



Cucurbit[6]uril as a functional monomer in molecularly imprinted polymers: synthesis, structural and thermal characterization

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Abstract

In a groundbreaking approach, Cucurbit[6]uril (CB[6]) has been successfully incorporated as a functional monomer to synthesize molecularly imprinted polymers (MIPs) through bulk polymerization, opening new avenues for advanced material development. Methacrylic acid (MAA) was used as a second monomer, with dimethylformamide (DMF), ethylene glycol dimethacrylate (EGDMA), and ammonium persulfate (APS) serving as the porogen, crosslinker, and initiator, respectively. In this study, two CB[6] to MAA ratios (MIP 1:80 and MIP 1:100) were tested, aiming for selectivity toward atrazine (AT) in aqueous media. The structure of the MIPs was analyzed using field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD) analysis and Fourier-transform infrared spectroscopy (FTIR), confirming that CB[6] was successfully polymerized. XRD analysis confirmed the amorphous nature of both MIPs, while FESEM revealed rough, wrinkled, and folded morphology. MIP 1:100 exhibited a rougher surface with less uniform pores than MIP 1:80. Thermal stability study demonstrated that increasing the MAA concentration reduces the polymer's thermal stability. A preliminary adsorption study was conducted under specific conditions (pH 6, initial AT concentration: 10 ppm, adsorbent dosage: 20 mg, contact time: 120 min, and room temperature). MIP 1:80 showed higher removal efficiency (28.9%) than MIP 1:100 (17.2%), suggesting that these MIPs are suitable for adsorption studies and can be further enhanced by optimizing the ratio and adsorption conditions in future research. This novel polymer could have significant potential for applications in selective adsorption, catalysis or as a sensor due to its unique structure and thermal properties.

Keywords Cucurbit[6]uril · Molecularly imprinted polymer · Bulk polymerization · Functional monomer

Introduction

Molecularly imprinted polymers (MIPs) are highly crosslinked polymers that contain imprinted cavities specifically designed for selective binding [1]. These cavities

give MIPs their exceptional affinity and selectivity for target molecules, making them ideal for applications requiring customized molecular recognition. The host–guest interaction concept is fundamental to the molecular imprinting technique (MIT), where specific binding sites are created within the polymer by imprinting a template molecule [2]. The goal of MIP development is to enable selective removal or recognition of target molecules.

The molecular recognition capabilities of MIPs arise from a template-controlled polymerization process. This process involves the formation of molecular binding sites through the cross-linking of functional monomers, which are pre-assembled around a template molecule. The complexation of template molecules and monomers is facilitated by covalent or non-covalent interactions [1]. MIP preparation typically involves bulk polymerization, beginning with the dissolution of the functional monomer, crosslinker, initiator and template in a porogenic solvent. The

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selection of functional monomers is crucial, as successful molecular recognition depends on the stable formation of a template-monomer complex via host–guest interactions [3]. Host–guest molecular recognition has garnered significant attention due to its high selectivity, specificity of the host structure and the unique structural relationships it establishes with guest molecules, including cations, anions or neutral molecules [4, 5].

Supramolecules are macrocyclic structures formed by linking building units through non-covalent interactions, resulting in macrocycles. These supramolecular macrocycles feature large recognition cavities, such as crown ethers, calixarenes, cyclodextrins and cucurbiturils [6]. The large cavity within these supramolecules enables them to function as hosts for guest molecules, making them ideal for studying host–guest molecular recognition through inclusion complexation. Previous studies have shown that β -cyclodextrin (β -CD) performs well in inner recognition, where its cavity can encapsulate various compounds, including drugs, pesticides, organic micropollutants, dyes, and heavy metals, based on its stereoscopic structure and size [7]. The inclusion process within the hydrophobic cavity of β -CD is influenced by the binding constant and strength, primarily governed by van der Waals forces, hydrophobic interactions, hydrogen bonding, and other non-covalent forces [8]. In aqueous environments, water molecules initially occupy the inner cavity but are displaced by non-polar guest molecules. This displacement is driven by factors such as the hydrophobic effect, the release of water energy, macromolecular stress relief, and van der Waals interactions between the guest and cavity [7].

Cucurbit[n]urils (CB[n]), previously known as cucurbiturils, form another family of supramolecules synthesized through an acid-catalyzed condensation reaction using glycouril and formaldehyde [9, 10]. Specifically, cucurbit[6]uril (CB[6]) is a hexameric organic compound from the cucurbitaceae family, consisting of six monomeric glycouril units (Fig. 1), which form a non-polar cyclic structure [11]. Cucurbit[6]uril (CB[6]) is an ideal functional monomer for molecularly imprinted polymers (MIPs) due to its unique structural and chemical features. The rigid, pumpkin-shaped structure of CB[6] provides a stable framework, ensuring consistent host–guest interactions during the polymerization process [12, 13]. Its large hydrophobic cavity offers an ideal environment for template molecules to be selectively encapsulated, allowing for high-affinity recognition. Furthermore, the presence of six carbonyl groups within the cavity introduces polar sites that enhance the stability of host–guest complexation via hydrogen bonding, van der Waals interactions, and dipole interactions [14, 15]. This dual character of CB[6], combining hydrophobicity with polar regions, is advantageous in tailoring molecular recognition sites, making

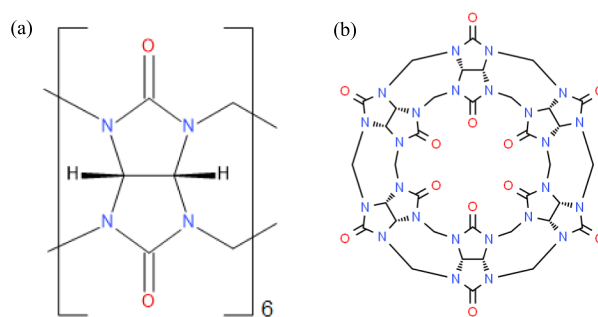


Fig. 1 The chemical structure of (a) glycouril monomer and (b) CB[6] macrocycle

it particularly useful in selective binding applications, such as the removal of herbicides or pollutants from solution [16, 17]. Moreover, its partial solubility in water and insolubility in organic solvents allows for efficient interaction with a variety of guest molecules, making it highly versatile in MIP synthesis. These features, coupled with their high thermal and chemical stability, make CB[6] a promising candidate for the development of highly selective, robust molecularly imprinted polymers.

