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Performance evaluation and application of molecularly imprinted polymer for separation of carbamazepine in aqueous solution

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ABSTRACT

A molecularly imprinted polymer (MIP) for selective adsorption of carbamazepine (CBZ) in aqueous solution was synthesized by precipitation polymerization using CBZ as a template molecule and methacrylic acid (MAA) as a functional monomer. The performance of the CBZ–MIP was evaluated in terms of selectivity, adsorption capacity, binding characteristics, loading volume, and elution volume. The CBZ–MIP exhibited a high affinity for CBZ over the competitive compound (Diclofenac) and was more suitable to remove low concentrations of CBZ in large-volume water samples. A binding performance experiment indicated that the adsorption of CBZ–MIP was characterized by both specific and non-specific binding interactions. Moreover, the regenerability of the MIP was affirmed in ten sequential cycles of adsorption/desorption without a significant loss in recovery. Finally, the CBZ–MIP was applied to enrich CBZ in environmental water samples, and the CBZ concentrations were subsequently determined using HPLC-UV. The results were in good agreement with corresponding LC–MS/MS data.

1. Introduction

In recent years, numerous studies have shown that the continual release of pharmaceuticals into the environment has the potential to create a constant exposure that could allow pharmaceuticals to resemble persistent organic pollutants [1,2]. Carbamazepine (CBZ), a drug widely used to treat epilepsy and bipolar disorder, is an important pharmaceutical drug in this respect because of its heavy use, high recalcitrance, and potential ecotoxicology. Studies have reported its presence in wastewater (up to 6.3 μg/L) [3], surface water (up to 1.1 μg/L) [3–5], and drinking water (30 ng/L) [3]. Its resistance to biodegradation and stability as it moves through different aquatic compartments causes CBZ to be a highly environmentally relevant pharmaceutical drug [6]. Because of its bio-refractory nature, numerous methods, such as ozonation, UV radiation, UV/H_2O_2 degradation [7], and photocatalytic degradation with TiO_2 [8], have been developed to remove this pollutant from water. However, current advanced processes are inefficient because they also remove high concentrations of other compounds of less environmental significance, which impacts treatment costs [9]. Usually, these advanced treatment processes do not completely mineralize the compounds of interest. Therefore, the loss of CBZ only partially accounts for treatment efficiency, because of the formation of transformation products that are more resistant to degradation. These stable transformation products may increase the overall toxicity of treated water and worsen the environmental and health impacts [10]. However, advanced removal methods are normally non-selective and increase the cost of wastewater treatment. Because of the environmental relevance of CBZ and the cost of current advanced removal methods, the development of highly selective removal methods is of great concern.

Molecular imprinting is a rapidly growing field relevant to science research as well as industrial applications related to separation, artificial receptors, catalysts, and sensors, since molecularly imprinted polymers (MIPs) have high selectivity, mechanical strength, and resistance to acids, bases, organic solvents, high pressures, and temperatures. Molecular imprinting forms selective recognition sites that are complementary both in shape and chemical structure to the template molecule, and after removal of the template, these sites can bind to the template molecule or closely related structural analogues with similar affinity and selectivity as natural antibodies [11]. Additionally, MIPs are stable, easy to prepare, inexpensive, and can be reused many times without decrease in performance. Therefore, molecular imprinting offers a versatile platform for creating a polymer matrix with molecule-specific recognition properties for applications ranging from removal of low concentrations of pollutants from aqueous solutions, to analytical techniques [12].

Selective removal of low concentrations of pollutants in water is an emerging technique with promising potential. MIPs imprinted

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with α-estradiol were used to remove estrogenic pollutants from spiked lake water [13]. Le Noir et al. employed MIPs to remove environmentally relevant concentrations of 17β-estradiol from aqueous solution using MIP adsorbent columns [14]. MIPs were also proposed to remove phenolic estrogen pollutants [15].

There are very few studies on the application of MIPs to remove CBZ from aqueous samples. Only two papers have reported the use of MIPs to selectively extract CBZ from wastewater and urine samples [16,17]. However, to the best of our knowledge, no studies have investigated the basic material properties of CBZ–MIPs related to their adsorbent capacity, rebinding of CBZ, equal and unequal opportunity competition of template, and the leakage of templates. Also, only a few studies have attempted to remove CBZ present in low concentrations in relatively large volume. This would allow the application of MIPs in the removal of CBZ from aqueous phases, especially, at low concentrations in wastewater, surface water, and ground water. In this study, MIP was synthesized by precipitation polymerization. The objective was to evaluate and confirm the applicability of CBZ–MIPs for the competitive separation of CBZ in an aqueous solution as mentioned above. Furthermore, the CBZ–MIPs were applied to extract CBZ from real water samples for HPLC analysis.

