

# Hybridization of a Macroporous Sponge and Spherical Microporous Adsorbents for High Throughput Separation of Ionic Solutes

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Hybrid materials using a macroporous sponge and spherical microporous adsorbents have been developed for an effective rapid pretreatment of water samples. Various adsorbents, including methacrylate series, divinylbenzene (DVB), and graphite particles, were utilized for hybridization with a macroporous sponge consisting of polyethylene and polyvinyl acetate, EVA resin. Both the EVA resin and each of the particles were thermally blended at 150°C with water-soluble pore templates, pentaerythritol and poly (oxyethylene, oxypropylene) triol. After molding as a columnar shape, the hybrid materials were observed by a scanning electron microscope both before and after washing with water/methanol sonication. Only methacrylate series could be effectively fixed onto the pore surface of sponge, whereas DVB and graphite particles were incorporated to the EVA matrix. We assume that the chemical interactions between EVA and adsorbents are very important for effective hybridization to fix the adsorbents onto the pore surface. Furthermore, we demonstrated the hybridization of ion-exchange resin and sponge for a high throughput purification of ionic compounds. The ion-exchangeable polymers prepared by methacrylic acid, 4-vinylpyridine, and *p*-styrene sulfonic acid with ethyleneglycol dimethacrylate could be fixed at a given ratio of “20, wt%”, and its effective adsorption based on the ion-exchange ability was observed under rapid elution (3 mL min<sup>-1</sup>).

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## Introduction

In environmental analyses, high-speed and low-cost analyses methods are strongly required because of an increase in the number of environmental pollutants. Especially, an effective rapid pretreatment for quantitative analyses is fairly important.<sup>1-4</sup> As recent research for novel separation media to achieve effective rapid separations, monolithic materials and core shell-type materials have been developed. Monolithic columns prepared of silica-based or polymer-based materials have been widely studied for rapid separation with high efficiency. In general, monolithic columns are suitable for high throughput separations by specific morphology consisting of a 3D continuous structure including a through pore and a skeleton.<sup>5-8</sup> According to the advantages of monoliths, several applications for biological separations have been mainly studied in recent studies.<sup>9,10</sup> On the other hand, recently developed core shell-type packing materials are attractive for ultra high performance liquid chromatography (UHPLC) at higher pressured separations.<sup>11,12</sup> In both cases, effective separations have been achieved, and thus they are useful for quantitative determination with sensitive detection, such as MS/MS.<sup>13,14</sup> However, for

simple and effective pretreatments of environmental samples, these separation media do not satisfied the requirements, because a large amount of samples should be treated to accomplish a selective concentration of pollutions.

In order to overcome this problem for rapid pretreatment, we recently reported a novel separation medium based on a sponge like polymer material, named spongy monolith.<sup>15-17</sup> Spongy monolith consisting of polyethylene and polyvinyl acetate, EVA resin, showed higher permeability compared to commonly used spherical adsorbents and monolithic columns. Also, the spongy monolithic column could be utilized for effective rapid preconcentration of an endocrine disrupter, bisphenol A upon using as a pretreatment column of on-line column switching chromatographic system, which is an attractive method for the quantitative analyses with real samples.<sup>16</sup> However, although the spongy monolith showed a similar hydrophobic property as a C<sub>18</sub> bonded silica monolithic column, the adsorption capacity based on the hydrophobic interaction was much lower than that of C<sub>18</sub> particles and a monolith. This disadvantage is a potentially significant problem if the spongy monolith is utilized for a pretreatment adsorbent of real environmental samples. Therefore, a novel concept for the development of a useful adsorbent to achieve effective rapid pretreatment is required. For example, once we tried to prepare the other sponge-based materials by the hydrolysis of ester on EVA, and modifications with functional groups; however, a significant increase of the

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adsorption capacity was not observed because of a low specific surface area of the EVA-based sponge.<sup>16</sup> For one of the possibilities as a new concept and further simplified preparation, we propose a hybrid material involving a macroporous sponge and microporous adsorbents.

In fact, as in previous studies, several composite materials using polymer-polymer and/or polymer-inorganic particles were reported.<sup>18-22</sup> In most of these cases, the objectives of the studies were modifications of the physical strength and the thermal stability of the basic materials. Furthermore, the detailed mechanisms of constructing of composite materials have been rarely discussed.

