Metal–Organic Gel-Modulated Synthesis of Hierarchically Porous Molecularly Imprinted Polymers for Efficient Removal of Sildenafil from Water

Libin Wan,* Huoliang Gao, Ge Yan, Haidong Gao, and Mantang Chen*

ABSTRACT: Molecularly imprinted polymers (MIPs) with high specific recognition capability are promising in environmental remediation. However, traditional MIPs usually show poor specific binding affinity toward templates in pure aqueous medium, thus greatly limiting their practical applications in wastewater treatment. Herein, we proposed a facile and versatile method to synthesize a water-compatible hierarchically porous MIP (HP-MIP), in which a metal–organic gel (MOG) was formed by in situ assembly and acted as a removable structural modulator. Remarkably, the integration of the MOG modulator and template imprinting defects significantly improved the specific template binding affinity of HP-MIP in water. The adsorption behavior of HP-MIP fitted well with the heterogeneous Freundlich isotherm, suggesting that HP-MIP possessed greater site heterogeneity to sildenafil than HP-NIP, which confirmed the efficiency of HP-MIP for the removal of sildenafil from water. This approach provides an important pathway to prepare water-compatible porous MIP for efficient removal of highly toxic organic pollutants from wastewater.

INTRODUCTION

As a new class of organic pollutants, pharmaceuticals and personal care products (PPCPs) have aroused extensive concerns over their adverse effects on wildlife and human beings. Due to their mass production and widespread use, PPCPs are frequently detected in environmental matrices, such as surface water, groundwater, and even drinking water. Sildenafil, a synthetic selective inhibitor of phosphodiesterase type-5 (PDE-5) used for the treatment of erectile dysfunction in males and also an illegal additive in the herbal dietary supplements and health care products, has been one of the most frequently detected PPCPs in the aquatic environment. It was found that the long-term exposure of sildenafil is pernicious to public health and may cause serious complications and even death for those with hidden diseases due to its side effects such as headache, flush, nasal congestion, and visual abnormalities. Therefore, it is necessary to develop efficient methods for the removal of sildenafil from water.

The adsorption method is one of the easiest and most economic methods for removing organic pollutants from water. Previous studies reported that the removal efficiency of organic pollutants greatly depended on the interactions between an adsorbent and a target molecule. Molecularly imprinted polymers (MIPs), also named artificial antibodies, have attracted great interest in recent years. Due to the presence of imprinting cavities in MIPs generated by template removal after polymerization, MIPs exhibited specific recognition capability toward the template, which made their promising efficiency in selective extraction, environmental separation, and sensing. For example, Ding et al. prepared a core–shell magnetic MIP by the surface molecular imprinting technique, and the obtained MIP showed high recognition ability to sildenafil from complex samples.

However, the traditional MIPs are usually only compatible in organic media and fail to show specific binding affinity toward the template in an aqueous environment, owing to that water can disrupt the noncovalent interaction (e.g., hydrogen bond) between the template and functional monomers. Considering that water is the main medium for most of PPCPs in the environment, the poor specific binding affinity of...
traditional MIPs to the template in pure water greatly limited their applications in wastewater treatment.36,27 To improve the specific template recognition ability of MIPs in an aqueous solution, several efforts, including using hydrophilic reactants (monomer and cross-linker),24,28 using specially designed functional monomer,29 grafting hydrophilic layer,30,31 and using interfacial Pickering emulsion polymerization,32 have been devoted to preparing the water-compatible MIPs. Despite some progress made in the development of water-compatible MIPs with enhanced specific template recognition ability in aqueous media,33 the development of MIPs with high specific surface areas (SSAs) and strong specific template binding affinity in a pure aqueous solution was still challenging.

Metal–organic gels (MOGs) are supermolecular gels with a periodic three-dimensional porous structure, which are prepared based on the coordination between metal ions and organic ligands.34 Due to their remarkable advantages of large SSA and excellent solubility, MOGs have been widely used to fabricate macroporous polymers.34–37 For example, a magnetic porous carbon composite was prepared using Fe-based MOG as both a precursor and a template, and the obtained material exhibited improved adsorption capacity to methyl orange in an aqueous solution.38 Ma et al. prepared a water-compatible MIP using levofloxacin and Fe-based MOG as a template and a porogenic solvent, respectively, and used it for drug release.39 Therefore, the emergence of MOGs provided a promising strategy to fabricate hierarchically porous MIPs (HP-MIPs) with high SSA and strong template binding affinity and promoted the potential application of MIPs in wastewater remediation.