2. Experimental

2.1. Chemicals

CBZ, diclofenac (DFC) sodium salt, methacrylic acid (MAA), divinylbenzene 80 (DVB-80), 2,2′-azobisisobutyronitrile (AIBN), HPLC grade acetonitrile (ACN), methanol, and toluene were all purchased from Sigma–Aldrich (Steinheim, Germany). Acetic acid and formic acid were purchased from Merck (Darmstadt, Germany). AIBN was recrystallized in methanol prior to use.

Standard stock solutions of CBZ (8 g/L) and DFC (4 g/L) were prepared in a methanol: water (1:1, v/v) mixture and Millipore water, respectively and were stored at −20 °C.

2.2. Apparatus and analytical methods

The HPLC analyses were carried out using an Agilent 1050 HPLC (Agilent Technologies, USA) equipped with a 79855A 21-Vial auto sampler, a G1303A Vacuum Degasser, a 79853C Variable Wavelength UV detector, and a 79852A Quaternary Pump. The UV detection wavelength was 254 nm and the column temperature was maintained at 30 °C. A Gemini-NX C18 column (250 mm × 4.6 mm, i.d., 5 μm) was used for separation. The elution conditions were described previously [18]. Briefly, the gradient mobile phase consisted of Millipore water with 26.5 mmol/L formic acid (solvent A) and acetonitrile (solvent B). The flow rate was 1.0 mL/min. The gradient was increased from 18% B to 20% B in the first 4 min followed by a gradual increase to 55% B over 3 min, an increase to 60% B in 5 min (holding for 3 min), an increase to 100% B in 3 min (holding for 4 min), and a return to the initial conditions of 18% B over 7 min; these conditions were maintained for 5 min to allow for equilibration before the next injection. The injection volume was 20 μL. Samples were filtered through a 0.45 μm syringe filter (Millipore) before injection. Quantification of CBZ and DFC was performed using an external standard method. The linear range was established between 0.1 and 1.0 mg/L with a correlation coefficient (R^2) of 0.9997. The limit of detection (LOD) was 0.01 mg/L for CBZ and DFC, and the limit of quantitation (LOQ) was 0.1 mg/L for CBZ and DFC. LC–MS/MS analyses of CBZ was carried out by an independent laboratory, using a previously published LC–MS/MS procedure [19].

A Baker SPE 12G system (Mallinckrodt Baker, Griesheim, Germany) with a vacuum manifold was used in this study to mimic water purifying equipment. Separation tests were performed using this SPE apparatus.

2.3. Preparation of MIP by precipitation polymerization

The MIP synthesis procedure used in this study was based on an established procedure [20], with slight modification. Briefly, for the preparation of CBZ–MIP, 151 mg (0.64 mmol) of CBZ was mixed with 0.33 mL (3.89 mmol) of the functional monomer MAA in a 250 mL screw-capped glass vial followed by the addition of 50 mL of porogen (a mixture of acetonitrile and toluene, 75:25, v/v). To this solution, 1.82 mL (13.06 mmol) of cross-linker DVB-80 and 92.5 mg (0.565 mmol) of initiator AIBN was added. The solution was purged with nitrogen in an ice bath for 5 min to remove oxygen, and subsequently sealed in the glass vial. The temperature was ramped from room temperature to 60 °C over a period of around 2 h and held at this temperature for 24 h while stirring. The resultant polymer was Soxhlet extracted with methanol to remove the template and filtered. This procedure was repeated several times until CBZ could not be detected in the filtrate. The remaining polymer was dried under vacuum at 60 °C and was used in subsequent experiments. The corresponding non-imprinted polymer (NIP) was prepared in the same manner but in the absence of template. To establish the reproducibility of the MIP preparation protocol, three batches of polymer strictly following the protocol outlined above were conducted.

2.4. MIP column preparation

Empty SPE cartridges (63 mm × 9 mm i.d.) were dry-packed with 71 mg of MIP or NIP. A Baker SPE 12G system with a vacuum manifold was applied to force solutions through the particle bed at a flow rate of 0.15–0.30 mL/min. Prior to loading the sample, the cartridges were pre-conditioned with 5 mL of methanol and 5 mL of acetonitrile, followed by 5 mL of Millipore water at 0.1 mL/min. If not used immediately, pre-conditioned MIP cartridges were sealed with appropriate stoppers and stored at 4 °C to prevent drying by solvent evaporation.

2.5. Performance of MIP

2.5.1. Confirmation of selectivity

The selectivity of the CBZ–MIP was evaluated through two different loading methods, defined as equal and unequal opportunity competition adsorption. DFC was used as a competitor. In the equal opportunity competition adsorption experiment, 5 mL of a mixture of CBZ and DFC in a methanol: water (1:1, v:v) solution with various concentrations (50, 500, 1000, 2000, and 4000 mg/L) was loaded onto the cartridge. In the unequal opportunity competition adsorption experiment, 5 mL of DFC (500 mg/L) was loaded onto the cartridge, followed by 5 mL of CBZ (500 mg/L). The filtrate was analyzed using HPLC. All the experiments were performed in triplicate.