In the present paper, we describe a novel preparation method of hybrid materials with a macroporous sponge material and spherical microporous adsorbents for effective/rapid pretreatments of water samples. The formulation of the hybrid materials are also discussed regarding the chemical interaction between sponges (EVA) and adsorbents. Moreover, we demonstrate high throughput analyses for ionic compounds with hybrid material of EVA based sponge and ion-exchangeable polymer particles.

## Experimental

### Materials

Ethylene glycol dimethacrylate (EDMA), divinylbenzene (DVB) as the crosslinking agent were purchased from Wako Chemicals (Osaka, Japan). These were distilled under a vacuum to remove the polymerization inhibitor. 2,2'-Azobis(isobutyronitrile, AIBN) as a radical polymerization initiator was re-crystallized by methanol. The other solvents including acetone, methanol, toluene, pyridine, tetrahydrofuran (THF), acetonitrile (MeCN) for high-performance liquid chromatography (HPLC), and benzoic acid were also purchased from Wako Chemicals. 4-Vinyl pyridine (4VP), methacrylic acid (MAA), and *p*-styrene sulfonic acid (SSA) as the functional monomers were purchased from Tokyo Kasei (Tokyo Japan). MAA and 4-VP were distilled under a vacuum to remove the polymerization inhibitor. Graphite particles with an average size of 7.9  $\mu\text{m}$  were supplied by Ito Graphite Co., Ltd.

### Preparation of polymer particles

We prepared the polymer particles for hybridization with EVA based sponge by a multi-step swelling and polymerization method.<sup>23,24</sup> Polystyrene seed particles were prepared by emulsifier-free emulsion polymerization. As shown in Table 1, polymerization was carried out at 70°C for 24 h using EDMA or DVB as a cross-linker, toluene as a porogenic solvent, MAA or 4VP as functional monomers, and AIBN "1.0, wt%" as a radical initiator. After the polymerization procedures, the polymer particles were washed with pure water, methanol, and THF to remove any porogenic solvent and unreacted compounds. The washed particles were dried at room temperature under a vacuum condition. The polymer particles were about 5.0  $\mu\text{m}$  in diameter. For SSA containing particles, the dispersion method was utilized.<sup>25,26</sup> By this method, the polymer chain of SSA can be modified on the pore surface of the base polymer. The polymer particles (13.0 g) with EDMA prepared by the method mentioned above were dispersed in methanol; then, SSA (2.10 g) and a radical initiator (AIBN, "1.0, wt%" against SSA) were added for a thermal reaction at 70°C for 24 h. After polymerization, the particles were washed with methanol and acetone before drying.

Table 1 Feed composition of the prepared polymer particles and polymerization condition

Abbreviation	Crosslinker	Functional monomer
EDMA	EDMA	—
EDMA-MAA	EDMA (75 mol%)	MAA (25 mol%)
EDMA-4VP	EDMA (75 mol%)	4VP (25 mol%)
DVB	DVB	—

### Hybridization of EVA-based sponge and particles

Hybrid material of EVA-based sponge and particles were prepared in a way similar to a previous method<sup>15-17</sup> shown as follows: polyolefin chips (EVA resin), pore templates (pentaerythritol), auxiliary of pore templates (poly (oxyethylene, oxypropylene) triol) and each of the particles were blended at 150°C and stirred. The resulting materials were extruded as a column shape at 130°C. The columnar materials were immediately cooled in water for solidification. Then, the stick-shaped materials were washed with water using ultrasonication to remove water-soluble compounds. The porosity of the obtained hybrid was about "74, %" and the diameter of its cross-section across its entire length was 4.8 mm. For packing the material into a stainless steel column, we utilized an empty column with an internal diameter of 4.6 mm. The diameter of the hybrid material (4.8 mm) was greater than that of the empty column (4.6 mm). In regard to the compositions, DVB, graphite, and EDMA-SSA particles were hybridized at "20, wt%" against the spongy monolith, whereas EDMA, EDMA-MAA, and EDMA-4VP were used at 1.0 to 20 wt%. The procedure for column packing was as follows. One end of each hybrid material was compressed with a thermal shrinkage tube at 120°C. After macerating the hybrid materials into water/MeCN (1/4, v/v), the shrunk portion of the hybrid material 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 hybrid material was cut, and the column-end module was connected.