Here, a water-compatible HP-MIP was prepared in the presence of Fe-based MOG as a structural modulator and was applied as an absorbent for the removal of sildenafil from water. In detail, this system used sildenafil, methacrylic acid (MAA), ethylene glycol dimethyl acrylate (EGDMA), and a mixture solution of methanol and ethanol as the template, monomer, cross-linker, and porogenic solvent, respectively. The introduction of Fe-based MOG could enhance the noncovalent interactions between MAA and sildenafil in polar solvents and create the structural defect and additional pore space inside MIP by removing Fe-based MOG after polymerization. Due to the synergistic effect of the porous structure and imprinting sites, HP-MIP showed excellent specific adsorption affinity toward sildenafil.

## RESULTS AND DISCUSSION

### Optimization of Polymerization Conditions.

In the present work, we adopted Fe-based MOG as a structural modulator to direct the construction of water-compatible HP-MIP through in situ cross-linking polymerization (Figure 1). Fe-based MOG was prepared using Fe3+ and H3BTC as the precursors. After polymerization, MOG and sildenafil inside MIP were eluted with a mixture solution of methanol and acetic acid (90:10, v/v) to get the water-compatible HP-MIP with a porous structure and specific imprinting cavities for sildenafil. To investigate the influence of MOG on the imprinting performance of HP-MIP, a series of polymers were prepared with different dosages of Fe3+ and H3BTC. As shown in Figure 2a, the resulting MIPs, which were prepared in the absence of both Fe3+ and H3BTC or in the presence of only H3BTC in the reaction system, showed almost no specific recognition performance, and both the resulting MIPs and NIPs displayed low adsorption capacity to sildenafil. When Fe3+ and H3BTC were both supplied during polymerization, the specific adsorption capability of the resulting HP-MIP to sildenafil was apparent. By fixing the molar ratio of Fe3+ to H3BTC, the effect of the MOG precursor dosage was also studied. It was found in Figure 2a that the imprinting factor (IF) (i.e., the binding capacity difference between MIP and the corresponding NIP) increased with increasing the dosage of Fe3+ and H3BTC in the tested range, whereas the highest adsorption capacity (17.8 mg g⁻¹) of HP-MIP to sildenafil with a satisfied IF value of 2.5 was obtained when the dosage of Fe3+ and H3BTC was 0.75 and 0.5 mmol, respectively. The improved specific adsorption performance of HP-MIP prepared in the presence of MOG might be due to the
creation of the porous structure through MOG forming and disappearing.

It was well known that the imprinting performance of MIP greatly depended on the polymerization conditions. To achieve the excellent specific recognition ability of HP-MIP, the molar ratio of the template to the functional monomer was also optimized. Figure 2b shows the effect of the molar ratio of sildenafil to MAA on the adsorption performance of the obtained polymers. It was found that the adsorption performance of HP-MIP for sildenafil increased with increasing the molar ratio of sildenafil to MAA from 1:12 to 1:2, while a further increase in the molar ratio induced a slight decrease in the adsorption capacity of HP-MIP to sildenafil. The highest adsorption performance and IF value of HP-MIP were achieved when the molar ratio of sildenafil to MAA reached 1:2. Overall, the above results suggested that relatively high use of sildenafil with a small size in the polymerization process favored high binding affinity of HP-MIP to a certain degree.

Characterization of HP-MIPs. The morphologies of HP-MIP, HP-NIP, MIP, and NIP were characterized by scanning electron microscopy (SEM). It can be clearly seen in Figure 3 that both HP-MIP and HP-NIP were clusters of porous polymer beads with a size of 30−100 nm, whereas both MIP and NIP were polymer bead agglomerates with a size of 1 μm.

Figure 3. SEM images of (a) HP-MIP, (b) HP-NIP, (c) MIP, and (d) NIP.

Figure 4. Characterization of adsorbents. (a) N₂ adsorption−desorption isotherm of HP-MIP, HP-NIP, MIP, and NIP; (b) DFT pore-size distribution of HP-MIP, HP-NIP, MIP, and NIP; (c) X-ray diffraction (XRD) pattern of sildenafil@MOG@HP-MIP (1), MOG@HP-NIP (2), HP-MIP (3), HP-NIP (4), MIP (5), and NIP (6); and (d) Fourier transform infrared (FT-IR) spectra of sildenafil@MOG@HP-MIP (1), MOG@HP-NIP (2), HP-MIP (3), HP-NIP (4), MIP (5), and NIP (6).
This confirmed that the introduction of Fe$^{3+}$ and H$_2$BTC significantly influenced the size of polymer particles, which may be due to the increased viscosity of the reaction system by the in situ formation of MOG, thus inhibiting the growth of polymers. 

