30 min. Then the moist spongy monoliths were packed into the empty column (30 or 250 mm × 4.6 mm I.D.). After removing the excess monomer solution, the columns were heated at 50 °C for 12 h.

The prepared columns were evaluated by a scanning electron microscopy (SEM) instrument, Miniscope from Hitachi (Tokyo, Japan) and a Mercury intrusion porosimetry instrument, PoreMaster 33P from Quantachrome Instrument (USA) to obtain pore information, and an ATR FT-IR instrument, FT/IR 4200 from Jusco (Tokyo, Japan) to observe the change in the appearance of the

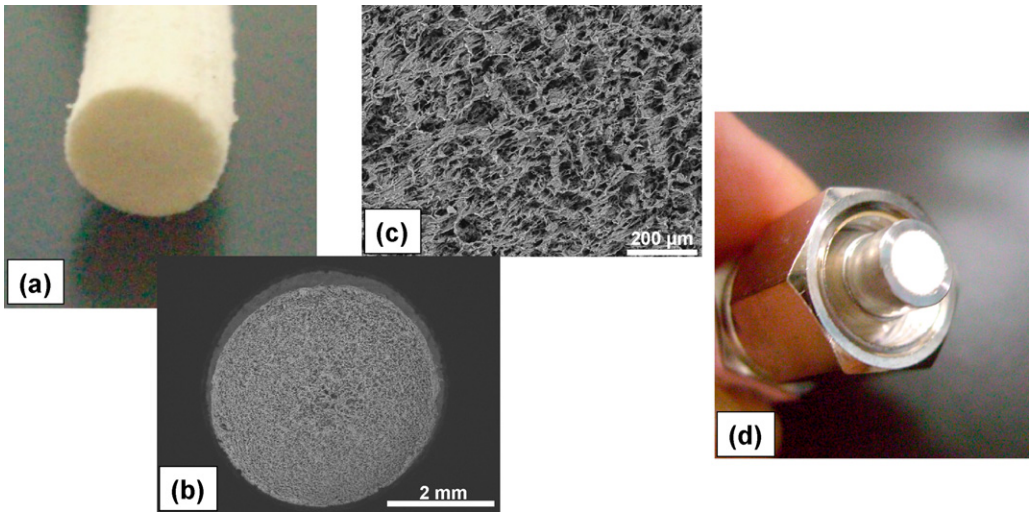

Fig. 2. Physical appearance and SEM images of spongy monoliths. (a) Physical appearance, (b and c) SEM image, and (d) photo of column end of the spongy monolithic column.

columns and confirm their absorbance based on GDMA polymers. In addition, the columns were evaluated by liquid chromatography to examine their adsorption capacity and physical strength.

3. Results and discussion

3.1. Physical appearance of spongy monoliths

Fig. 2 shows the physical appearance and SEM images of spongy monoliths and the packed column-end. SEM images show that the spongy monolith has large pores, more than 10 μm in diameter whereas the pore size of commonly used monolithic materials is less than a few micrometers. In addition, we can easily control the pore size of the spongy monolithic material by changing the composition of the EVA and water-soluble compounds used in its preparation. Also, results from mercury intrusion porosimetry are shown in Fig. 3. These results also support that the spongy monolith has over 10 μm sized pores. Additionally, the image of the column-end suggests that the spongy monolith was effectively packed into the column with no void between the surface of the spongy monolith and the inner wall of the column. At this end, the diameter of the spongy monolith was less than that of the stainless steel column, thus; the spongy monolith was completely packed in the column by the outward pressure generated by the expansion of the spongy monolith. In fact, seepage was not observed on chromatographic evaluations as shown in our previous study [24]. The ease of column packing is attributed to the flexibility and operationality of the spongy monolith. Therefore, we propose that the spongy monolith is superior to commonly used particles or monolithic materials with respect to simplified packing.

