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SELECTIVE RECOGNITION OF BISPHENOL A USING MOLECULARLY IMPRINTED POLYMER PREPARED BY BULK POLYMERIZATION PROTOCOL

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ABSTRACT

Molecularly imprinted polymer (MIP@MAA-β-CD) was synthesised via a simple non-covalent imprinting approach using methacrylic acid functionalized beta-cyclodextrin (MAA-β-CD) as functional monomer, bisphenol A (BPA) as template molecule, trimethylolpropane trimethacrylate (TRIM) as a crosslinker, benzoyl peroxide (BPO) as initiator and toluene as the porogen. The synthesised polymers were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) and thermogravimetric analysis (TGA). The FT-IR results revealed the presence of similar functional groups for MIP@MAA-β-CD and NIP@MAA-β-CD. This indicated that there was complete template removal during the washing process. The obtained SEM micrographs of MIP@MAA-β-CD and NIP@MAA-β-CD showed dissimilar features, indicating the existence of specific binding sites formed by the template on the MIP. The result obtained for the TGA analysis showed that MIP@MAA-β-CD is thermally stable.The selectivity study showed that an imprinting factor of 1.91 was obtained in addition to the high binding capacity and selectivity of the template towards its imprinted polymer compared to its structurally similar analogues. The achieved level of selectivity proved that MIP@MAA-β-CD is efficient for practical applications.

Keywords: Binding capacity, characterisation, non-covalent interactions, selectivity.

INTRODUCTION

Molecular imprinting is a technique inspired by the mechanism of enzyme catalysis and antibody formation. Researchers have been committed to exploring similar synthetic approaches to obtain tailor-made binding materials by chemical means [1]. Molecularly imprinting techniques appear to be ideally suited to provide sorbent materials that are tailorable in their recognition properties to a wide range of hazardous pollutants. These materials are comparatively easy to produce and provide sufficient robustness ensuring storage endurance and applicability at harsh conditions.

To date, molecular imprinting has proven to be the most efficient and versatile technique for incorporating specific molecular recognition sites into polymers leading to polymeric artificial receptors [2-3].

Molecularly imprinted polymers (MIPs) are prepared by co-polymerization of cross-linking monomer and a complex which is pre-formed between the template molecule and functional monomers using covalent, non-covalent or semi-covalent interactions [4]. When the template molecule is removed from the imprinted material after polymerization, it leaves behind specific cavities that are complementary to the template in size, shape and chemical functionality [4-5]. The most widely used technique for preparing MIPs is non-covalent imprinting due to its relative simplicity on the experimental level [6]. In this process, the complex of the template and functional monomer is formed in situ by non-covalent interactions, such as hydrogen bonding, electrostatic forces, van der Waals forces, or hydrophobic interactions [7]. Synthesis of MIP is a relatively straightforward and inexpensive procedure [8]. The MIP is prepared by mixing the functional monomer, template, cross-linker, and initiator in a proper solvent [9]. There are several advantages of this technique including easy preparation of the template monomer complex, easy removal of the templates from the polymers, fast binding of templates to MIPs, cost-effectiveness and its potential application to a wide range of target molecules [10].

The goal of molecular imprinting is to obtain an imprinted polymer with some practically useful features. Very often, this feature is the separation of a compound (or of a group of compounds) from a matrix (by solid phase extraction, chromatography and binding assay), or the determination of a compound by the selective interaction with MIP sensor [11]. In virtually every application, the MIP is expected to demonstrate some sort of selectivity for the target compound against other compounds in the matrix [12].

The aim of this study therefore, is to prepare MIP@MAA-β-CD selective for bisphenol A via the bulk polymerisation in a non-covalent approach to establish an interaction between the template and the monomer. The achieved level of selectivity in this study proved that the synthesised material will be efficient in real-life applications.

EXPERIMENTAL

Reagents and materials

β-cyclodextrin (99%), trimethylolpropane trimethacrylate (99%), methacrylic acid, toluene 2,4-diisocyanate (98 %), toluene (98%), Bisphenol A, Phenol, 2,4-Dinitrophenol and 2,4-Dichlorophenol and dibutyltin dilaurate were supplied by Sigma Aldrich USA. Benzoyl peroxide, methanol and acetic acid obtained supplied by Brightchem.1000 mg L^{-1} Stock Solution of Bisphenol A, Phenol, 2,4-Dinitrophenol and 2,4-Dichlorophenol were prepared by dilution of the respective standards in methanol and stored at 4 °C prior to analysis. Fresh working standards were prepared daily by diluting with deionized water. All reagents and chemicals were of analytical reagent grade and used without further purification.