N$_2$ adsorption–desorption isotherms and density functional theory (DFT) pore-size distributions of HP-MIP, HP-NIP, MIP, and NIP are shown in Figure 4a–b, respectively, and the corresponding pore features are summarized in Table 1. It could be noticed that the Brunauer–Emmett–Teller (BET) SSA of HP-MIP was calculated to be 219.6 m$^2$ g$^{-1}$, being over 4 times that of HP-NIP (50.6 m$^2$ g$^{-1}$) and about 50 times that of MIP (4.5 m$^2$ g$^{-1}$) and NIP (4.1 m$^2$ g$^{-1}$). In addition, the total pore volumes of HP-MIP, HP-NIP, MIP, and NIP were 0.71, 0.16, 0.011, and 0.0098 cm$^3$ g$^{-1}$, respectively. These results confirmed that the formation and elution of MOG during the polymerization significantly increased the SSAs and the total pore volume of MIP, which could enhance the adsorption performance of HP-MIP.

XRD was employed to characterize the removal of MOG in the fabrication of HP-MIP and HP-NIP. As shown in Figure 4c, both sildenafil@MOG@HP-MIP and MOG@HP-NIP matched well with the reported pattern of Fe$_2$H$_2$BTC-MOG. After the elution treatment by a mixture solution of methanol and acetic acid, XRD patterns of HP-MIP and HP-NIP were broad and less defined, the same as those of MIP and NIP, and the diffraction peaks of MOG disappeared. Figure 4d shows the FT-IR spectra of sildenafil@MOG@HP-MIP, MOG@HP-NIP, HP-MIP, HP-NIP, MIP, and NIP. The characteristic stretching vibration peaks at 3436 and 1729 cm$^{-1}$ were attributed to O–H in MAA and C=O in EGDMA, respectively. Besides, the peaks at 1259 and 1159 cm$^{-1}$ could be assigned to the symmetric and antisymmetric stretching vibrations of $\equiv$C–O–C in EGDMA. In both sildenafil@MOG@HP-MIP and MOG@HP-NIP, the symmetric and antisymmetric stretching vibrations of O–C=O were observed at 1632 and 1557 cm$^{-1}$ ($\Delta v = \Delta v_{as} - \Delta v_{s} = 75$ cm$^{-1}$), indicating the bidentate coordination mode between Fe$^{3+}$ and H$_2$BTC, which are the typical characteristic bands in Fe-based MOG. After the elution treatment, these peaks disappeared in both HP-MIP and HP-NIP. The above analysis indicated that MOG could be removed by solvent elution treatment. The static contact-angle experiments of HP-MIP and HP-NIP were also performed. As shown in Figure 5, the static contact angles of HP-MIP and HP-NIP were 39 and 49.5°, respectively, which revealed the successful preparation of water-compatible imprinted polymers. This may be attributed to the metal ion-mediated interaction between a template and a monomer. Although MOG inside the polymer was eluted after polymerization, Fe$^{3+}$ might act as a mediator between MAA and sildenafil during prepolymerization. The metal ion-mediated imprinting method can effectively avoid the disturbance caused by polar solvents in the interaction between the template and the monomer and improve the molecular imprinting effect of MPs in polar environmental media, which was in accordance with the previous studies.

**Effect of a Binding Solution.** The effect of a binding solution on the adsorption behavior of HP-MIP to sildenafil was studied. As observed in Figure 6a, HP-MIP provided much higher adsorption capacity to sildenafil than HP-NIP in all tested solutions, suggesting the presence of specific template imprinting sites in HP-MIP. It should be noted that the amounts of sildenafil bound on both HP-MIP and HP-NIP were much higher than those observed in other tested media, including ethanol/water (1:1, v/v), methanol/water (1:1, v/v), acetonitrile/water (1:1, v/v), and methanol/ethanol (2:1, v/v), which may be attributed to not only the surface hydrophilicity of HP-MIP using MOG as a structural modulator but also the competitive binding of an organic solvent.