This study investigates the synthesis and characterization of a novel molecularly imprinted polymer (MIP) designed for the selective recognition of atrazine, a widely used herbicide. In this work, atrazine serves as the template molecule, and cucurbit[6]uril (CB[6]) along with poly(methacrylic acid) (MAA) are used as functional monomers to create two different MIP formulations with varying CB[6]:MAA ratios (Fig. 2). The resulting MIPs are thoroughly characterized by examining morphology, the incorporation of CB[6] into the polymer matrix, as well as their thermal stability, crystallinity, and pore structure. This research lays the groundwork for utilizing the developed MIPs in future applications for selective recognition and removal of atrazine, offering potential for environmental monitoring and remediation.

Experimental

Materials

Cucurbit[6]uril (CB[6]), ammonium persulfate (APS), ethylene glycol dimethacrylate (EGDMA) and atrazine (AT) were obtained from Sigma Aldrich (St. Louis, MO, USA). Methacrylic acid (MAA), dimethylformamide (DMF), acetone and methanol were purchased from R & M Chemicals (Essex, UK), while acetic acid was from QR&C (ASIA) Sdn. Bhd. (Selangor, Malaysia). Ethanol was acquired from Systerm Chemicals (Selangor, Malaysia).

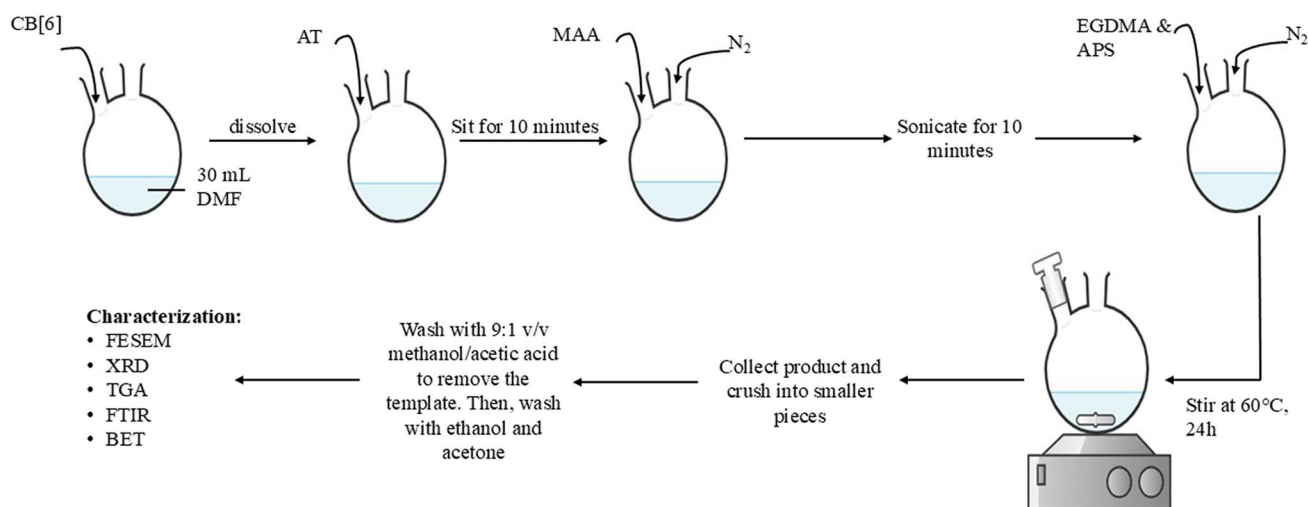


Fig. 2 General synthesis method of CB[6] based MIPs

Instrumentations

Morphologies and chemical composition of samples were observed by field emission scanning electron microscopy (FESEM, JEOL JSM-7600 F) was carried out to study the surface morphology of the samples. The elemental composition was studied using energy dispersive X-ray spectroscopy (EDX) analysis. The crystallinity of the samples was studied by using X-ray diffraction (XRD, Shimadzu X-ray diffractometer) analysis. The thermal stability of the samples prepared in this study was carried out by performing thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA851 thermal analyzer) with a heating rate of $10^{\circ}\text{C min}^{-1}$ at a temperature range of 0–800°C under continuous nitrogen atmosphere. To study the structural characteristics of all the samples, Fourier transform infrared analysis (FTIR, Perkin-Elmer FT-IR spectrophotometer coupled with UATR accessory) was conducted. The specific surface area and the pore structure were analyzed using a Brunauer-Emmet-Teller (BET) analyzer (Micromeritics, Tristar II Plus).

Synthesis of MIP/CB[6]

Firstly, 0.05 mmol of CB[6] were dissolved in 30 mL of DMF using a round bottom flask. Then, MAA (4 mmol and 5 mmol) and 0.05 mmol of AT were added into the mixture, swirled and let to sit for 10 min. The mixture was then ultrasonicated for 10 min and deoxygenated through nitrogen purging. 2 mL of crosslinker (EGDMA) was dissolved and the mixture was swirled. Initiator, 40 mg APS were added into the pre-polymerized mixture and sealed. The mixture was allowed to perform polymerization at 60°C for 24 h under nitrogen atmosphere.

After polymerization, the resulting white polymer was collected and crushed. The crushed solid polymer was then washed using 9:1 v/v methanol and ethanoic acid through Soxhlet extraction and ultrasonication to remove template molecules and unreacted monomers. The template removal process was performed until no peak was observed at wavelength 222 nm under UV–VIS analysis (Fig. 3). The polymer was collected and washed with ethanol and acetone alternately to remove the last residue of AT. Finally, the polymer dried in the desiccator and ground into powder.