3.2. Linear velocity versus back pressure

In order to examine the possibility of high throughput elution using the spongy monolithic column, we investigated the back pressure at several linear velocities. The results were compared with those of a commonly used particle-packed column and those of a monolithic column (Chromolith, Merck Ltd.) with the same column dimensions. The plot of linear velocity vs. back pressure is shown in Fig. 4. Here, the original pressure of equipment on each flow rate without column was corrected in this figure. The particle-5 μm packed type column could not be used at a linear velocity exceeding 7.0 mm/s because of the high back pressure. Additionally, the properties of each column, theoretical plate number, and permeability K_F were summarized in Table 1. The values of K_F were estimated by the following equation,

$$K_F = \frac{F\eta L}{\pi r^2 \Delta P}$$

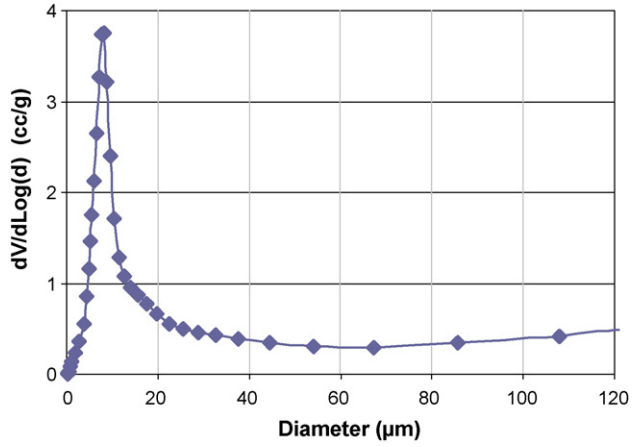

Fig. 3. Pore distribution of spongy monoliths measured by mercury intrusion porosimetry.

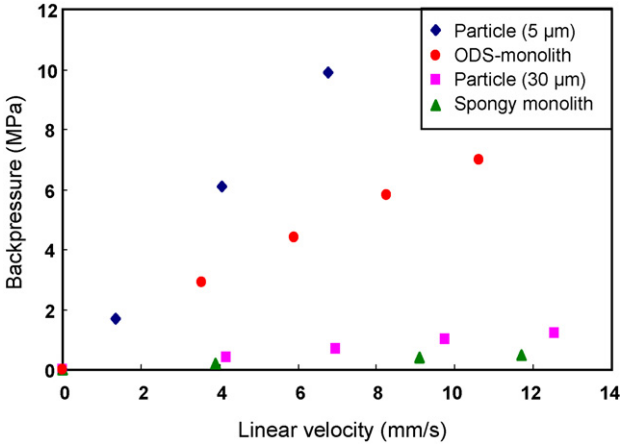

Fig. 4. Linear velocity and back pressure in each column. *LC conditions*: Column size, 100 mm × 4.6 mm I.D.; mobile phase, MeCN/H_2O = 7/3; temperature, 40 °C.

Table 1
The properties of each column.

Column	Pore diameter (average)	Theoretical plate number N^*	Permeability (m^2)
Polymer particle—5 μm	3.6 nm	2620	2.4×10^{-14}
ODS-monolith (Chromolith)	Macropore 2 μm, mesopore 13 nm	4400	6.1×10^{-14}
ODS particle—30 μm (LC-SORB:SP-A-ODS)	9.0 nm	364	3.5×10^{-13}
Spongy monolith	10.5 μm	280	8.5×10^{-13}

N was determined from result of t_0 (acetone).
LC conditions: column size, 100 mm × 4.6 mm I.D.; mobile phase, MeCN/H_2O = 7/3; temperature, 40 °C.

where K_F is the permeability, F is the flow rate of the pump, η is the solvent viscosity [25], L is the column length, πr^2 is the cross-sectional area of the column, ΔP is the back pressure. As shown in Table 1, although the separation efficiency was very low on spongy monolith, the highest permeability was observed on spongy monolithic column. These results clearly showed that the spongy monolithic column was more suitable for high throughput elution than particle-packed and commonly used monolithic columns.

