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Novel surface modified molecularly imprinted polymer focused on the removal of interference in environmental water samples for chromatographic determination

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Abstract

Uniformly sized molecularly imprinted polymers (MIPs) for bisphenol A (BPA) with surface modification and immobilized intervals of functional monomers afforded by utilizing 4,4′-methylenebisphenol as a pseudo component have been prepared. MIPs for BPA were prepared using 4-vinyl pyridine immobilized in the most effective interval and ethylene glycol dimethacrylate as a functional monomer and cross-linking agent, respectively. Prepared MIPs showed significant selectivity for BPA retention and removal performance for interference in actual samples as the HPLC stationary phase compared to those of ordinary MIPs. These MIPs were employed as pretreatment media of column switching HPLC and the HPLC system provided a detection limit of 0.36 ppt when electrochemical detection was used. Actual samples, including Suwannee River natural organic matter (NOM), were applied and BPA was detected in the NOM even if widely used UV detection was employed.

Keywords: Bisphenol A; Molecularly imprinted polymers; Surface modification; Column switching HPLC

1. Introduction

Molecularly imprinted polymers (MIPs) are widely used for the selective concentration and pretreatment of target compounds existing in complex matrix such as plasma [1]. In environmental analysis, very low concentration of target chemicals contained in actual samples such as river and lake waters occurs serious difficulties in the sample preparation due to substantial interference [2].

Bisphenol A (BPA) is frequently detected in environmental water and is attracting attention as an endocrine disrupter because it has rapidly entered the environment, food chains, and therefore the human diet. It has recently been reported that BPA shows estrogenic activity even at concentrations below 1 ng/l (ppt) [3–5], therefore, monitoring ultra low concentration of BPA in environmental water samples is important.

To overcome these difficulties, MIPs with highly specific binding capacity and the ability to remove interference is one of the solutions [6]. Combined pretreatment with specific MIPs and chromatographic determination is the most promising procedure. We have developed newly designed MIPs for BPA pretreatment and applied them to the actual determination of BPA. In trace analysis, leakage of the residual template molecule, which is the same as the target molecule, prevents the accurate determination of the target compound [7]. Consequently, a structurally related analog, which can be separated in the subsequent chromatographic process, is employed as an alternative template molecule. Previously *p-tert*-butylphenol (TBP) was used as a pseudo-template [8,9], however, we used 4,4′-methylenebisphenol

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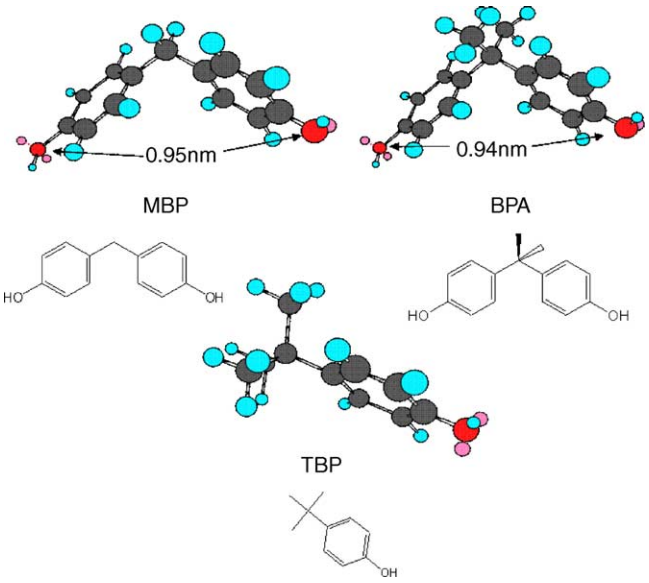

Fig. 1. Three-dimensional structures of pseudo-templates and BPA.

(MBP). As is shown in Fig. 1, MBP is structurally closer to BPA than TBP. The uniformly sized MIP was prepared by a two-step swelling method [10]. During this process, 4-vinylpyridine (4VP), functional monomer, was introduced into ethylene glycol dimethacrylate (EDMA) as a cross-linking agent in the form of a complex with MBP template providing an effective interval of 4VP, which interacts with hydroxyl group of BPA. Imprinted sites were then created by removing MBP after polymerization. Created appropriate interval of 4VP afforded increase of interaction with BPA due to the effective hydrogen bonding with 4VP and hydroxyl group of BPA. Figs. 2 and 3 show simplified schematics of imprinted sites created with TBP and MBP, respectively.