For the synthesis of the molecularly imprinted polymer (MIP@MAA-β-CD) and non-molecularly imprinted polymer (NIP@MAA-β-CD), a water bath Memmert (Schwabach, Germany) was used. Upon adsorption, the residual concentrations of phenol, BPA, 2,4-DNP and 2,4-DCP (at 271, 276, 358, 286 nm respectively) were measured using the Uv-vis spectrophotometer (Perkin Elmer Lambda 35). Deionized water collected by deionized water dispenser Sartorius Stedim, Milli-Q method (Arium 611 DI). The pH meter (Eutech pH 700) was used to obtain the pH-values. Shaker Incubator (IKA, KS4000 I control) for agitation at 250 rpm and variable temperatures of the adsorbent-adsorbent mixture. A 2000 FTIR spectrometer (Perkin Elmer) was used to measure the FTIR spectra of all the synthesized polymers. The samples were combined with KBr powder and formed into pellets before analysis, while the analysis was carried out for the liquid sample using a Bruker FTIR fitted with an Attenuated Minimum Reflectance (ATR) diamond (Billerica, USA). The SEM Quanta FEG 650 was used to evaluate the morphology of the polymers. TGA Q 500 (Perkin Elmer, Waltham, MA, USA) was used to study the thermal stability of the materials synthesized.

Preparation of molecularly imprinted polymer

MIP@MAA-β-CD was prepared according to a method by Asman et al. [13] with slight modifications. The reaction molar ratio of the template, functional monomer and cross linker for the preparation of MIP was 1: 4: 20 was adopted. BPA (0.14 mmol), was dissolved in 20 mL toluene in a round bottom flask. Exactly 0.56 mmol of MAA-β-CD monomer, crosslinker, TRIM (2.80 mmol), and BPO initiator (1 g) was added. The contents of the flask were purged for at least 10 min with nitrogen gas and then sealed and allowed to polymerize for 24 h in a water bath at 70 °C. The final product was crushed and ground. The polymer was sieved to get regular-sized particles. Then, the template was removed by washing the polymer with methanol/acetic acid (9:1 v/v) solution. The MIP@MAA-β-CD (MIP) was washed several times until no BPA was detected at 276nm using a UV Visible Spectrophotometer. The particles were then washed a few times with water. For the preparation of non-imprinted polymer (NIP@MAA-β-CD), a similar procedure was followed except that the template was omitted. The proposed interaction between the monomer and bisphenol A in the synthesis of MIP@MAA-β-CD is depicted in Figure 1.