Results and discussion

Synthesis of MIP/CB[6]

The synthesis process for the molecularly imprinted polymer (MIP) begins with the dissolution of CB[6] in DMF, followed by the addition of methacrylic acid (MAA) at varying molar concentrations. This step is critical for establishing functional groups within the polymer network. MAA, as a hydrophilic functional monomer, plays a key role in forming the binding sites within the polymer matrix. The incorporation of CB[6] as a second monomer enhances the structural integrity and selectivity of the resulting MIP, as its macrocyclic structure can provide specific recognition sites for target molecules.

CB[6] has rigid and highly symmetrical cavities, providing the ability to form host–guest interactions with AT molecules via hydrophobic interactions. The addition of MAA enhances the binding performance of the MIP as it introduces carboxyl (–COOH) groups, providing more selective binding properties by hydrogen bonding and electrostatic

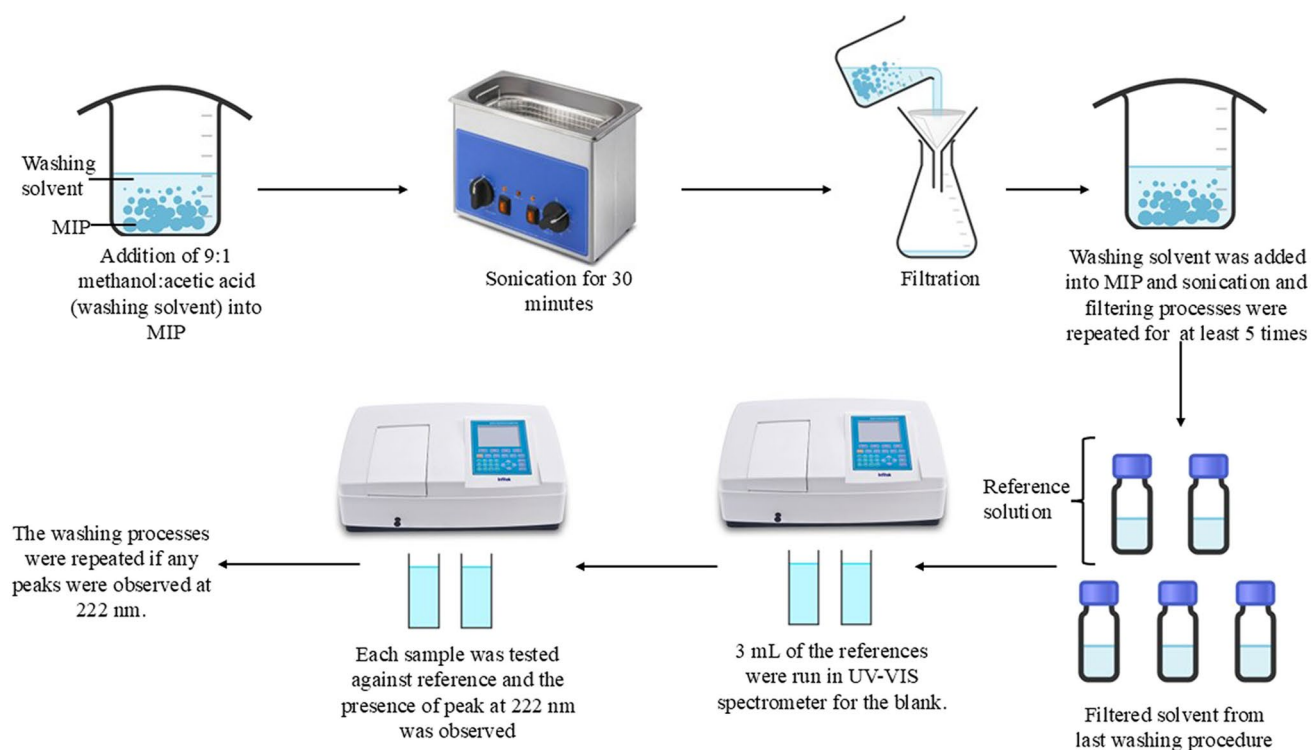


Fig. 3 Schematic diagram on MIPs' washing procedure

interactions. It is a synergistic effect between both monomers to improve the affinity of the MIP towards the AT.

The ultrasonication and nitrogen purging steps are essential for ensuring that the polymerization mixture is well-dispersed and free from oxygen, which could interfere with the polymerization process. The addition of the initiator (APS) and a crosslinker (EGDMA) initiates the free radical polymerization and promotes the formation of a stable and well-defined polymer network, respectively.

After the polymerization step, the removal of template molecules and unreacted monomers is achieved through Soxhlet extraction and ultrasonication with a methanol/ethanoic acid solution. This purification process ensures that only the MIP remains free from any residual template molecules that could affect the selectivity of the polymer. The use of ethanol and acetone alternately ensures thorough washing to remove any remaining monomers or impurities, guaranteeing the purity of the final polymer product. The template removal process was performed until no peak was observed at wavelength 222 nm under UV–VIS analysis. The polymerization under a nitrogen atmosphere at 60 °C for 24 h ensures the formation of a robust polymer network, while the subsequent drying and grinding steps yield the final powdered MIP product. These procedures ensure that the resulting MIP has a high degree of selectivity and porosity for the target molecule, making it suitable for use in adsorption and molecular recognition applications.

The final polymer product appears white in color, and it is then sent for physical–chemical characterization. The selection of MIP formulations with CB[6]: MAA ratios of 1:80 and 1:100 reflect an optimized balance between the functional monomers and the crosslinker, which is critical for achieving selective binding and effective polymerization. In these ratios, CB[6] is the functional monomer providing recognition sites for the template, while the template molecule itself establishes the imprint for selective adsorption.

