NOTE

Convenient Method for Removing and Concentrating Hydrophobic Organic Compounds from Water with Amphiphilic Polymers

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INTRODUCTION

Because hydrophobic organic compounds (HOCs) sparingly dissolved in aqueous media are regarded a source of environmental pollution and endocrine disruptors,[1] they must be removed from water. In addition, because of the extremely dilute concentrations of HOCs, expensive apparatus to detect or complicated operations to concentrate them have been needed to analyze them. Therefore, convenient methods and materials for efficiently removing and concentrating HOCs from water have been strongly required.

Solid adsorbents have been widely used to remove HOCs from aqueous media.[2–5] The use of a solid adsorbent, however, is not suitable for preparing concentrated solutions of HOCs because of strong adsorption. Recent reports have suggested that the use of hydrophobic interactions is effective for the removal of HOCs from aqueous media.[6–16] Because the hydrophobic bonds are weak, the hydrophobic materials are expected to make convenient concentration of HOCs in water possible. Therefore, our strategy for a facile method to remove and concentrate HOCs slightly dissolved in water employs an amphiphilic block copolymer. Amphiphilic polymers generally form micelles in aqueous media. In the micelle solutions, hydrophobic domains are in liquid–liquid phase equilibrium with the hydrophilic phase in nanospace.[17–19] Hence, the interfacial area between the hydrophobic and hydrophilic phases becomes much higher than that in a general water–oil system. Therefore, micelle solutions of amphiphilic polymers are expected to efficiently capture HOCs in hydrophobic domains. In addition, the micelles capturing HOCs should easily release the HOCs

with an appropriate solvent. Hence, amphiphilic polymers are favorable for removing and concentrating HOCs. Thus, in this article, we propose a facile method for removing and concentrating HOCs sparingly dissolved in water with an amphiphilic block copolymer.

EXPERIMENTAL

Materials

Poly(ethylene glycol) monostearate with the 25-mer of poly(ethylene glycol) (HM–PEO or **2**; Tokyo Chemical Industry Co., Ltd., Tokyo) was used as a model amphiphilic block copolymer. A hydrogel of poly(acrylic acid) (PAA gel) was synthesized with acrylic acid as a monomer, methylene bisacrylamide as a crosslinking agent, potassium peroxodisulfate as an initiator, and hexane and water as solvents under vigorous stirring at 90°C; the monomer/crosslinking agent/initiator molar concentration ratio was 100/1/1.

Method

Preparation of the solution

A water solution containing bisphenol A (BPA) was prepared through the dissolution of BPA in distilled water at a concentration of 10.0 mg/L (10 ppm). The resulting solution was denoted **1**. An aqueous solution of **2** was prepared through the dissolution of HM–PEO in distilled water at a concentration of 1.00 g/L.

Analysis

To determine the BPA concentration, absorbance spectra in the ultraviolet–visible (UV–vis) region were measured for the solutions with a Waters 996 UV–vis spectrometer (Japan Waters Co., Tokyo, Japan). In the concentrations in this study, a linear relation between the integrated absorbance intensity and BPA concentration held at least one significant figure.
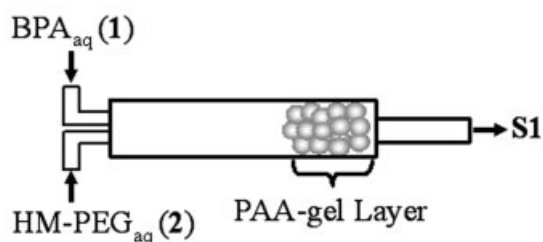

Process 1

Process 2

Figure 1 Schematic illustrations of the process for the removal of HOC from water.

Procedure

Figure 1 shows schematic illustrations of our procedure for removing and concentrating BPA from aqueous solutions. In process I, **2** is introduced to **1**. The resulting solution is denoted **1–2**. In this process, the poly(ethylene glycol) monostearyl ester (HM–PEG) micelle should capture BPA in hydrophobic domains because of the hydrophobic interaction. Subsequently, **1–2** is passed through the PAA gel layer in process II. In this process, HM–PEG is removed from the water because of the formation of a hydrogen-bonded HM–PEG/PAA gel complex.[20] BPA should also be removed from the water accompanying HM–PEG. The resulting water is denoted **S1**. Subsequently, a small amount of methanol passes through the PAA gel layer. In this process, BPA should be extracted to methanol, and a concentrated methanol solution should be obtained. The resulting methanol solution of BPA is denoted **S2**.