2.5.2. Adsorption capacity

A series of spiked water samples (from 50 to 4000 mg/L CBZ) were prepared. Aliquots of each sample (5 mL) were passed through the MIP and the NIP cartridges. The filtrate was analyzed using HPLC. The adsorption efficiency was calculated to assess the adsorption capacity of the CBZ–MIP. All the experiments were performed in triplicate.

2.5.3. Loading volume

A series of aqueous solutions (100, 300, 500, 700, and 1000 mL) spiked with 1 μg of CBZ were loaded onto the MIP and NIP cartridges. The cartridges were washed with 5 mL of Millipore water

to remove non-specific interactions, and eluted with five 1 mL aliquots of methanol. The extract was concentrated under a gentle nitrogen flow to dryness, reconstituted in 1 mL of methanol, and analyzed using HPLC. The recovery of CBZ was calculated. All the experiments were conducted in triplicate.

2.5.4. Binding performance study

To investigate the adsorption isotherm of the CBZ–MIP, 71 mg of CBZ–MIP was equilibrated with varied initial concentrations (5–4000 mg/L) of CBZ in each cartridge, and sealed with an appropriate stopper. After 2 h, a vacuum was applied to force the solutions through the particle bed. The filtrate was analyzed using HPLC. The binding of CBZ to the NIP was also measured in the same way. All the experiments were carried out in triplicate. The adsorption capacity was calculated using the following equation:

$$Q = \frac{V(C_0 - C)}{m} \quad (1)$$

where Q (mg/g) is the adsorption capacity; V (L) is the volume of the CBZ solution; m (g) is the weight of the MIP; C_0 (mg/L) is the initial concentration of CBZ; and C (mg/L) is the free concentration of CBZ in the solution.

2.6. Determination of elution volume

After 5 mL of a spiked water sample (1 mg/L CBZ) was loaded onto the MIP and NIP cartridges, the cartridges were washed with 5 mL of Millipore water. Five 1 mL aliquots of methanol were allowed to percolate through the cartridge. The extract was concentrated under a gentle nitrogen flow, reconstituted in 1 mL of methanol, and analyzed using HPLC. The recovery of CBZ for every 1 mL methanol aliquot was calculated separately. All the experiments were conducted in triplicate.

2.7. Leakage of the template and regeneration of MIP

To test the leakage of the template in water and organic solvent, 3 mL of Millipore water and 3 mL of methanol were allowed to percolate through the MIP cartridge at flow rates of 0.08–0.10 mL/min, respectively. The filtrates were analyzed using HPLC.

A single MIP cartridge was employed to investigate the regenerability of the CBZ–MIP. The cartridge was washed with Millipore water and methanol several times until the template could not be detected in the filtrate using HPLC. The cartridge was dried in vacuum and reused for the adsorption of CBZ. The regenerability of the CBZ–MIP was determined by the recovery of CBZ in the same cartridge after regeneration.

2.8. Application of CBZ–MIP to real water samples

Surface water samples were collected from the Landwehr-Channel near Charlottenburger Tor of Berlin, and a lake in Schloss Charlottenburg of Berlin. Treated wastewater samples were collected from the effluent of the Schönerlinde Sewage Treatment Plant in Berlin in November of 2009. All the water samples were filtered through a cellulose acetate filter to eliminate any solid impurities. One liter of surface water along with treated water samples were loaded onto the CBZ–MIP cartridges. The cartridges were then washed with Millipore water and the CBZ was eluted with five 1 mL aliquots of methanol. The extracts were subsequently concentrated under a gentle nitrogen stream and reconstituted in 1 mL of methanol for the HPLC-UV analysis.

3. Results and discussion

3.1. Performance of CBZ–MIP

3.1.1. Confirmation of selectivity

We evaluated the selectivity of CBZ–MIP for the binding of CBZ through the equal and unequal opportunity competition experiments prior to any other experiments. DFC was selected as the competitive molecule because its chemical molecular structure is somewhat similar to CBZ (Fig. 1), and it also widely coexists with CBZ in water bodies. In the equal opportunity competition experiment, DFC and CBZ (concentrations varied from 50 to 4000 mg/L) had the same opportunity to reach the binding sites. Therefore, DFC was allowed to compete with CBZ for the adsorption sites. The results are shown in Fig. 2. As expected, the adsorption efficiency of CBZ on the MIP was significantly higher than it was for the NIP, and no selective behavior occurred between CBZ and DFC on the NIP. This suggested that the higher efficiency and selectivity of the MIP for CBZ was due to the specific binding sites. As shown in Fig. 2a, both CBZ and DFC had high adsorption efficiencies at lower concentrations (50 mg/L) in the MIP column, due to the excess binding sites on the CBZ–MIP. Therefore, there was no competition under this condition. However, both the adsorption efficiency decreased with the increase of CBZ and DFC concentrations, and there was a difference in the degree of variation between CBZ and DFC. When the concentrations of CBZ and DFC were between 50 and 500 mg/L, the adsorption efficiency of CBZ on MIP reduced slightly from 98.5% to 83.0%, whereas the adsorption efficiency of DFC reduced dramatically from 98.3% to 6.7%. These results demonstrated that the competition was initiated by increasing the CBZ and DFC concentrations; DFC was only slightly adsorbed onto the CBZ–MIP surface in the presence of high CBZ concentrations under equal opportunity conditions. With the further increase of CBZ and DFC concentrations, the adsorption efficiency of CBZ declined gradually and the adsorption efficiency of DFC remained low. This indicated that the binding sites were saturated by CBZ, which caused the excess CBZ and DFC to pass directly through the column during the loading steps; similar results were observed by Prasad et al. [21].