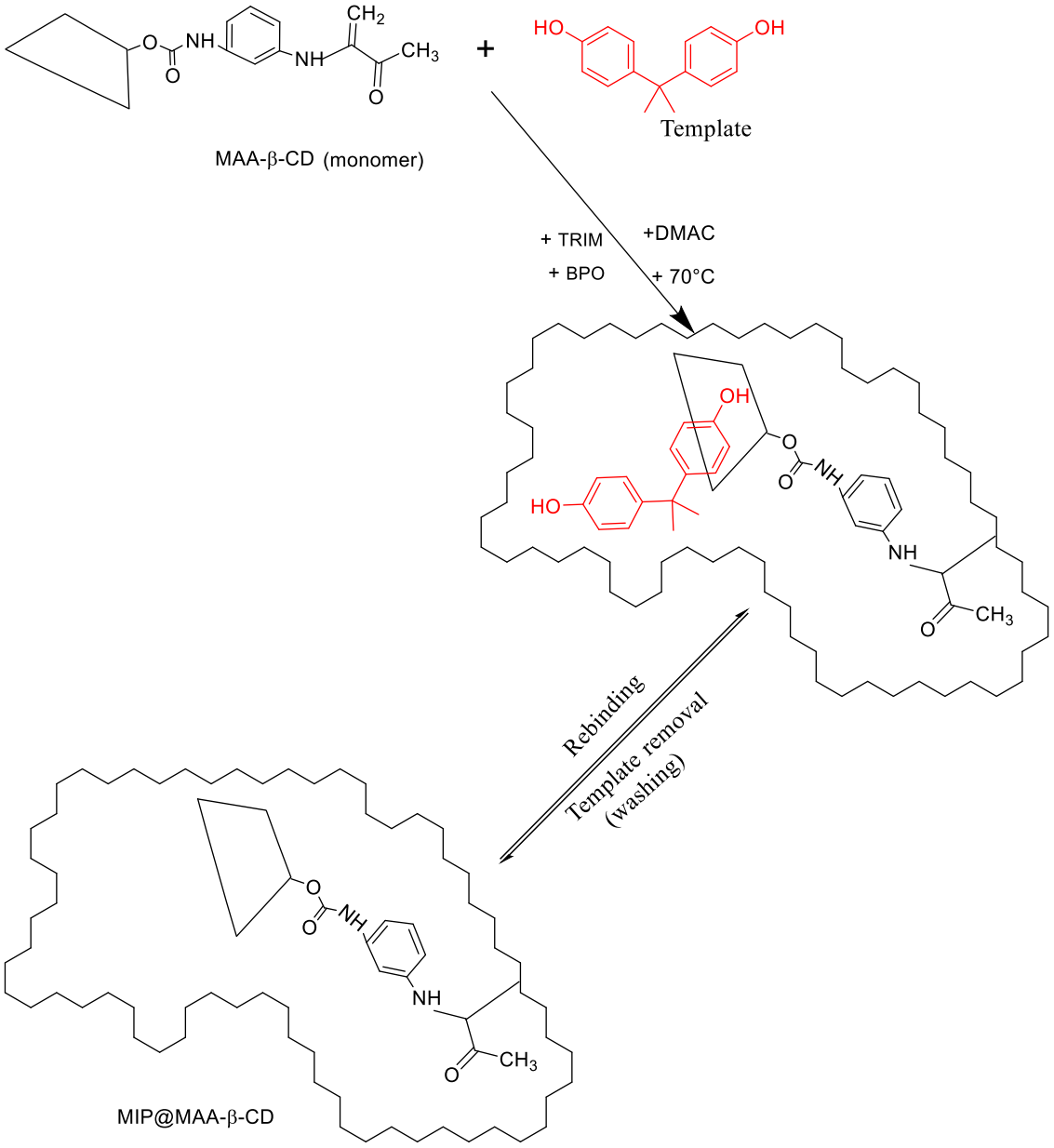

Figure 1: Proposed interaction between the monomer and bisphenol A in the synthesis of MIP@ MAA-β-CD.

Selectivity study

Phenol, 2,4-dinitrophenol and 2,4-dichlorophenol were used to determine the relative selectivity of MIP@MAA-β-CD. Exactly 10 mL of selected solvent (Phenol, 2,4- dinitrophenol or 2,4-dichlorophenol) of known concentration was added to 20 mg of MIP@MAA-β-CD in vials. The

content was shaken using a shaker at 180 rpm for 30 min at room temperature and then filtered through a 0.45µm membrane filter. The supernatant was measured using a UV-Vis spectrophotometer. The evaluation of the NIP was conducted using a similar procedure [14].

All experiments were performed in triplicates.

The bound amount of the analyte was calculated by subtracting the unbound amount from the initial amount of the analyte. The values of K_d, K and K' were calculated using the listed Equations (3)–(5):

$$K_d = \frac{[C_i - C_f]}{m} \times V \quad (1)$$

$$K = K_{d(BPA)} / K_{d(phenolic)} \quad (2)$$

$$K' = K_{MIP} \text{ and } K_{NIP} \quad (3)$$

where C_i (mg/L) and C_f (mg/L) are the initial and final concentrations. V (L) is the volume used, and m (g) is the weight of adsorbents. $K_{d\ (BPA)}$ and $K_{d\ (phenolic)}$ are the static distribution coefficients of BPA and competitive compounds (phenol, 2,4-dichlorophenol and 2,4-dinitrophenol representing phenolic compounds), respectively. While K_{MIP} and K_{NIP} represent the selectivity coefficients of MIP and NIP, respectively.