### Chromatographic measurements

HPLC measurements were carried out with an LC-VP HPLC system from Shimadzu (Kyoto, Japan), consisting of an LC-10AcP, a solvent delivery pump; a CTO-10Avp, a 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-M 10A, and a photodiode array detector. Acetone, benzoic acid and pyridine were utilized for fundamental evaluations of each hybrid monolithic column.

In this study, the retention factor,  $k$ , was defined as follows:

$$k = (V_{\text{retention volume of solute}} - V_{\text{void volume}}) / V_{\text{void volume}}$$

The physical morphologies of the prepared hybrid materials were evaluated by scanning electron microscopy, SEM (TM-1000, Hitachi, Japan).

## Results and Discussion

### Basic properties of particles and physical appearance of hybrid materials

The results of SEM observations of the prepared particles, as expected, showed that uniform sized and porous particles were obtained at around 5.0  $\mu\text{m}$  in diameter. Additionally, we

measured the ion-exchange capacity of particles that were prepared with functional monomer, MAA, 4VP, and SSA. An authentic titration was employed for the evaluation. The results are summarized in Table 2. All of the polymers had a certain degree of ion-exchange capacity though the capacities were different from each other. We thus expected that hybrid materials with macroporous sponge might also provide the ion-exchange functionality.

Then we examined the possibility of the hybridization of the polymer particles and an EVA-based sponge. SEM images of hybrid materials are summarized in Figs. 1 and 2. Figure 1 shows the images of hybridization with EDMA-based particles in different contents of particles. As shown in these images, EDMA particles were effectively attached on the pore surface. During the washing process of hybrid materials with sonication, no particles fell off. Therefore, we assumed the most of the particles were incorporate in the hybrid materials. Additionally, the number of particles was increased visually as higher content of particles by SEM. In fact, although we tried to prepared hybrid materials including further content of particles, the porous structure did not exist at more than "20, wt%" content of the particles.

On the other hand, when we utilized DVB-based particles or graphite carbon particles, these particles were completely filled in the EVA backbone, as shown in Fig. 2. Here, we discuss a reason for the differences of hybridization, when the particles were situated on the pore surface or inside of backbone. In our previous studies, we described that EVA-based sponge materials can be used for adsorption media, and have a specific retention ability for polycyclic aromatic hydrocarbons.<sup>17,27</sup> As an easy

consideration, DVB and graphite has many aromatic rings; therefore, the interaction between these particles and EVA might be stronger, and thus most of the particles were imported into the backbone. Similarly, EDMA-based particles have a certain degree of affinity with aromatic compounds;<sup>28</sup> resulting EDMA particles were situated on the surface of the EVA backbone. Furthermore, when we employed bare silica particles, no particles were attached and incorporated to EVA; most of the particles fell off because of much less affinity with EVA. Consequently, we assumed that the distribution of particles to EVA or the pore template was fairly important to obtain the hybrid materials. The possibility of a detailed mechanism should be examined as future work.

#### Adsorption functionality of the hybrid materials

The hybrid materials prepared with EDMA and functional monomers clearly showed effective hybridization, in which the particles were situated on the pore surface, as well as the EDMA particles. Then, the hybrid materials were packed into empty columns *via* a similar method in previous<sup>16</sup> work, and we evaluated the retention ability by HPLC analyses. The retention factors of pyridine or benzoic acid toward each column are summarized in Fig. 3. Here, EVA, EDMA-MAA, EDMA-4VP show the columns packed with bare EVA sponge, just EDMA-MAA, and just EDMA-4VP, respectively. Additionally, Arabic numerals of each column indicate the ratio of particles (wt%) in the preparation of hybrid materials. In evaluating the EDMA-4VP series, we employed "1.0, vol%" of formic acid because the retention for benzoic acid was too strong to be detected without an acid in the mobile phase. As shown in Fig. 3, the ionic interaction was clearly observed on the column that included ion-exchangeable particles. The retention factor of each solute was gradually increased as a higher content of particles, while EVA did not retain both solutes at all. The linear relationship between the retention factor and the content of particles was thus confirmed. Based on these results, we propose that the hybridization process utilized in this study