3.3. Basic properties of spongy monoliths

As expected, spongy monoliths were unstable in non-polar organic solvents because spongy monoliths were made exclusively from non-crosslinked polymers. In fact, spongy monoliths easily dissolved in non-polar solvents such as toluene, hexane, tetrahydrofuran, etc. Therefore, the spongy monolithic columns cannot be used for normal phase separation in LC. On the other hand, spongy monoliths were relatively stable in polar solvents such as water, MeCN, MeOH, ethanol, isopropanol, etc. Therefore, we expected that spongy monolithic columns could be used for reverse-phase separation and examined the hydrophobicity of the spongy monolithic column by simple chromatographic analyses of alkybenzenes; the results were presented in a previous report [24]. As shown in this report, the logarithm of the retention factor k' linearly increased with an increase in the number of carbon atoms on alkylbenzene alkyl chains. In this study, k' was defined as follows:

$$k' = \frac{v(\text{retention volume of solute}) - v(\text{void volume})}{v(\text{void volume})} \quad (1)$$

Although the hydrophobicity of the spongy monolithic column was confirmed in a previous study, the relative hydrophobicity compared to that of commonly used columns was not elucidated. Therefore, we determined the separation factor, α, of CH_2 by comparing the k' values of a commercially available octadecylsilylated (ODS) monolithic column and that of the spongy monolithic column [26,27]. Here the separation factor α was defined as follows:

$$\alpha\left(\frac{a}{b}\right) = \frac{k'a}{k'b} \quad (2)$$

where $k'a = k'$ of a, $k'b = k'$ of b.

The plot for $\log k'$ and the number of carbon atoms in the alkyl chains of alkylbenzene is shown in Fig. 5. The results indicate that hydrophobic interactions of the spongy monolithic column were similar to those of the ODS monolithic column. Moreover, the value of the separation factor, α, for CH_2 (hexylbenzene/pentylbenzene) of each column also was almost the same: 1.47 for the spongy monolithic column and 1.49 for the ODS monolithic column. Therefore, we expected that the spongy monolithic column could be utilized as a separation medium in reverse-phase mode.

3.4. Adsorption capacity of the spongy monolith

In order to examine the potential adsorption capacity of the spongy monolith, we carried out frontal analyses using a certain concentration of BPA aqueous solution. The conditions are shown as follows; sample—500 mg/L BPA solution (in 5.0% aqueous MeOH), flow rate—0.5 mL/min, temperature—40 °C. The breakthrough curve on 100 mm-length column of spongy monoliths was indicated in Fig. 6. As result of 1.0% breakthrough, the adsorption capacity for BPA was estimated at 6.34 mg per column (10.5 mg/1.0 g of spongy monolith). Additionally, linear relationship was observed on each spongy monolithic column including 50 and 30 mm-column length (coefficient of correlation, $R^2 = 0.999$). Furthermore, in order to compare the adsorption capacity with commercially available media, ODS monolithic column and particle packed column were also evaluated with same frontal analysis. The results are summarized in Table 2. It was anticipated that the adsorption

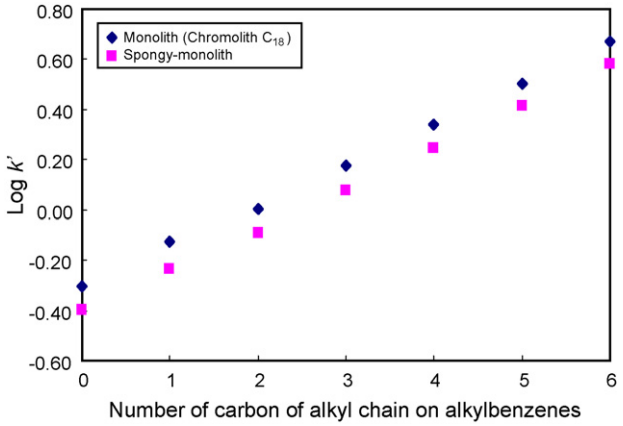

Fig. 5. Log k' versus number of carbons in alkylbenzene alkyl chains. *LC conditions*: Column, spongy monolithic column (100 mm × 4.6 mm I.D.), or Chromolith (100 mm × 4.6 mm I.D.); mobile phase, MeCN/H_2O = 7/3; flow rate, 1.0 mL/min; detection, UV 254 nm; temperature, 40 °C; solutes, 1.0 μL alkylbenzenes (0.1 mg/mL).