RESULTS AND DISCUSSION

Characterization of Materials

Fourier Transform Infrared Spectroscopy Analysis

FTIR spectroscopy is a suitable method to determine the functional groups and types of bonds present in MIP [15]. BPA, MIP (MIP@MAA-β-CD) and NIP@MAA-β-CD were used as a reference to confirm if the polymerisation and interaction with the template have occurred. The results were obtained in the range of 400- 4000 cm^{-1} as shown in Figure 2. Strong peaks of 3148 cm^{-1}, 1718 cm^{-1}, 1606 cm^{-1}, 1386 cm^{-1}, 1240 cm^{-1} and 1151 cm^{-1} corresponding to O-H, C=O, C=C, C-H and C-O respectively were observed. There were no mark spectral differences observed between the MIP and NIP. Also, no functional group belonging to the BPA was observed. This suggests that the template was completely removed, and the imprinting of BPA onto the MIP was effective.

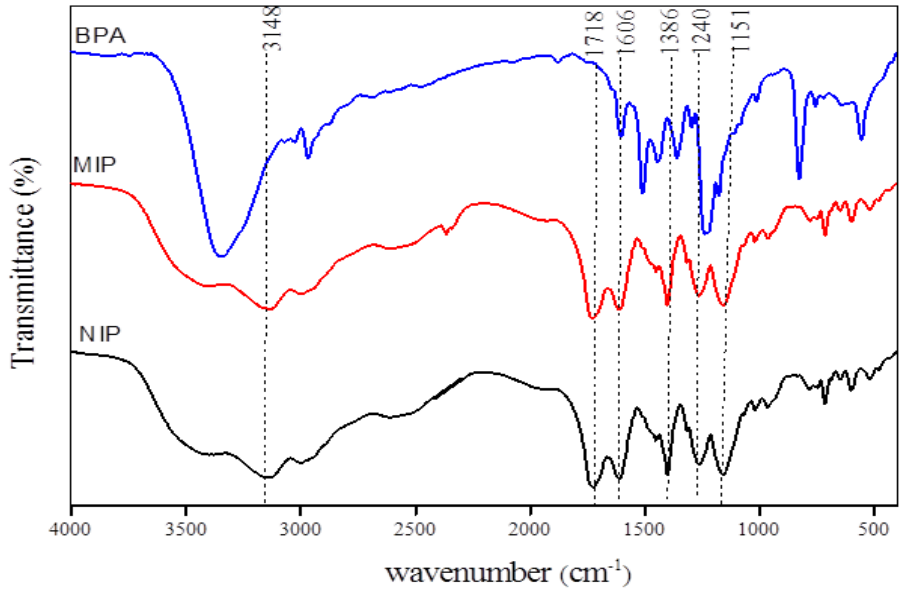

Figure 2: FT-IR spectra of bisphenol A (BPA), MIP@ MAA-β-CD and NIP@ MAA-β-CD.

Scanning Electron Microscope Analysis

SEM is a powerful visualisation tool used in material and polymer sciences [16]. It is an essential and valuable analysis technique for unfolding the understanding of the morphology and texture of the polymers. The obtained micrographs (Figure 3) showed distinct morphological differences between MIP@MAA-β-CD and NIP@MAA-β-CD. The MIP had a rough surface with cavities while the NIP had a smoother surface (Figure 3b) indicating that there were no specific binding sites formed by the template [17]. The cavity formed in the MIP (Figure 3a) was due to the imprinted sites created by the template molecule after it was removed [18].