Table 2 Ion exchangeable capacity of the polymer particles

Polymer	EDMA-MAA	EDMA-4VP	EDMA-SSA	EDMA
Capacity/meq g <sup>-1</sup>	0.38	0.59	0.12	—

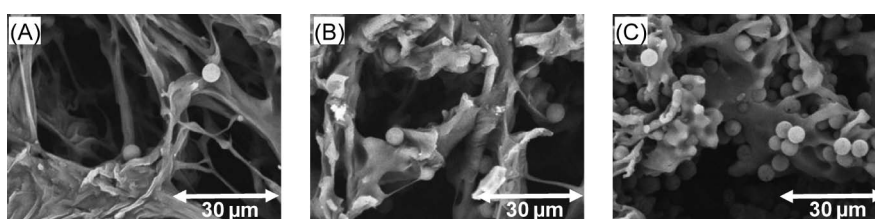


Fig. 1 SEM images of the hybrid materials with EDMA particles. The ratios of EDMA particles were (A) 1, (B) 5, and (C) 20 wt%, respectively.

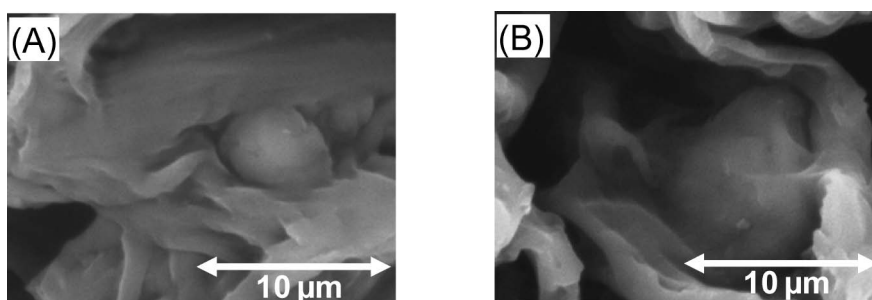


Fig. 2 SEM images of hybrid materials with DVB or graphite particles. (A) Including DVB based particles, (B) including graphite particles.

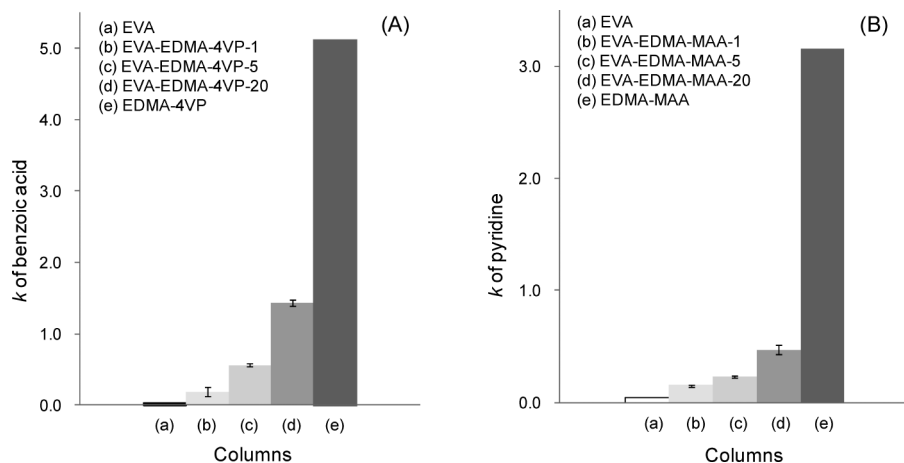


Fig. 3 Retention factor on each column. (A)  $k$  of benzoic acid on 4VP based column, (B)  $k$  of pyridine on MAA based column. LC conditions: column size, 100 mm  $\times$  4.6 mm i.d.; mobile phase, (A) MeCN/0.1% formic acid aq. = 99/1 (v/v), (B) 100% MeCN; flow rate, 0.5 mL min<sup>-1</sup>; detection, (A) UV 228 nm, (B) UV 254 nm; temperature, 40°C; solutes, 5  $\mu$ L benzoic acid or pyridine (0.1 mg mL<sup>-1</sup>).