For the unequal opportunity competition, DFC was loaded to the column first, to give DFC the opportunity to reach or occupy the binding sites before the subsequently added CBZ. Therefore, CBZ may flow out with the filtrate if its binding affinity to the CBZ–MIP is weaker than the previously adsorbed DFC. Interestingly, the adsorption efficiency of the MIP for DFC dropped sharply after the loading of CBZ, whereas there was no significant variation in the adsorption efficiency of DFC on the NIP (Fig. 2b). The results indicated that the adsorbed DFC was replaced by CBZ due to the higher molecular recognition selectivity of the MIP to CBZ.

The equal and unequal opportunity competition experiments demonstrated two important implications. First, the MIP adsorption sites are generally specific to the template molecules in high concentrations rather than other environmental pollutants. This gives the template molecules the priority to occupy the limited binding sites, especially in applications such as wastewater from

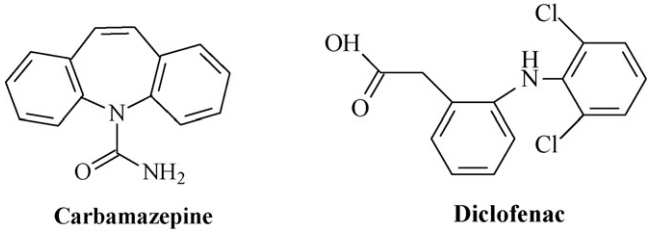

Fig. 1. Chemical structures of CBZ and DFC.

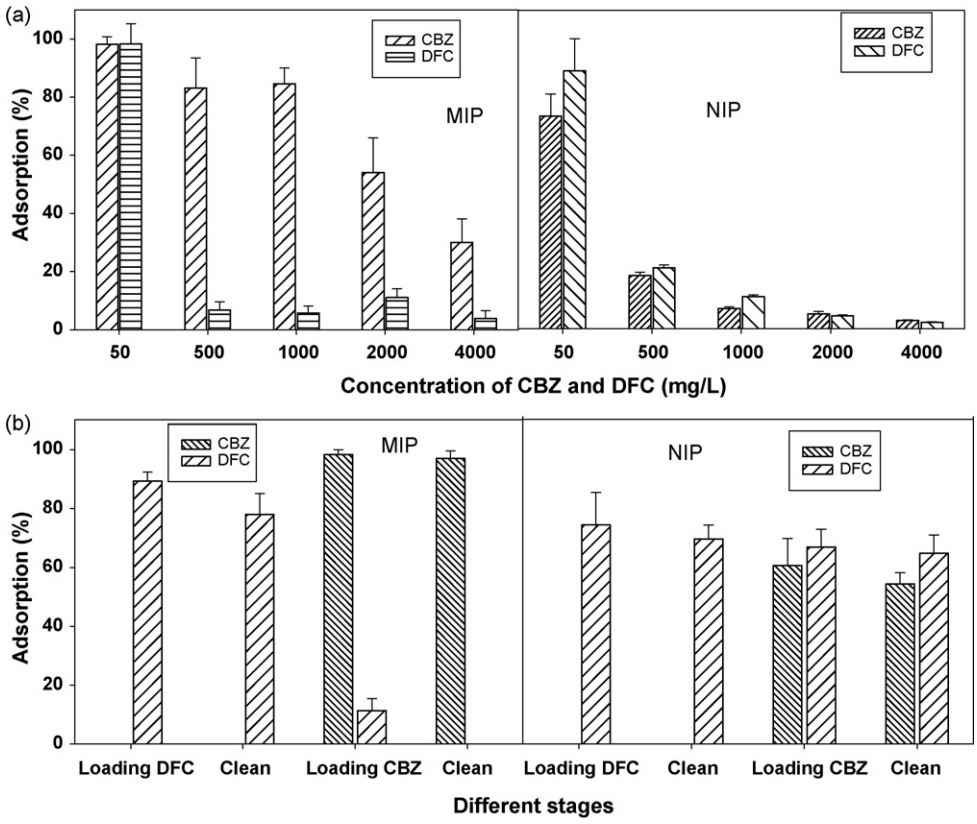

Fig. 2. Adsorption of CBZ and DFC on MIP and NIP with different loading methods: (a) equal opportunity and (b) unequal opportunity competition between CBZ and DFC.

the manufacturing of the template compound or special wastewater. Second, when the template and other environmental pollutants are in relatively low concentrations, the MIP adsorption sites are first occupied by the templates compounds, whereas excess adsorption sites are occupied by other pollutants (competitors). The amounts of templates and other pollutants increased with increasing water sample volumes. Because of the high selectivity of the MIP, the competitors adsorbed at first were replaced by the template molecules until the binding sites were occupied by the template molecules, and the material was completely loaded.