The higher ratio of CB[6] to MAA (e.g., 1:80 and 1:100) is designed to ensure better polymer network formation between functional monomers and crosslinkers. The increase in CB[6] maximizes the availability of binding sites without overloading the polymer matrix, which could compromise the structural integrity or cause steric hindrance during binding. These ratios were selected based on preliminary tests to ensure the balance between structural robustness and functional efficiency, making them ideal candidates for further evaluation in adsorption studies.

Characterization of MIP/CB[6]

Morphology analysis

The surface morphologies of CB[6], MIP 1:80, and MIP 1:100 were examined using field emission scanning electron

microscopy (FESEM), with the results depicted in Fig. 4a. CB[6] displayed a distinct crystalline structure characterized by smooth surfaces and a rectangular geometry, indicative of its organized molecular framework. In contrast, both MIP 1:80 (Fig. 4b) and MIP 1:100 (Fig. 4c) exhibited rough, wrinkled and folded surface structures, typical of highly crosslinked polymer networks formed during bulk polymerization. MIP 1:80 exhibited more uniform pores compared to MIP 1:100. In addition, the MIP 1:100 displayed a more folded and thicker surface with lower number of pores in comparison with MIP 1:80. Despite these textural differences, there were no observable variations in particle size and shape between the two MIPs, suggesting that the polymerization conditions did not significantly affect their macroscopic morphology.

Further analysis was performed using energy-dispersive X-ray (EDX) spectroscopy to determine the elemental composition of the samples (Table 1). CB[6], as an organic molecule, is composed of carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) atoms. Due to the limitations of EDX in detecting hydrogen, the analysis focused on the relative atomic concentrations of C, N, and O. The EDX results confirmed the successful incorporation of CB[6] into both MIPs, as evidenced by the presence of nitrogen atoms (a signature element of CB[6]). The atomic concentration of nitrogen in MIP 1:80 was recorded at 2.48%, while MIP 1:100 exhibited a slightly lower concentration of 1.27%. This difference reflects the relative quantities of CB[6] used during polymerization and further validates the role of CB[6] as a functional monomer in the formation of these MIPs.

These findings underline the successful integration of CB[6] into the polymeric framework of the MIPs, providing structural insights that correlate with their morphological and compositional characteristics. Such data are critical for understanding the material properties of the MIPs, particularly their ability to form selective recognition sites through host–guest interactions.

Table 1 EDX analysis of CB[6], MIP 1:80 and MIP 1:100

Samples	C (%)	O (%)	N (%)
CB[6]	43.73	23.64	32.63
MIP 1:80	77.36	20.16	2.48
MIP 1:100	81.66	17.07	1.27

Crystallinity analysis

The crystalline and amorphous nature of the materials was analyzed using X-ray diffraction (XRD) patterns, as presented in Fig. 5a. The XRD spectrum for CB[6] exhibits three sharp diffraction peaks at $2\theta = 15^\circ$, 23° , and 31° , which are characteristic of its highly ordered crystalline structure [18]. These distinct peaks arise from the regular molecular arrangement of CB[6], reflecting its symmetrical and rigid framework.

In contrast, the XRD patterns for both MIP 1:80 and MIP 1:100 (Fig. 5b) displayed broad diffraction peaks centered around $2\theta = 20^\circ$, indicative of their amorphous nature. The lack of sharp peaks in the MIP samples suggests a significant reduction in crystalline order due to the crosslinking and polymerization processes. This transformation highlights the effective integration of CB[6] within the polymer matrix, where its crystalline nature is disrupted during the formation of the MIPs.

These observations are consistent with the intended design of the MIPs, as amorphous polymers are typically preferred for their irregular surface morphology and enhanced ability to accommodate template molecules within their imprinted cavities. The XRD data thus provides critical insight into the structural changes associated with the polymerization process and the successful formation of molecularly imprinted sites tailored for host–guest interactions.