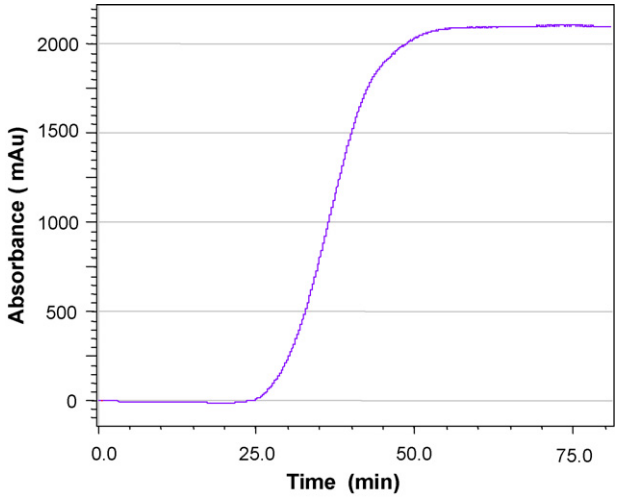

Fig. 6. Breakthrough curve of BPA solution on spongy monolithic column. *LC conditions*: Column size, 100 mm × 4.6 mm I.D.; flow rate, 0.5 mL/min; detection, UV 274 nm; eluent, BPA aqueous solution (500 mg/L in 5.0% aqueous MeOH), temperature, 40 °C.

Table 2
Adsorption capacity of BPA on each column.

	Chromolith	ODS particle—30 μm	Spongy monolith (original)	Spongy monolith (modified)
Adsorption capacity (mg/column)	36.5	127	6.34	12.5

Frontal analysis condition: column size, 100 mm × 4.6 mm I.D.; flow rate, 0.5 mL/min; detection, UV 274 nm; eluent, BPA aqueous solution (500 mg/L in 5.0% aqueous MeOH), temperature, 40 °C, The capacities were estimated by the 1.0% breakthrough of each column.

capacity of spongy monolith was much less than that of the other media. This smaller capacity was due to morphology of spongy monolith as above-mentioned results. In fact, the spongy monolith has only macropore without meso- and micro-pore so that the relative surface area was pretty lower than other porous media. Therefore, we tried to increase the adsorption capacity of spongy monolith by the additional chemical modification. The effect of the modification is discussed later. However, if we use the spongy monolithic column as a pretreatment media for BPA, the adsorption capacity is enough for practical use because the concentration of BPA in environmental water is much lower than 1.0 mg/L.

3.5. Recovery of BPA with column-switching LC system

As shown in the above discussion, the spongy monolithic column is hydrophobic in nature. Although we expected that the column could be used for high throughput LC analyses, the separation efficiency was very low; therefore, the column could not be utilized as an analysis column. Actually, the theoretical plate number of the spongy monolithic column (100 mm × 4.6 mm I.D.) was 280. However, the high porosity and hydrophobicity of this column makes it useful for high throughput preconcentration in SPE or on-line column-switching systems.

In this study, we investigated the utility of a spongy monolithic column as a preconcentration column in an on-line column-switching system. In this evaluation, BPA, which is a popular endocrine disrupter, was utilized as the objective compound. Our previous study indicated that, BPA could be completely and selectively concentrated from real environmental water samples by an on-line column-switching system using surface-modified molecularly imprinted polymers as preconcentration column media [1,5,6]. In these studies, we utilized uniform-sized polymer particles as preconcentration media and achieved an effective preconcentration at 3.0 mL/min (maximum flow rate of preconcentration because of upper pressure). However, in order to analyze a large number of samples, it is necessary to modify the size of polymer particles and their packing procedures. Therefore, if the spongy monolithic column with easier preparation and packing procedures functions effectively as a preconcentration column in high throughput elution, the availability of the on-line analysis system could be increased.

In this study, we used an aqueous solution of BPA with a concentration of 1.0 μg/L to 0.50 mg/L BPA as the sample and a high flow rate of 1.0–9.9 mL/min for preconcentration. The results of the preconcentration analysis for the recovery of BPA at a concentration of 0.5 mg/L are shown in Table 3. These results suggest that more than 95% recovery of BPA was achieved at each flow rate

Table 3
Recovery of BPA at each flow rate.