The selective mechanism has been presented in previous studies [22,23]. Structural analysis of MIP binding sites is difficult due to the amorphous nature of the materials and the heterogeneous distribution of binding site structures. Liu et al. [22] confirmed that the shape and size of the cavity in addition to the strength of the interaction between target molecule and binding sites determine the selectivity of MIP. Simon et al. [23] evaluated the binding site structure by employing molecular probes in structure-binding correlation studies. Their investigations illustrated that both pre-organization and shape selectivity are important in predicting the behavior of MIPs. An important observation was that the shape selectivity appeared to be the dominant mechanism for selectivity by the imprinting effect for MIP elicited towards templates with fewer template–functional monomer interactions. Alternatively, the selectivity of MIP to templates, that contain a greater number of functional groups, appears to depend on the pre-organization of functional groups.

3.1.2. Adsorption capacity and loading volume

The adsorption capacity and loading volume are two important parameters that characterize the MIP adsorbent bed. The adsorption capacity characterizes the amount of solute that can be loaded onto the adsorbent bed without loss of the analytes, whereas the loading volume refers to the maximum volume of a water sample that can be introduced into the adsorbent bed under given hydraulic conditions. Breakthrough occurs when the breakthrough threshold of the adsorbent bed has been reached [24]. The adsorbent capacity and loading volume for a given packed bed are valuable in determining the adsorption parameters such as adsorbent amounts and bed thickness [25]. The adsorption capacity corresponds to the maximum amount of a compound that can be retained on a MIP in equilibrium. A simple adsorbent capacity study was conducted to investigate the capacity of CBZ–MIP to effectively retain CBZ without overloading the active sites. Fig. 3 shows the adsorption efficiencies of MIP and NIP. It is obvious that the MIP adsorbed more CBZ than the NIP. The difference between

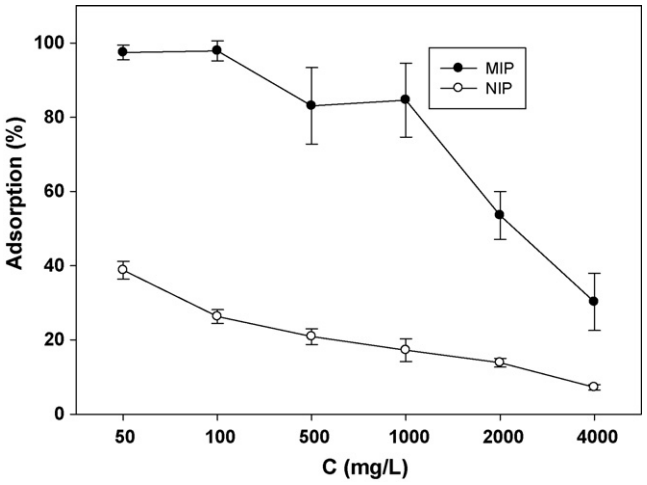

Fig. 3. Adsorption of CBZ on MIP and NIP with different CBZ concentrations.

the adsorption efficiencies of CBZ in MIP and NIP was up to about 70% at a CBZ concentration of 100 mg/L. The adsorption efficiency of MIP for CBZ at concentrations of 50 and 100 mg/L were around 98%; the losses of CBZ probably occurred during washing. The log K_{ow} of CBZ is 2.45, belonging to medium polarity or weak polarity. In this study, a small amount of CBZ was lost from MIP columns after washing with basic Millipore water, which may have been caused by hydrophobic interactions. When the concentration of CBZ was increased to 500 and 1000 mg/L, the adsorption efficiency of MIP for CBZ declined from 90% to 80%. A dramatic decrease in the adsorption efficiency of CBZ–MIP was found when the CBZ concentration increased from 1000 to 2000 mg/L. This indicated that there was a saturation point for the selected adsorbent in this concentration range.

An accumulated loading experiment was carried out to validate if the adsorbent bed selected on the basis of the above analysis had reached the saturation point. Five solutions with the same volume (5 mL) and concentration (2000 mg/L) were consecutively loaded onto the MIP column, and the filtrates were collected from every loading step. According to the results, when the first 5 mL of the solution passed through the MIP column, the percentage of CBZ bound to the adsorbent bed was 58.3%, which was higher than the other four batch loadings (retained percentage ranged from 9.8 to 3.9%). This indicated that the adsorbent was close to saturation. However, additional small quantities of CBZ were adsorbed onto the MIP during the subsequent loadings. This may be due to the slow kinetics caused by some difficult-to-reach binding sites. In addition, the polymer may experience swelling with longer exposures to the organic solvent (methanol), which may also expose binding sites [26].