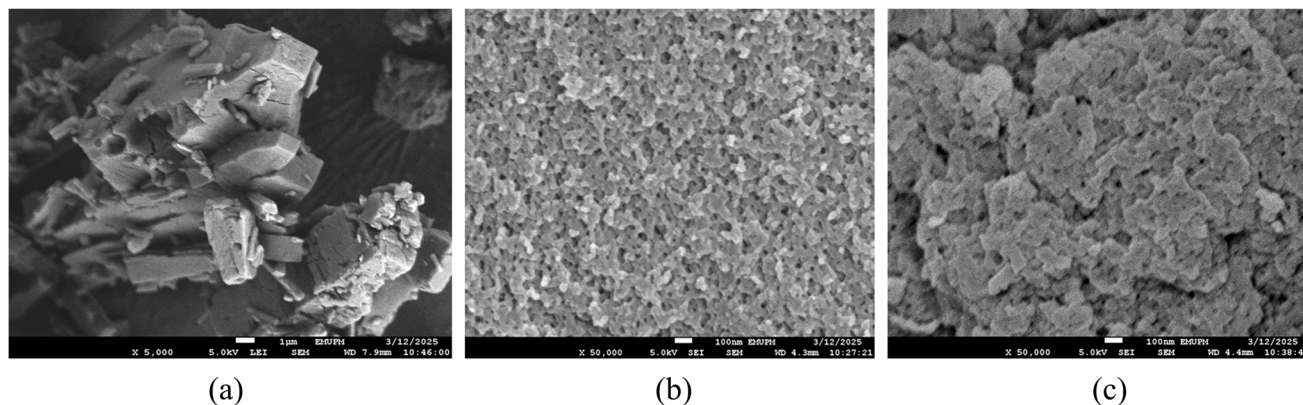


Fig. 4 FESEM images of (a) CB[6], (b) MIP 1:80 and (c) MIP 1:100

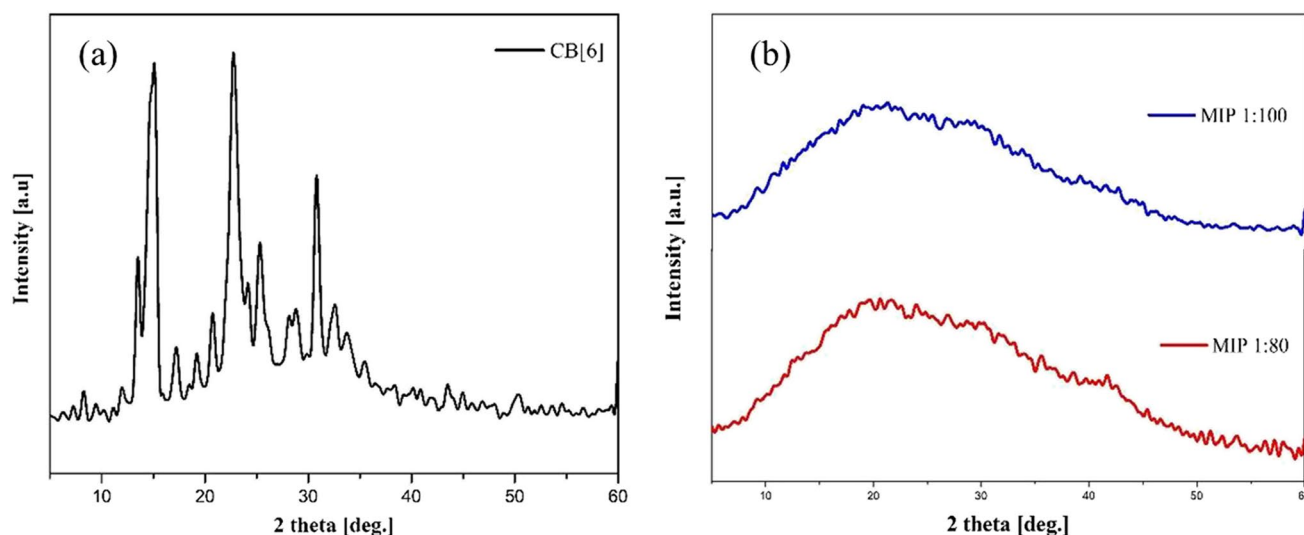


Fig. 5 XRD patterns of (a) CB[6] and (b) MIP 1:80 and MIP 1:100

Thermal stability

Thermal stability analysis of CB[6], MIP 1:80, and MIP 1:100 was conducted via Thermogravimetric Analysis (TGA) under a nitrogen atmosphere, with the temperature increasing up to 800°C. The TGA curves in Fig. 6a reveals a consistent initial weight loss between approximately 50°C and 150 °C across all samples, which is attributed to the evaporation of water molecules. CB[6] exhibits a two-stage weight loss pattern, with the first stage occurring at 50.76°C, accounting for an 8.36% loss in mass, primarily due to the evaporation of water. The second stage spans from 296.48°C to 579.64 °C, with a significant weight loss of 72.85%, corresponding to the decomposition of the polymer itself [19]. These thermal degradation stages are consistent with previous studies on polymethacrylic acid (PMAA), which exhibit a three-stage decomposition. The first stage involves dehydration and the scission of polymer side chains below 250°C, followed by decarboxylation at 250 - 400°C, which releases CO₂ and small hydrocarbons. The final stage, above 400°C, represents the complete breakdown of the polymer backbone [20–22].

From Fig. 6b-c, both MIP 1:80 and MIP 1:100 show initial weight loss between 50°C and 100°C, indicating the evaporation of water molecules from the polymer matrices. However, MIP 1:100 demonstrates a higher weight loss (40.41%) compared to MIP 1:80 (12.61%), suggesting that the higher methacrylic acid (MAA) concentration in MIP 1:100 results in greater water entrapment within the polymer structure. MAA, being a hydrophilic monomer, increases the hydrophilicity of the polymer, thereby enhancing the trapping of water molecules in the matrix [23, 24].

In the second stage of decomposition, starting around 200°C, the breakdown of polymer backbones formed by MAA and the degradation of polymer side chains occurs. A sharp decline in weight is observed around 400°C, which marks the decomposition of CB[6] macrocycles. MIP 1:80 exhibits a significant weight loss (89.53%) compared to MIP 1:100 (57.56%), indicating that the MIP 1:80 composition contains a higher amount of CB[6]. This suggests that CB[6] contributes more to the thermal stability of the polymer in MIP 1:80 than in MIP 1:100. Overall, CB[6] demonstrates the highest thermal stability, while MIP 1:80 is more thermally stable than MIP 1:100. This decline in thermal stability with increasing MAA concentration is primarily due to the presence of carboxylic groups in MAA, which are more susceptible to thermal degradation at lower temperatures. An increase in MAA concentration results in a higher number of thermally labile sites, thereby reducing the overall thermal stability of the MIP [25].

General structure by Fourier-transform infrared spectroscopy

FTIR spectra in Fig. 7 reveal the distinct vibrational features of the materials studied, highlighting key differences in functional groups and polymer interactions. All samples exhibit a broad O–H stretch peak between 3700 and 3100 cm^{−1}, attributed to water crystallization. Notably, the O–H stretch peak is broader and more intense in MIP 1:80 and MIP 1:100 compared to CB[6], indicating enhanced hydrogen bonding in the poly(methacrylic) acid (PMAA) segments of the polymer chains. These hydrogen bonding interactions typically occur due to the presence of carboxyl groups in MAA, which