	Flow rate of preconcentration (mL/min)				
	6.0	7.0	8.0	9.0	9.99
Recovery of BPA (%)	99.8	97.5	97.9	97.5	95.0

LC conditions: Analysis—column, Mightysil (150 mm × 4.6 mm I.D.); mobile phase, MeOH/H_2O = 6/4; flow rate, 1.0 mL/min; detection, UV 274 nm; temperature, 40 °C. Concentration—column, spongy monolithic column (100 mm × 4.6 mm I.D.); temperature, 40 °C; sample, 0.5 mg/L BPA aqueous solution (50 mL).

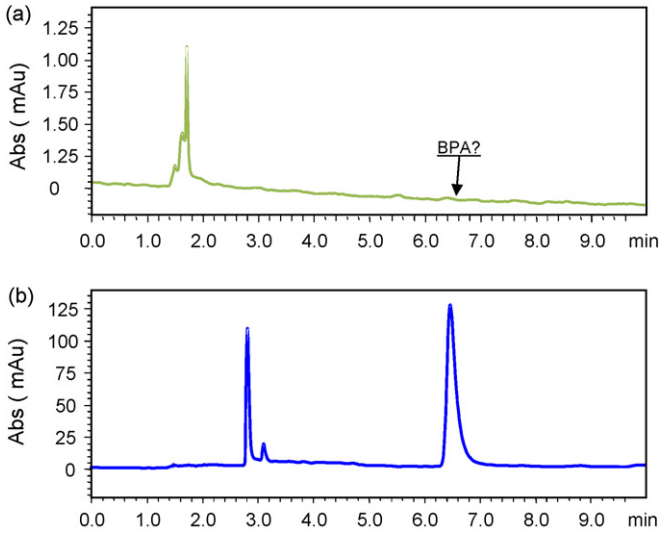

Fig. 7. Chromatograms of pseudo environmental water. Analysis conditions were the same as in Table 3. The BPA 1.0 mg/L solution was used as pseudo environmental water. (a) Before pretreatment (injection: 50 μL) and (b) after pretreatment on spongy monoliths (50 mL).

with the above concentration. Furthermore, the reproducibility of the high recovery was also confirmed at a flow rate of 5.0 mL/min (n = 20), and the relative standard deviation (RSD) was 2.4%. In addition, we could confirm reproducibility of BPA recovery concerning batch-to-batch preparations on spongy monoliths (RDS; 2.6%, n = 3) and column-to-column (RSD; 3.2%, n = 3). On the basis of these results, it can be inferred that spongy monoliths could be used as a preconcentration column in an on-line column-switching system. Furthermore, we investigated the practical use of a similar system using a pseudo environmental water sample. The chromatograms as shown in Fig. 7, demonstrate that BPA was completely recovered from pseudo river water samples. Then, the flow rate and back pressure on concentration procedures were almost the same as using authentic BPA aqueous solutions.

3.6. Chemical modification of spongy monoliths

As mentioned above, the novel spongy monolithic column was suitable for high throughput preconcentration in the on-line column-switching system. However, the dimensions of the column, particularly the column length, were much more than that of commonly used preconcentration columns. Therefore, we prepared a shorter column (30 mm × 4.6 mm I.D.) and utilized it in an on-line column-switching system under similar conditions. The results indicated that the recovery was much lower than the previous column (100 mm × 4.6 mm I.D.). Additionally, we also prepared another longer column (250 mm × 4.6 mm I.D.) to confirm the physical stability at high flow rates. In these cases, the back pressure was not stable at a high flow rate and the pressure gradually increased for a few minutes at an elution flow rate of 9.0 mL/min. These problems depend on the fundamental properties of spongy monoliths. For example, the adsorption capacity of the spongy monolith may be lower than that of porous particles because there are no

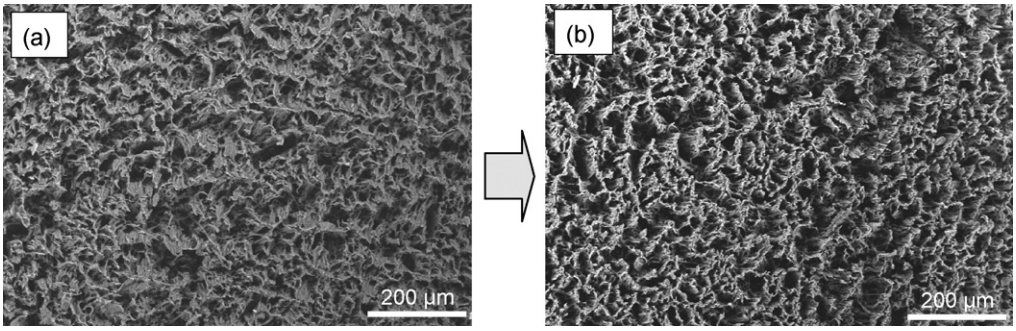

Fig. 8. Scanning electron microscopy images of modified spongy monoliths. (a) Original spongy monoliths and (b) modified spongy monoliths.