RESULTS AND DISCUSSION

Figure 2 shows absorbance spectra for **S1**, **1**, and a reference aqueous solution (**R**) prepared by the passage of **1** through the PAA gel layer. **S1** was obtained by the passage of **1–2** prepared by the addition of **2** (1 mL) to **1** (10 mL) through the PAA gel layer. Therefore, the weight ratio of HM–PEG to BPA was equal to 10. **1** and **R** show absorbance peaks attributed to the BPA absorbance. Because the absorbance of **R** is slightly weaker than that of **1**, the PAA gel scarcely has the ability to remove BPA. On the contrary, **S1** does not show any absorbance peaks. Therefore, BPA is almost perfectly removed from **1** by the combination of HM–PEG and PAA gel. This result means that BPA is captured in the hydrophobic domain of HM–PEG and removed from the water with the micelle because of the formation of a hydrogen-bonded complex of HM–PEG and PAA gel. Thus, the BPA-removing ability in the process is dominated by that of HM–PEG. Therefore, the BPA-removing ability of HM–PEG is examined by the
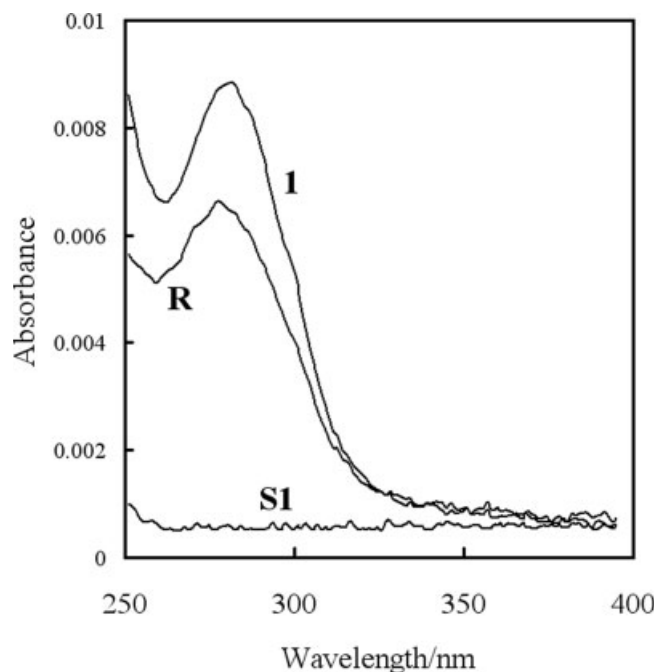
Figure 2 UV–vis spectra for **1** and **S1**.

variation of the weight ratio of HM–PEG to BPA in **1–2** ($R_{HM–PEG/BPA}$).