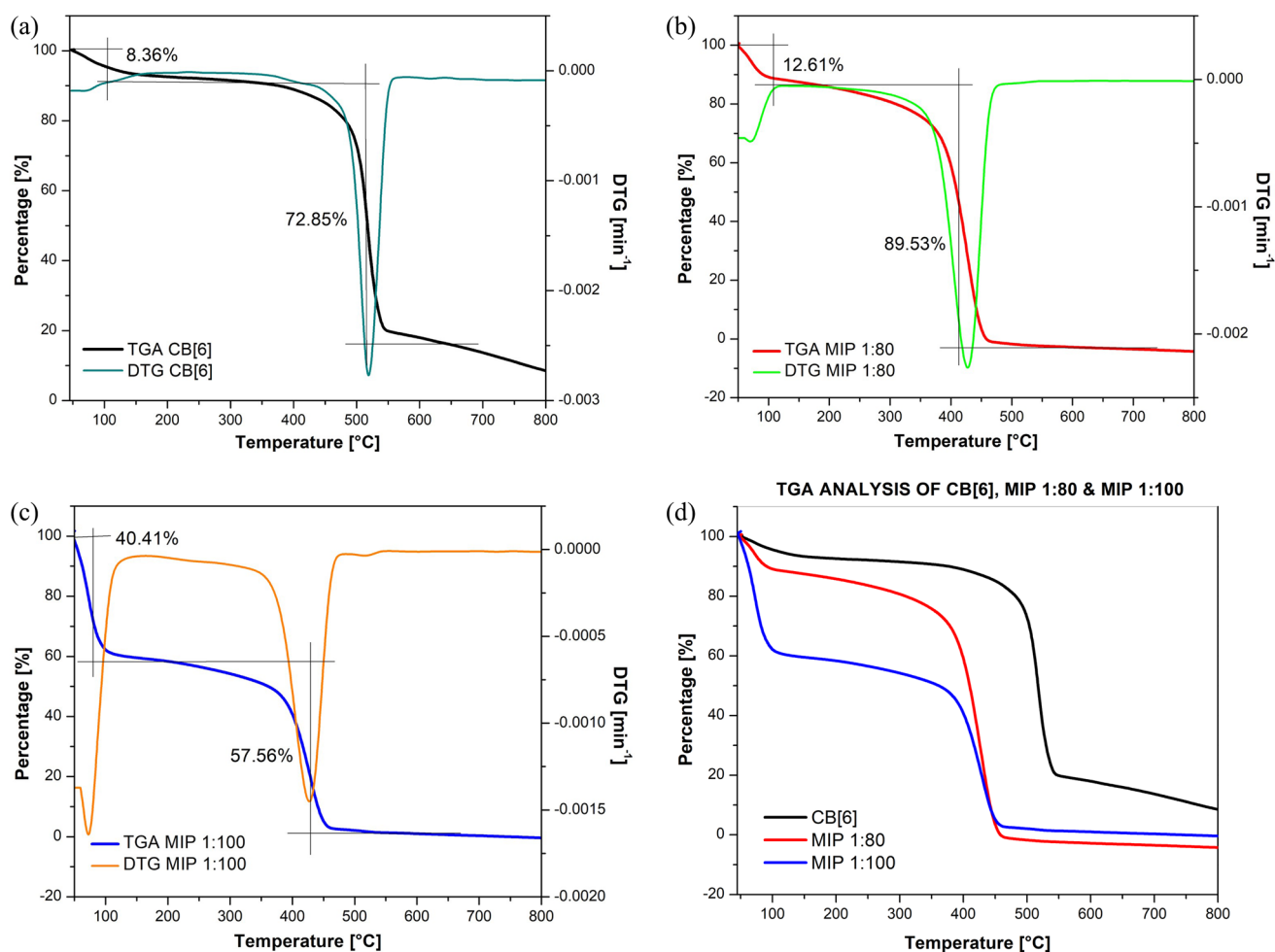


Fig. 6 The TGA and DTG curve of (a) CB[6], b MIP 1:80, c MIP 1:100 and (d) thermal stability comparison of the materials

interact with water molecules or other polymer functional groups (Fig. 7).

Both MIPs (1:80 and 1:100) show more prominent peaks in the 3000–2800 cm^{-1} region, reflecting an increased number of aliphatic C-H bonds in the polymer matrix. This suggests that the incorporation of MAA, which contributes aliphatic groups, enhances the presence of C-H bonds within the MIP structures [26]. Additionally, all materials demonstrate a strong sharp peak near 1700 cm^{-1} , corresponding to the stretching vibration of the C=O groups from the glycoluril units in CB[6]. This peak is a clear indication of the carbonyl group's presence in the molecular structure of CB[6] and is similarly observed in the MIPs, suggesting that CB[6] is successfully incorporated into the polymer network [27].

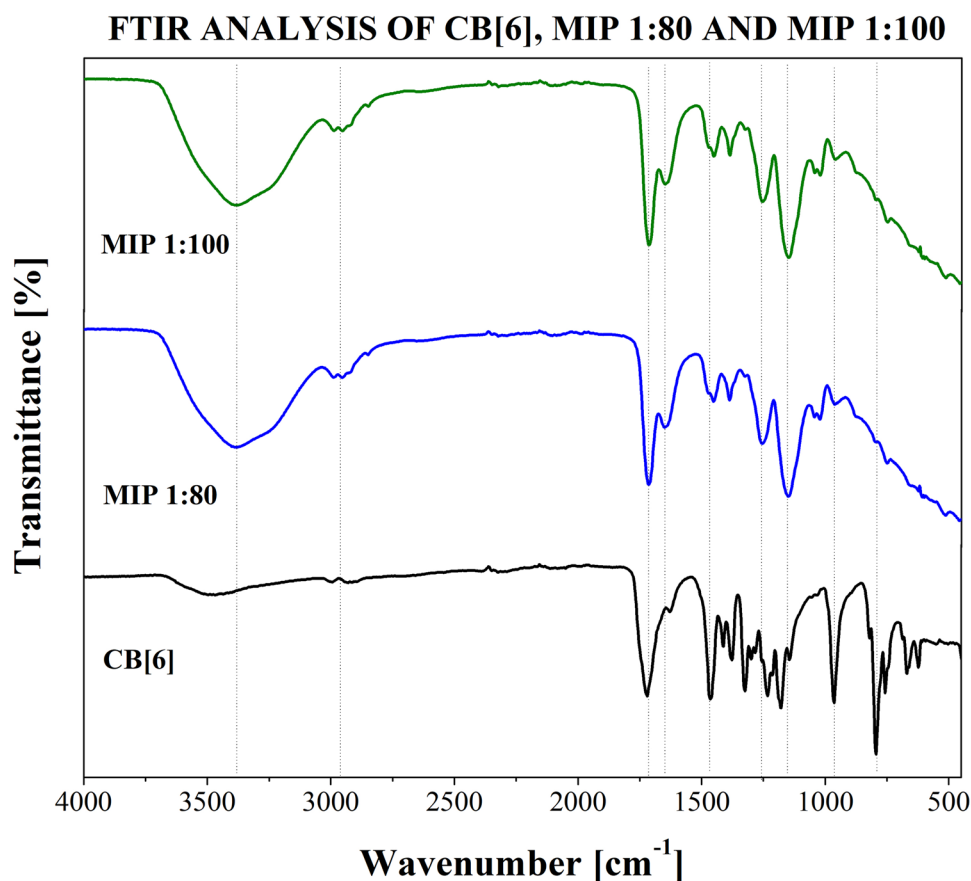
In the 1200–1150 cm^{-1} range, peaks corresponding to the C-N stretching vibrations of the polymer chains are observed. These peaks confirm the presence of the amide functional group within the MIP structure, particularly linked to the CB[6] monomer. A strong and sharp peak near 1500 cm^{-1} , characteristic of C-H bending vibrations from