A high loading volume can prevent losses from taking place during sample loading and washing steps as observed for selected cartridges. Five different sample volumes (100, 300, 500, 700 and 1000 mL) containing the same amount of CBZ (1 μg) were percolated through MIP and NIP cartridges; the results are summarized in Fig. 4. The recovery of CBZ in the MIP cartridges remained between 81% and 97%, which was significantly higher than the recovery with the NIP cartridges. For the NIP cartridges, the recovery decreased from 39% to 7.2% by increasing the sample volume. The results demonstrated that the capacity of the MIP is high enough to achieve almost complete sorption even at low concentrations whereas NIP recovery decreased with lower initial concentrations. Moreover, it is obvious that MIP had better removal efficiency using large volumes of low concentration (1000 mL at 1 μg/L). The results provided an important enlightenment to the application of MIP in the reuse of CBZ from the aqueous phase, especially, at the low concentrations found in wastewater, surface water, and tap water. Similar results were also found in the removal of phenolic estrogen using MIP [15].

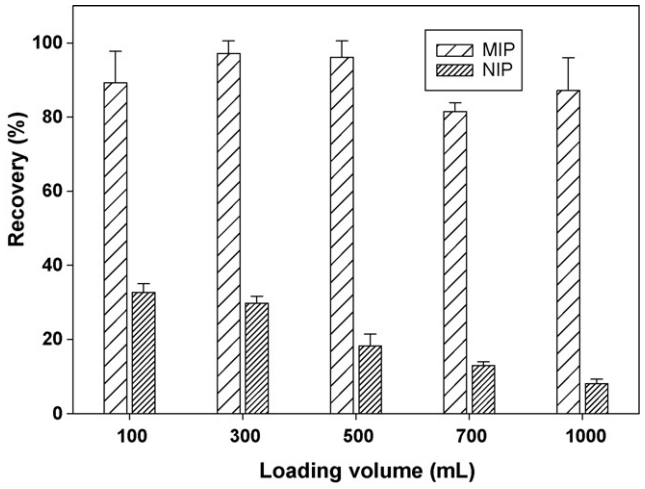

Fig. 4. Adsorption of CBZ on MIP and NIP with different loading volumes.

3.2. Binding performance of CBZ–MIP

The binding isotherm for CBZ on CBZ–MIP is useful for understanding the theory of the adsorption process and optimizing the adsorption materials. It is also an important index to assess the adsorption properties of the adsorbents, such as the binding affinity and the adsorption behavior. The Freundlich isotherm (Eq. (2)) is believed to be the better model for MIP [27–30].

$$Q = aC^{1/n} \tag{2}$$

$$\log Q = \log a + \frac{1}{n} \log C \tag{3}$$

where Q (mg/g polymer) is the adsorption capacity; a and n are adsorption coefficients; and C (mg/L) is the concentration of free CBZ in the solution.

The binding isotherms for CBZ in aqueous solution are shown in Fig. 5. The maximum binding site capacity of the MIP for CBZ was 86 mg/g when the final CBZ concentration was 4000 mg/L using 71 mg of adsorbent. The adsorption isotherm was successfully depicted by Freundlich adsorption model (R = 0.998) (Fig. 5b).

The observed binding of MIP is often based on both specific and non-specific interactions [31]. MIPs are specific to the template molecules due to the presence of memory cavities with a fixed size, shape, binding sites, and specific binding interactions between the target molecule and sites. The specific binding originates from the imprinting procedure and takes place in the selective recognition sites for the template. This suggests that the imprinted cavities of the MIP may be responsible for the high binding affinity of the template to the polymer. An MIP and an NIP were compared to investigate whether the polymerization process created CBZ imprinted sites that specifically recognized the template. The specificity of the MIP over the NIP was evaluated in terms of its ability to re-accommodate CBZ. As shown in Fig. 5a, the adsorption capacities of both absorbents increased with increasing CBZ concentrations, but the adsorption capacity of the CBZ–MIP was much greater than it was for the NIP. The result is consistent with the investigations carried out by Bravo et al. [32]. The difference in adsorption capacities between MIP and NIP for CBZ was approximately 60% at a CBZ concentration of 4000 mg/L. The results of the present study showed that MIP was very sensitive to the presence of its template. In the absence of imprinting, rebinding was driven solely by hydrophobic binding. Corresponding blank polymers were unable to differentiate between analytes, which suggested that the imprinting phenomenon was responsible for the recognition properties. However, the NIP was also capable of binding a certain amount of CBZ, which indicated that the MIP may also adsorb CBZ through non-specific binding interactions [33]. Also, hydrophobic interactions can contribute to the relatively high adsorption capacity due to the strongly hydrophobic properties of CBZ as well as the hydrophobic properties of the MIP surface [27].