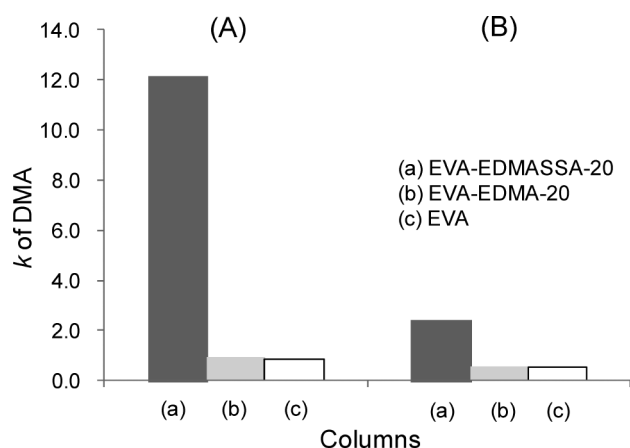


Fig. 4 Retention factor of DMA on each column. LC conditions: column size, 100 mm  $\times$  4.6 mm i.d.; mobile phase, (A) MeCN/0.1 mM HCl aq. = 90/10 (v/v), (B) MeCN/water = 90/10; flow rate, 0.5 mL min<sup>-1</sup>; detection, UV 260 nm; temperature, 40°C; solutes, 5  $\mu$ L *N,N*-dimethylaniline (DMA) (0.1 mg mL<sup>-1</sup>).

effectively worked, and the adsorption functionality also existed after hybridization, because the particles were attached onto the pore surface.

#### *Ionic interaction under a high throughput condition*

Another hybrid material including the particles, which was prepared with SSA, also showed an effective hybridization of EVA sponge and particles. Therefore, HPLC analyses were carried out as well. Firstly, the columns were evaluated with a mobile phase containing pure water. As shown in Fig. 4(B), the ionic interaction based on SSA was observed against the basic solute, *N,N*-dimethylaniline (DMA). Additionally, a significant retention effect was confirmed when an acidic solution was utilized as a mobile phase. These results clearly show that a strong ionic interaction by SSA effectively worked on the hybrid material. Finally, in order to know the possibility of high throughput analyses, we demonstrated a change of the retention ability on various flow rate conditions. Figure 5 shows the relation between the retention factor of DMA and the flow rate

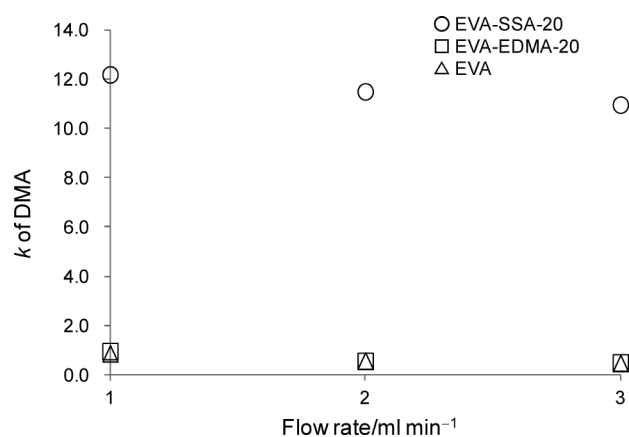


Fig. 5 Retention of DMA under various flow rates. LC conditions: column size, 100 mm  $\times$  4.6 mm i.d.; mobile phase, MeCN/0.1 mM HCl aq. = 90/10 (v/v); flow rate, 1.0 to 3.0 mL min<sup>-1</sup>; detection, UV 260 nm; temperature, 40°C; solutes, 5  $\mu$ L DMA (0.1 mg mL<sup>-1</sup>).

on HPLC analyses. This figure suggested that the hybrid material prepared with EVA sponge and EDMA-SSA is available for ion-exchangeable adsorption under the high throughput condition.

## Conclusions

We proposed novel separation media that were prepared by the hybridization of a macroporous sponge like material and microporous polymer particles. Methacrylate-based particles were available for effective hybridization, and the polymer-polymer hybrid materials could be utilized for the separation of high throughput elution. We strongly expect that the hybrid materials proposed in this study will be suitable for rapid separation and purification, especially for the environmental water samples.

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