the methylene groups in the symmetric cyclic structure of CB[6], is evident in the CB[6] spectrum [28]. This peak is also present in both MIP 1:80 and MIP 1:100, albeit with reduced intensity, which can be attributed to the lower concentration of CB[6] in these MIP formulations.

The region between 800 and 670 cm^{-1} exhibits characteristic C-H out-of-plane bending vibrations, indicative of the rigid, symmetric structure of the CB[6] macrocycle. These vibrations are consistent with the cyclic nature of the CB[6] monomer and further confirm its incorporation into the MIP matrix [29]. Additionally, CB[6] features a cyclic tertiary amide structure, and since no N-H bonds are present within the structure, no N-H stretching vibrations are detected at the region between 3700 and 3100 cm^{-1} in the FTIR spectra. This lack of N-H bond detection is consistent with the molecular structure of CB[6] and further supports the assignment of the observed peaks.

Overall, the FTIR analysis confirms that CB[6] is successfully incorporated into the MIP structure as a functional monomer, with key functional groups such as C=O, C-N, and C-H

Fig. 7 FTIR spectra of CB[6], MIP 1:80 and MIP 1:100



contributing to the characteristic spectral features observed in the MIPs. The variations in peak intensities between CB[6] and the MIPs suggest successful polymerization and interaction between the monomers in the polymer matrix.

BET analysis, pore size, and volume distribution

The Brunauer-Emmet-Teller (BET) surface area analysis provides valuable insight into the porosity and surface characteristics of the materials under study. The data in Table 2 shows that all the materials, including CB[6], MIP 1:80, and MIP 1:100, exhibit pore sizes in the range of 1–100 nm, which confirms that all are nanoporous in nature.

Table 2 The specific surface area, pore volumes and pore sizes of CB[6], MIP 1:80 and MIP 1:100 obtained from BET analysis

Sample	BET SA ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore size (nm)
CB[6]	3.3008	0.001506	1.8249
MIP 1:80	1.0823	0.000466	1.7220
MIP 1:100	0.0451	0.000185	1.6332

SA surface area

CB[6], as a single component, exhibits the largest BET surface area ($3.3008 \text{ m}^2/\text{g}$), which suggests that its molecular structure and crystalline form create a relatively open, less dense network, offering more surface area for interaction. In contrast, the incorporation of poly(methacrylic) acid (MAA) as a second functional monomer in MIP 1:80 and MIP 1:100 leads to a denser polymer network. The hydrophilic nature of MAA promotes stronger intermolecular interactions between polymer chains, which can reduce the surface area of the MIPs ($1.0823 \text{ m}^2/\text{g}$ for MIP 1:80 and $0.0451 \text{ m}^2/\text{g}$ for MIP 1:100) by restricting the formation of larger pores within the polymer matrix. This behavior has been observed in several studies [30].

The pore size and pore volume distribution follow a similar trend to the BET surface area. CB[6], as a single component, exhibits larger pores and greater pore volume, reflecting its more open and crystalline structure. With a BET surface area of $3.3008 \text{ m}^2/\text{g}$, CB[6] has relatively large adsorption sites that provide ample space for guest molecules. In contrast, the incorporation of poly(methacrylic) acid (MAA) into the MIP formulations (MIP 1:80 and MIP 1:100) leads to a denser polymer network, which restricts the formation of larger pores and reduces the overall pore volume. The pore size for MIP 1:80 (1.7220 nm) and MIP 1:100 (1.6332 nm) is smaller compared to CB[6] (1.8249

nm), reflecting the effects of the more compact polymer structure induced by MAA.

Similarly, the pore volume decreases significantly for MIP 1:80 ($0.000466 \text{ cm}^3/\text{g}$) and MIP 1:100 ($0.000185 \text{ cm}^3/\text{g}$) compared to CB[6] ($0.001506 \text{ cm}^3/\text{g}$). This reduction can be attributed to the hydrophilic interactions between MAA molecules, which can lead to tighter packing of the polymer chains and a corresponding decrease in pore volume. As the MAA content increases, the polymer matrix becomes denser, leaving fewer and smaller voids available for adsorption [31]. This reduction in pore size and pore volume directly impacts the polymer's ability to adsorb target molecules, making the structure less selective and tailored for specific recognition tasks.