3.3. Elution volume during desorption

An ideal sample elution methodology should be fast, accurate, precise, and should consume little solvent. To reduce the consumption of methanol, the elution was tested with 5 mL of methanol. The recovery for every 1 mL aliquot of methanol was calculated separately. As shown in Fig. 6, both the MIP and the NIP demonstrated a high percentage of recovery for the first 1 mL aliquot of methanol and reached a plateau for the other four methanol aliquots. The

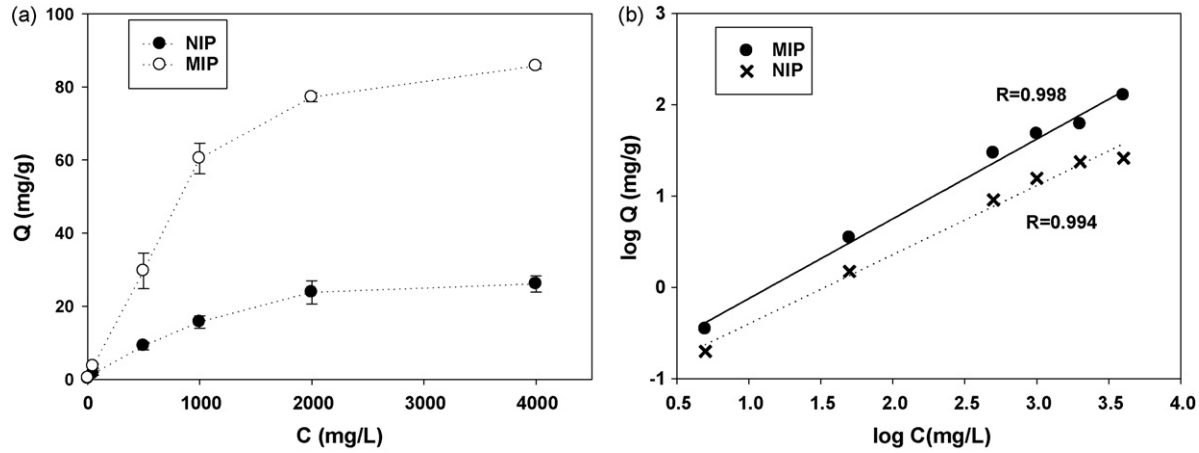

Fig. 5. Adsorption isotherms of CBZ on MIP and NIP for CBZ: (a) adsorption isotherms without the fitting curve and (b) adsorption isotherms with the fitting curve by the Freundlich model.

recovery of CBZ on the MIP column reached 88.3% after the first 1 mL of methanol passed through the column. The recovery was only 10.5% for the second methanol aliquot. The results indicated that 1–2 mL of methanol was enough to completely elute CBZ for the selected amount of MIP and, thus, provided a special significance for industrial application.

3.4. Leakage of template and regeneration of MIP

The MIP was synthesized with large quantities of the template, which may cause a small number of template molecules to remain in the polymer after extraction and leak later during adsorption and desorption. Leakage of the template compound can impair the accuracy and precision of assays for the target substances. This has been observed in several cases [27,34]. In our study, leakage of templates was not detected in aqueous solutions or methanol in an experiment to evaluate leakage (data not shown).

The major advantages of MIPs compared to adsorption materials are their physical stability (mechanical resistance to high pressures and temperatures) and high chemical robustness, which give MIPs the ability to be cleaned and reactivated under relatively harsh conditions for multiple uses in adsorbent applications [35,36]. The recovery of CBZ indicated that the CBZ–MIP could be reused after elution with methanol, and the recovery of CBZ varied slightly (89.3–98.9%) after ten cycles of adsorption and desorption (Fig. 7). The slight decrease in recovery was probably related to the loss of imprinted cavities during the regeneration process [22].

3.5. Application of CBZ–MIP to environmental water samples

The use of MIP in the solid-phase extraction of CBZ has been well described [20,37]. However, to the best of our knowledge, very few studies have demonstrated the potential use of CBZ–MIP for decontamination. The feasibility of applying CBZ–MIP to remove CBZ from real water samples was evaluated by comparing the concentrations of CBZ measured using MIP-HPLC/UV to literature data and those measured on LC–MS/MS. Resulting LC/UV chromatograms are shown in Fig. 8. The CBZ concentrations in the Landwehr-Channel and the lake in Berlin were 0.8 and 0.57 μg/L (MIP-HPLC/UV), respectively, which were in the range of the CBZ concentration (0.025–1.076 μg/L) reported in surface water in Berlin [38]. As for the treated water, the average concentrations of CBZ in two effluent water samples were 2.39 and 2.23 μg/L. Analysis of the two corresponding effluent water samples using LC–MS/MS was performed by an independent laboratory (Berlin Water Company) and revealed CBZ concentrations of 2.30 and 1.90 μg/L. These values were in reasonable agreement with the MIP-HPLC/UV discussed above. The recoveries of CBZ in the two surface and effluent water samples were higher than 96%. Therefore, the results indicate that