Figure 3 shows plots of the ratio of removed BPA to BPA in **1** ($R_{Removed\ BPA}$) against $R_{HM–PEG/BPA}$. $R_{Removed\ BPA}$ is determined by the absorbance spectra. When $R_{HM–PEG/BPA}$ is greater than or equal to 2, BPA dissolved in **1** is almost completely removed from water. Thus, a trace amount of HM–PEG can capture BPA sparingly dissolved
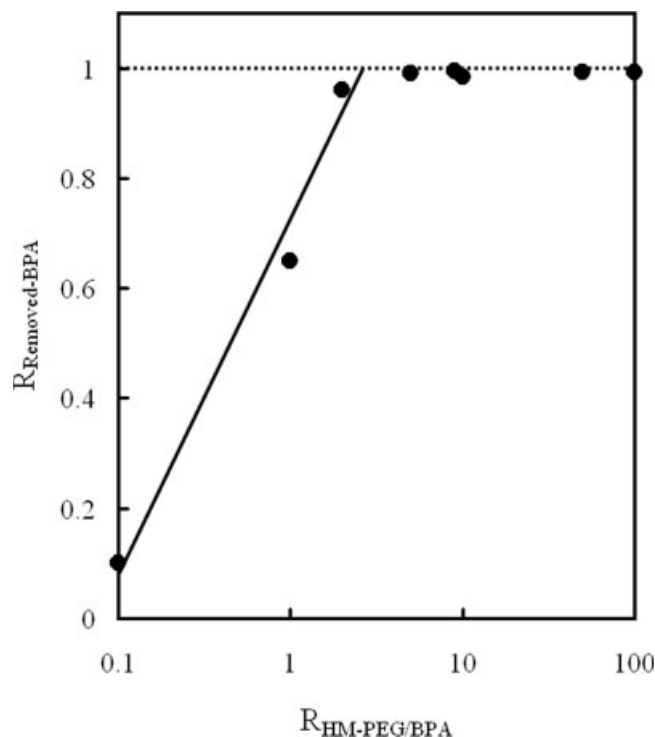
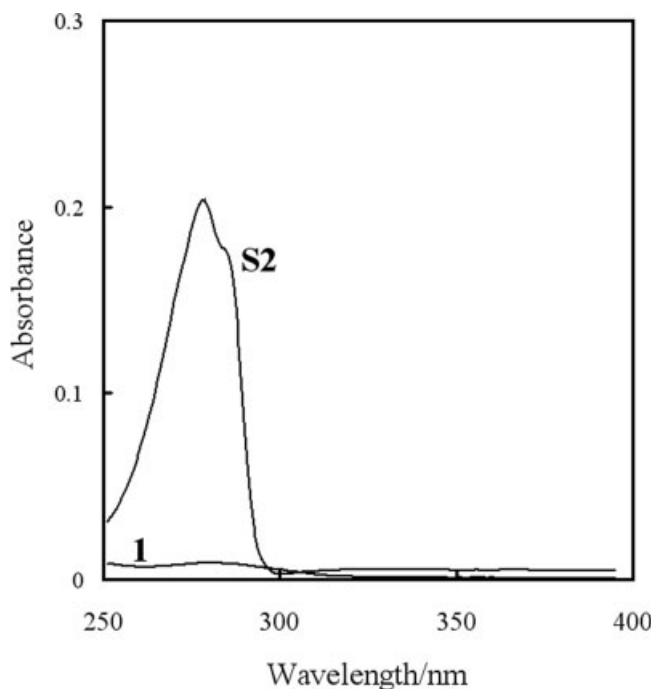**Figure 3** $R_{Removed\ BPA}$ versus $R_{HM–PEG/BPA}$.

Figure 4 UV–vis absorbance spectra of **1** and **S2**.

in water. If the removal of BPA were caused by physical adsorption on the surface of the micelle, such high removal efficiency should not be achieved. Because of hydrophobic interactions, BPA can dissolve into the hydrophobic domain to a high concentration. On the contrary, BPA saturates at less than 100 ppm in water. Therefore, the distribution coefficient of the hydrophobic phase to water should be high. For example, the distribution coefficient of octanol to water is 3.3. In addition, because the hydrophobic phase forms nanosized domains and they homogeneously disperse in water, the specific interface area between hydrophobic and water phases is extremely large. Therefore, the hydrophobic interaction and extremely large specific interface area of hydrophobic domains should achieve such highly efficient removal of BPA sparingly dissolved in water.

The features of the process proposed in this study are the efficient removal and facile preparation of concentrated solutions of HOCs sparingly dissolved in water. The former feature has already been confirmed, as mentioned previously. Then, another feature is discussed. Figure 4 shows the absorbance spectra of **1** and **S2**. The absorbance spectrum of **1** is identical to that shown in Figure 2. **S2** was prepared by the passage of 1.00 mL of methanol through a PAA gel layer holding BPA-capturing HM–PEG prepared from **1** (100 mL) and **2** (10.0 mL). Therefore, if BPA is quantitatively extracted into **S2**, the concentration of BPA in **S2** is 100 times higher than that of **1**. As can be seen in Figure 4, the absorbance peak attributed to BPA in **S2** is much more extensive than that of **1**. Therefore, **S1** is regarded as the solution in which the concentration of BPA is much higher than that of **1**. The concentration of BPA in **S2**, estimated from the area of the absorbance peak, is about 0.1 g/L, which is about 100 times higher than the concentration of BPA in **1**. Therefore, an almost quantitative concentration is achieved by the proce-

dure proposed in this study. Because the solubility of BPA in methanol is much higher than that of an aliphatic solvent, the efficient extraction of BPA from hydrophobic domains of HM–PEG to methanol should be achieved.

CONCLUSIONS

The method proposed in this study achieves an almost quantitative removal and concentration of BPA sparingly dissolved in water. The key elements leading our procedure to the expected results are hydrophobic interactions between the targeted molecule and hydrophobic chain of the amphiphilic block copolymer and an extremely high specific interface area between hydrophobic and water phases. Therefore, this method can be applied to other HOCs, such as perchlorobenzene. Thus, the method proposed in this study is expected to be an efficient method for water purification and sample preparation for analyses of water quality.

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