Preliminary adsorption study

A preliminary study on the adsorption of atrazine has been conducted to test the adsorptive ability of the MIPs that have been prepared in this study. The preliminary study was carried out under pH 6, with adsorbent dosage and initial concentration of adsorbate were 20 mg and 10 ppm, respectively. Under room temperature, the adsorbent was stirred

using a multi-stirrer for 120 min and the removal efficiency was calculated. Both MIPs depicted the ability to perform adsorption in aqueous solution. The obtained removal efficiency for MIP 1:80 and MIP 1:100 was 28.9% and 17.2%, respectively. The lower adsorption efficiency may be due to the lower amount of CB[6] in the polymer chain. Although the adsorption efficiency is lower, it can be improvised in the future study by optimizing the synthetic ratio of MAA and CB[6], also by optimization of adsorption conditions such as initial concentration of adsorbate, adsorbent dosage, temperature, pH and contact time.

During the adsorption, the atrazine molecules are loaded onto the cavities of the CB[6] (Fig. 8) through non-covalent interactions. Atrazine is a moderately hydrophobic molecule due to the presence of non-polar hydrocarbon groups in its structure, along with the chlorine atoms and triazine structure, contributing to lower water solubility [32]. This hydrophobic structure allows the occurrence of host–guest interaction between CB[6] cavity and atrazine molecules, also aided by the hydrogen bonding between hydrogen (attached to nitrogen atom in atrazine) and oxygen atom (from carbonyl group of CB[6]) (Fig. 9). The presence of MAA

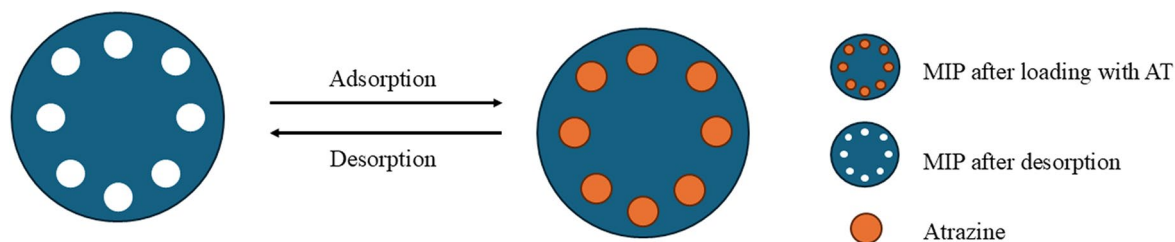
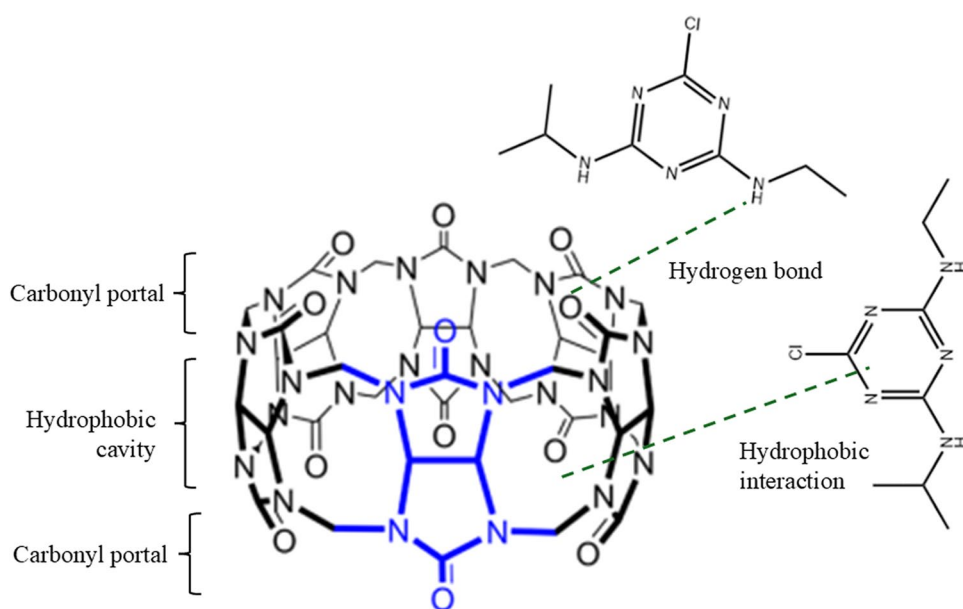


Fig. 8 General schematic representation of selective adsorption–desorption of atrazine into the cavities of MIPs

Fig. 9 Possible interaction mechanisms of CB[6] in MIPs with atrazine molecules



within the polymer structure further improves the binding of atrazine through hydrogen bonding and π -stacking [33].

Conclusion

Based on the comprehensive characterization results, the molecularly imprinted polymers (MIPs) incorporating CB[6] exhibit promising properties for selective molecular recognition. The FTIR analysis confirmed the successful incorporation of CB[6] into the MIP structure, evidenced by key functional group peaks. The BET surface area and pore size distribution analysis revealed that the polymer network's porosity is influenced by the addition of MAA, which leads to a denser network with reduced surface area and pore volume. This is consistent with the expected behavior of MIPs, where the balance between functional monomers, crosslinkers, and the template dictates the polymer's adsorption characteristics. The physical and chemical characterization of the synthesized MIPs, particularly their porosity and functional group composition, suggests that these materials are well-suited for selective adsorption applications. However, further studies are needed to evaluate their performance in real adsorption scenarios, specifically targeting environmental contaminants such as atrazine. Future work could focus on optimizing the polymer formulation for increased efficiency in atrazine removal, through both adsorption capacity studies and desorption experiments. This would ensure the development of a highly efficient, environmentally friendly solution for selective molecular recognition and environmental remediation.

By refining the synthesis and characterization of MIPs, particularly for target pollutants, this study lays the foundation for their use in practical applications, such as water treatment and sensor technologies. Further research into the specific interactions between the MIPs and target molecules like atrazine will be crucial to their success in real-world applications.

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Data Availability No supplementary data for this paper. All data has been provided in the paper.

Declarations

Conflict of interests The authors declare no competing financial or nonfinancial interests that are directly or indirectly related to this work.

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