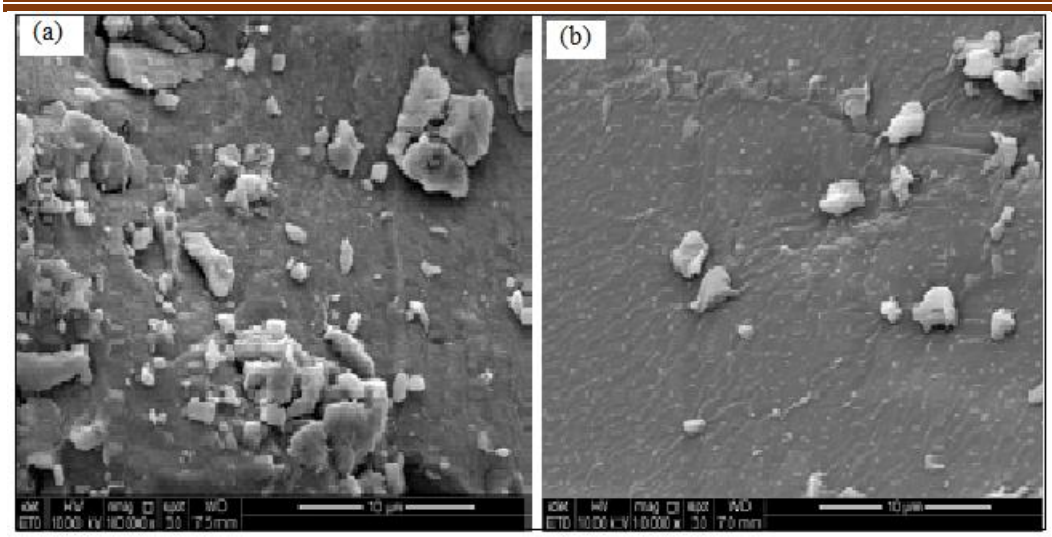

Figure 3: SEM Images of (a)MIP@MAA-β-CD(b) NIP@MAA-β-CD

Thermogravimetric Analysis

The thermal degradation behavior of (a) MIP@MAA-β-CD (b) NIP@MAA-β-CD was recorded in a nitrogen atmosphere in the range of 50–900 °C and are shown in Figure 4. Two stages of weight loss were observed, such a behavior has been observed formerly in TGA analysis similar to polymer backbone based on methacrylate monomers [19]. The materials were thermally unstable and started to lose mass upon heating below100 °C in the first stage due to the adsorbed water molecules [20]. The second stage of weight loss occurred in the range of 278–433 °C for NIP@MAA-β-CD and 278–501°C for MIP@MAA-β-CD, which might be owing to the decomposition of the polymer backbone. The MIP@MAA-β-CD showed higher thermal stability than the NIP@MAA-β-CD due to higher decomposition temperature, confirming that imprinted polymer layers were successfully synthesized similar results have been demonstrated elsewhere [19-22].

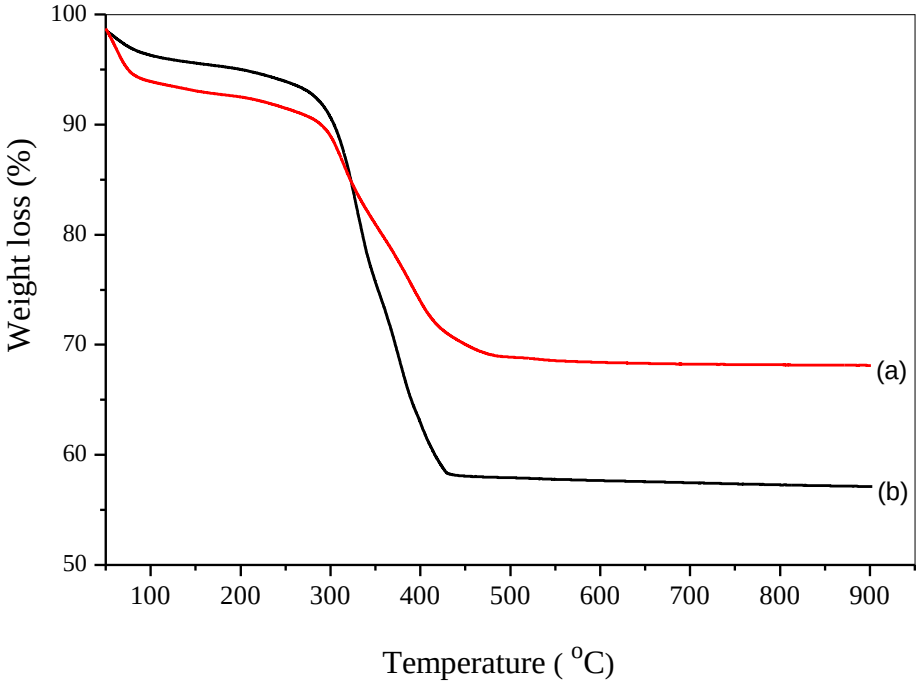

Figure 4: TGA curves of (a) MIP@MAA-β-CD(b) NIP@MAA-β-CD

Selectivity/ rebinding studies

The ability of any sorbent/adsorbent material to recognise and quantify its analyte in the presence of any other interferent in its matrix is known as selectivity [23]. The selectivity can be modified by enhancing the specific interactions situated inside imprints while minimizing the non-specific interactions with the bulk polymer [23-24].