To remove interference in environmental water samples, a portion of the MIPs was surface modified with methacrylic acid 3-sulfopropyl (MAS) and other hydrophilic monomers of glycerol dimethacrylate (GDMA) and/or glycerol monomethacrylate (GMMA).

Obtained surface modified MIPs were evaluated through HPLC, nitrogen adsorption method and Schatchard analyses. Pretreatment columns packed with the MBP imprinted polymer and with its surface modified polymers were used for column switching HPLC [2], which provided highly reliable results for BPA determination when combined with electrochemical detection [11–13]. The detection limit for this method was 0.36 ppt [14,15].

We have reported that trace amounts of BPA in environmental water sample such as river and lake water can be determined with column switching HPLC coupled with electrochemical detection involving MIP as pretreatment media [15]. But due to interference in actual samples, widely used UV detection could not be applied in general. In this study, we tried to confirm the effect of surface modification onto MIPs by applying them to actual HPLC analysis of BPA in environmental samples such as Suwannee River natural organic matter (NOM), which was collected from the same site that was used originally to collect the standard Suwannee River humic and fulvic acids and frequently used as a reference matrix in environmental analysis.

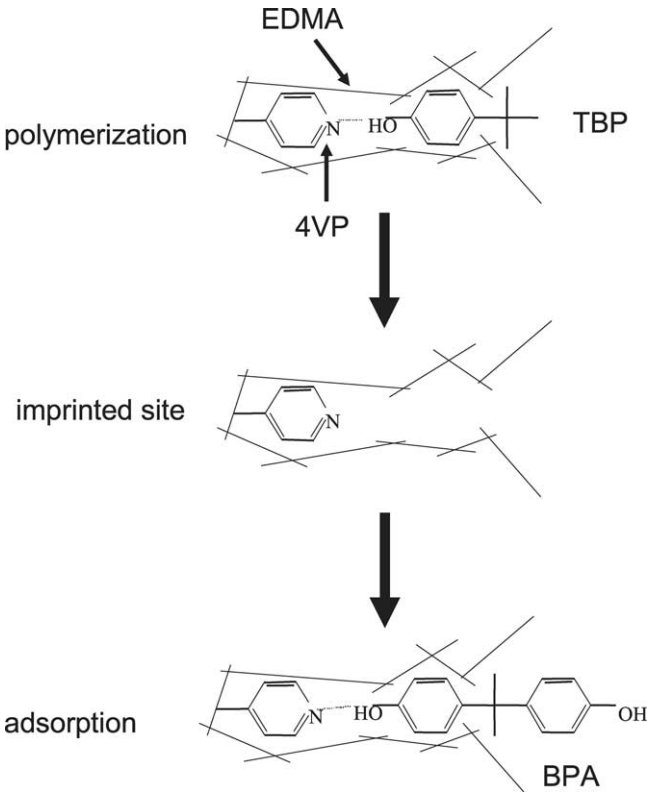

Fig. 2. Simplified schematics of creating TBP imprinted procedures.

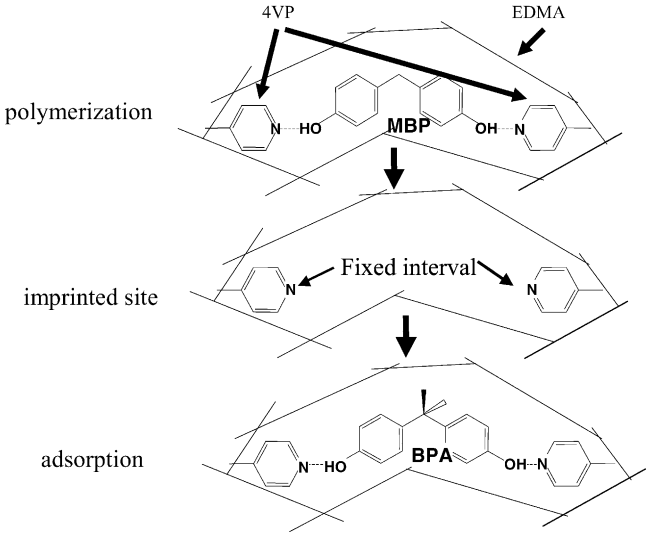

Fig. 3. Simplified schematics of MBP imprinted sites.