meso- and micro-pores in spongy monoliths. Additionally, most spongy monolith pores are obliterated after shrinking. This means that pores were easily compressed with lower pressures just as in a sponge. Therefore, the back pressure increased gradually at a high flow rate when the longer column was utilized. In order to solve these problems, spongy monoliths were modified with another crosslinkable monomer, GDMA. We selected GDMA as the crosslinker because other non-polar crosslinkers dissolved spongy monoliths and other hydrophilic crosslinkers were not suitable for increasing the capacity of hydrophobic adsorption. Here, although GDMA is well known as a relatively hydrophilic crosslinker, in fact, polymer packing materials prepared from GDMA could be utilized for separating hydrophobic compounds in previous papers [28,29]. Additionally, as shown in the above discussion, because the spongy monolith easily dissolved in non-polar crosslinkers such as ethylene glycol dimethacrylate, we selected GDMA as a crosslinker.

SEM images of the modified spongy monolith are shown in Fig. 8. SEM images indicate that the physical appearance of the modified spongy monolith was almost the same as that of the original spongy monolith. Additionally, the elasticity of modified monolith was also almost the same as an original spongy monolith. This is very important for maintaining permeability. FT-IR results are shown in Fig. 9, and as shown in Fig. 9(d), the differential spectrum of original and modified spongy monolith materials indicated that the specific absorbance was around 1200 and 1750 cm^{-1}. These IR spectra clearly show that surfaces of spongy monoliths were modified using GDMA. Additionally, the weight of modified spongy monolith was increased 5.9% against non-modified one. This result also supported that GDMA was modified to spongy monolith. Modified spongy monoliths were packed into 3 types of empty columns (30 or 100 or 250 mm × 4.6 mm I.D.), and the recovery of BPA and back pressure was re-evaluated. First, when the short column (30 mm × 4.6 mm I.D.) was used as the preconcentration column in the on-line column-switching system, the recovery of BPA was apparently improved by the modified spongy monolithic column as shown in Fig. 10. The aforementioned result suggests that the adsorption capacity of the spongy monolith increased after modification with GDMA. In fact, according to the evaluation of adsorption capacity for BPA, the capacity was increased almost 2 times as compared to non-modified spongy monoliths (Table 2). This also supported that the modification effectively increased the adsorption capacity. Second, when we used the longer column (250 mm × 4.6 mm I.D.) at a high flow rate, the continuous stable flow was achieved even at 9.0 mL/min. Modification