A competitive adsorption experiment was carried out to demonstrate the selectivity of MIP@MAA-β-CD for BPA. From the results exhibited in Figure 5 and Table 1, it can be seen that the adsorption capacity of MIP toward BPA was the highest (4.00 mg/g) in addition to high imprinting effect of (1.91) obtained compared to other substrates, while the binding amount of these compounds onto NIP@MAA-β-CD were very poor (2.09 mg/g) this is attributed to the specific binding for BPA possessed by the MIP@MAA-β-CD, which was absent in the NIP@MAA-β-CD[25]. The synthesized MIP@MAA-β-CD can selectively recognize and separate BPA in the presence of its structurally related compounds. Similar findings were also observed by some researchers [21-27].

Table 1: Selectivity for competitive removal OF BPA onto MIP@ MAA-β-CD and NIP@ MAA-β-CD

Phenols	MIP@MAA-β-CD		NIP@MAA-β-CD		
	K_d (mg/g)	K	K_d (mg/g)	K	K'
Bisphenol A	4.00		2.09		1.91
2,4- Dichlorophenol	2.68	1.49	1.96	1.07	1.37
2,4-Dinitrophenol	2.17	1.85	1.59	1.31	1.36
Phenol	2.22	1.80	1.63	1.29	1.37

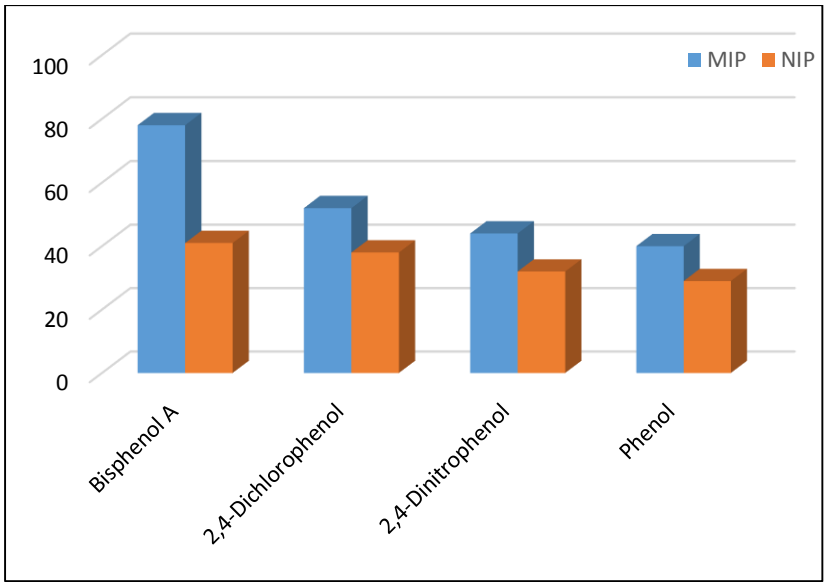

Figure 5: Selectivity study of MIP@ MAA-β-CD and NIP@ MAA-β-CD for BPA removal.

CONCLUSION

In this study, MIP@ MAA-β-CD was prepared by bulk polymerization technique using a molar ratio of the template molecules to the functional monomers to the cross-linking agents of 1:4:20 and characterized by SEM, FT-IR and TGA. The selectivity studies demonstrated that MIP@ MAA-β-CD contains a binding site that exactly matches the size and shape of the template molecule, compared to its structural analogs due to the higher imprinting factor (1.91) and maximum adsorption capacity (4.00 mg/g) obtained. Moreover, the modification of the polymer with β-Cyclodextrin increased the hydrophilicity of the polymer so that MIP can be applied to the adsorption of BPA in a water environment, which expands its practical applications.

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