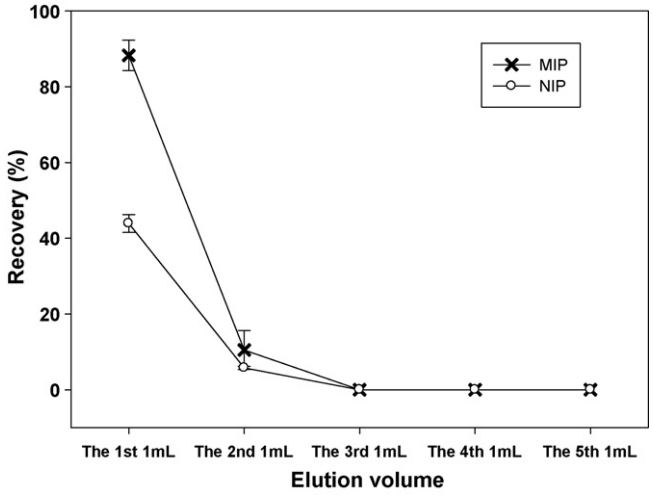

Fig. 6. Recoveries of CBZ using MIP and NIP with different elution volumes.

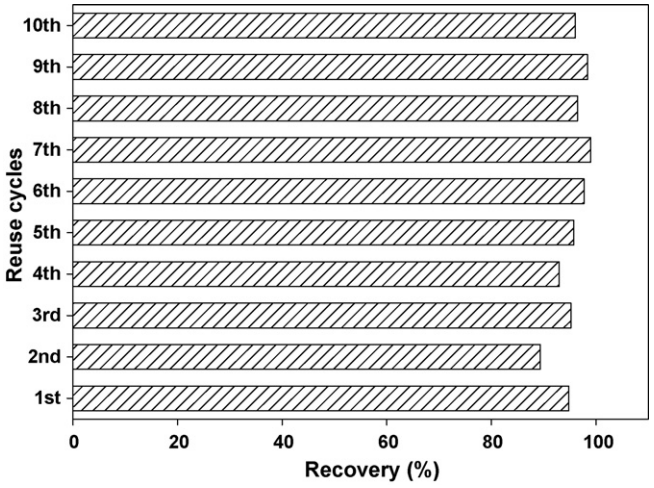

Fig. 7. Regeneration cycles for CBZ–MIP.

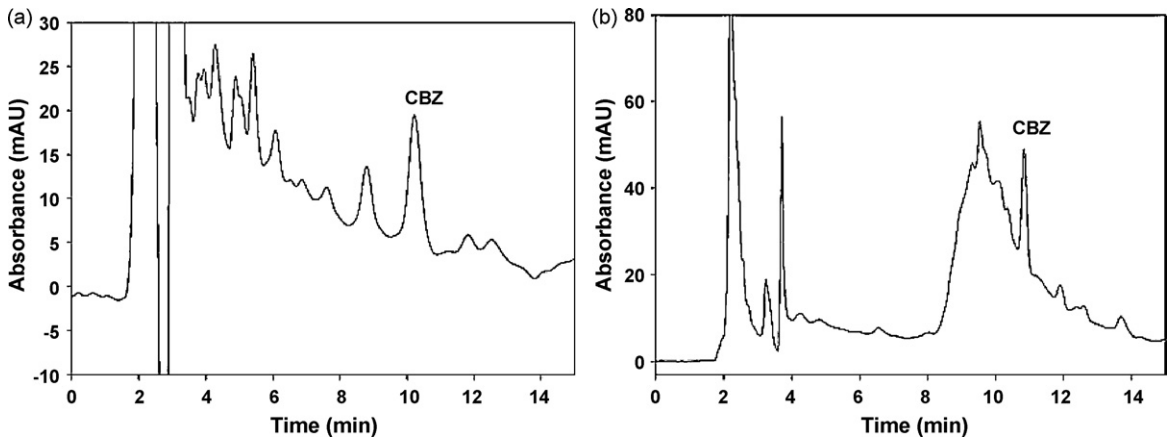

Fig. 8. Chromatograms of obtained by extracting CBZ from 1000 mL real water samples spiked with 0.5 μg/L CBZ using MIP: (a) lake water and (b) effluent water.

MIP is applicable to the removal or extraction of low concentrations of CBZ in environment water samples.

4. Conclusions

This study confirmed the applicability of CBZ–MIP for the removal of CBZ in water samples. The results obtained from the competitive binding experiment demonstrated that the synthesized MIP exhibited high affinity and selectivity for CBZ. High recovery (>80%) of CBZ was achieved with the sample volume as high as 1000 mL, which demonstrated that the MIP had a good removal efficiency on large sample volumes of low CBZ concentrations (1000 mL at 1 μg/L). In addition to applications for water treatment, the CBZ–MIP was successfully applied to concentrate CBZ in surface water and effluent wastewater followed by HPLC-UV detection. The results compared well with a highly selective and sensitive LC–MS/MS analysis that was performed in parallel. Therefore, our results suggested that the MIP provided a reliable and effective solution to remove and enrich low concentrations of CBZ in aqueous solutions.

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