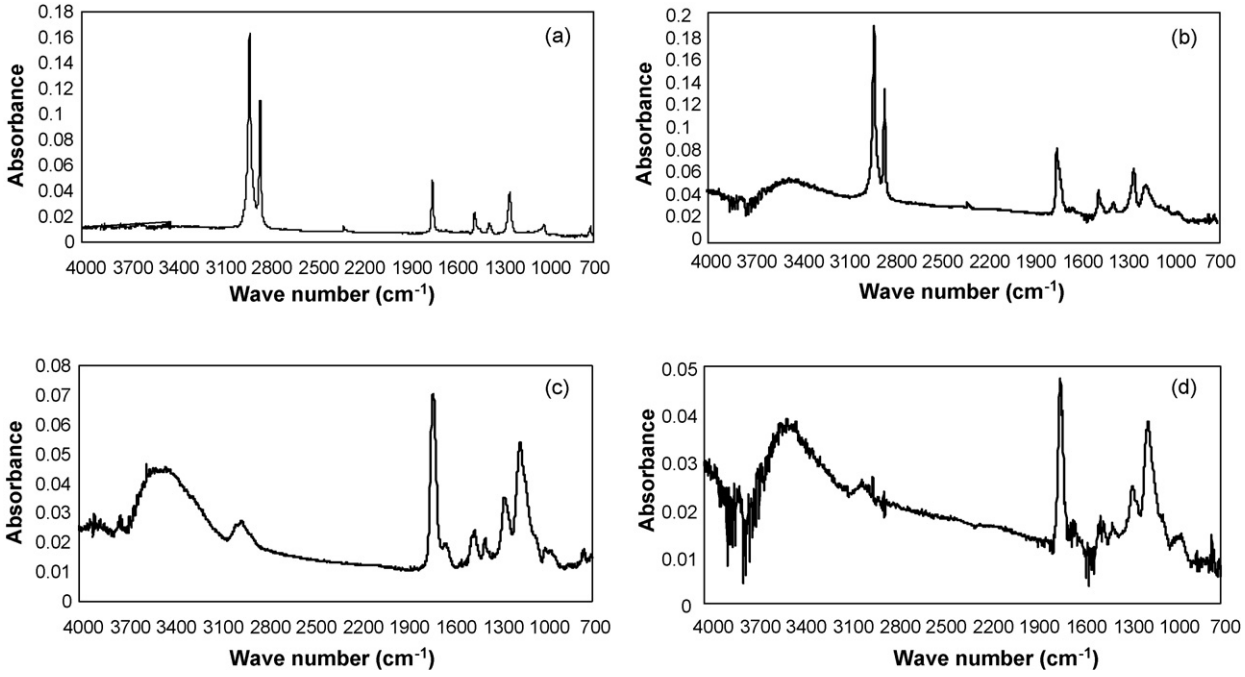

Fig. 9. Fourier-transform infra-red (FT-IR) spectra of GDMA and spongy monoliths. (a) Original spongy monoliths, (b) modified spongy monoliths, (c) standard GDMA, and (d) differential spectrum (modified spongy monoliths–original spongy monoliths).

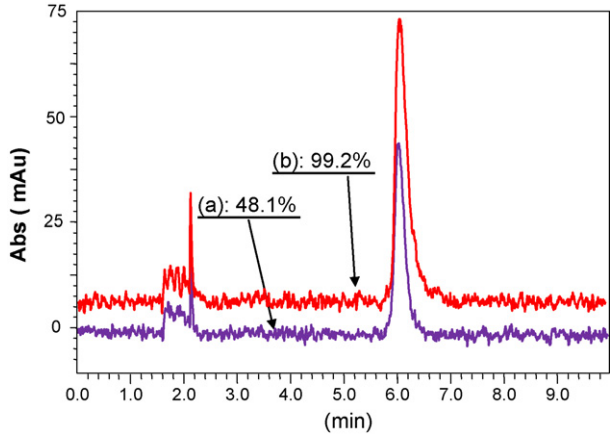

Fig. 10. Chromatograms of concentrated BPA on short column (30 mm). (a) Original spongy monoliths and (b) modified spongy monoliths. LC conditions were the same as described in Table 3 except the column size of concentration.

of the spongy monolithic material using a GDMA-based polymer improved the physical strength of the material and eliminated the unstable increase in back pressure.

4. Conclusion

In this study, we describe novel adsorption media, spongy monoliths for high throughput analyses. Results from chromatographic evaluations suggest that spongy monoliths had higher permeability than the commonly used separation media, and hydrophobicities of spongy monoliths were similar to those of ODS monolithic columns. Moreover, spongy monoliths could be used for the preconcentration of BPA in a column-switching LC system. Additionally, we chemically modified spongy monoliths by using a crosslinked polymer coating, and confirmed improvements in adsorption capacities and physical strengths via this method. Although results shown in this paper are preliminary, we demonstrated the potential application of spongy monoliths in high throughput analyses. In future studies, we hope to optimize pore size, pore homogeneity, physical strength, and chemical characterization by modifying the basic polymer, pore template, and preparation conditions, to develop a practical separation medium. Additionally, although we described the advantages of spongy monolith using a column-switching LC system we will try to apply the spongy monoliths as commonly used media of SPE. We expect that spongy monoliths will be used as separation media in SPE.

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