**Adsorption Kinetics and Isotherms of HP-MIPs.** The equilibrium adsorption experiments of HP-MIP and HP-NIP were performed in pure water, and their adsorption isotherms are presented in Figure 6b. It was found that the adsorption capacity of sildenafil on both HP-MIP and HP-NIP increased linearly with increasing the initial concentration of sildenafil, and HP-MIP bound more template than HP-NIP. According to the previous studies, the binding data of the template on imprinted polymers commonly fitted well with the Freundlich isotherm, and its equation is given as follows

$$\ln q_e = \ln K_f + (1/n) \ln c_e$$

where $q_e$ (mg g$^{-1}$) is the amount of sildenafil bound on the adsorbent at equilibrium time, $c_e$ (µmol L$^{-1}$) is the equilibrium concentration of sildenafil, and $K_f$ and $n$ are the Freundlich constants, reflecting the adsorption capacity and the heterogeneity of binding sites of the adsorbent, respectively.

The Freundlich isotherm parameters ($K_f$ and $1/n$) were calculated and are summarized in Table 2. It was found that the correlation coefficient values ($R^2$) for sildenafil on HP-MIP and HP-NIP were 0.995 and 0.998, respectively, indicating that the adsorption of sildenafil on HP-MIP and HP-NIP could be fitted well to the Freundlich isotherm. The $K_f$ value for HP-

![Figure 5. Profiles of a water drop on HP-MIP (a) and HP-NIP (b) films.](https://dx.doi.org/10.1021/acsomega.0c06000)
MIP was 2.361, being much greater than that for HP-NIP (0.0655), indicating that HP-MIP possessed much higher adsorption capacity for sildenafil than HP-NIP. The $1/n$ values for HP-MIP and HP-NIP were 0.669 and 0.977, respectively, indicating that the binding sites in HP-MIP were more heterogeneous than those in HP-NIP. These observations were in accordance with the reports of Shimizu et al. and Shen et al.

The adsorption kinetics of sildenafil on HP-MIP and HP-NIP were shown in Figure 6c. The adsorption of sildenafil on both HP-MIP and HP-NIP was rapidly increased in the first 3 min, and the adsorption/desorption equilibrium was quickly reached in 30 min with an adsorption capacity of 17.8 mg g$^{-1}$ in HP-MIP, which was more than 2.5 times of that in HP-NIP (7.2 mg g$^{-1}$). Figure 6d shows that the adsorption kinetics of sildenafil in both HP-MIP and HP-NIP was able to be fitted well to the pseudo-second-order kinetic model, and the equation is given as follows

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e} \ln \left(\frac{1}{q_t}\right)$$

where $q_t$ (mg g$^{-1}$) and $q_e$ (mg g$^{-1}$) are the adsorption capacities of sildenafil on the adsorbent at time $t$ and at equilibrium, respectively, and $K_2q_e^2$ (mg g$^{-1}$ min$^{-1}$) is the rate constant of the pseudo-second-order adsorption. The pseudo-second-order kinetic adsorption parameters were calculated and are displayed in Table 3. It showed that the initial adsorption rate of sildenafil on HP-MIP (66.7 mg g$^{-1}$ min$^{-1}$) was much higher than that on HP-NIP (34.0 mg g$^{-1}$ min$^{-1}$). These results greatly supported the higher affinity of HP-MIP toward sildenafil as compared with HP-NIP. The higher adsorption capacity and the faster initial adsorption rate of HP-MIP were due to the template imprinting cavities and porous structure.

**Selectivity Study of HP-MIPs.** To evaluate the selective recognition capability of HP-MIP, the selective adsorption experiment of HP-MIP was conducted in single systems (only one substance existed in a solution) using five compounds (vardenafil, tadalafil, ofloxacin, sulfadimidine, and bisphenol A) as interferences of sildenafil. Figure 7 illustrates that the adsorption capacities of sildenafil and its interferences on HP-MIP (7.3–17.8 mg g$^{-1}$) were much higher than that on HP-NIP (1.2–7.2 mg g$^{-1}$), except for tadalafil and bisphenol A. The potency for the IF of the analytes was in the order ofloxacin > vardenafil > sildenafil > sulfadimidine > tadalafil > bisphenol A, and no obvious differences between HP-MIP and HP-NIP for adsorption of tadalafil and bisphenol A were observed. It is noted that tadalafil and bisphenol A displayed no selectivity on the HP-MIP, and HP-MIP provided better selectivity to vardenafil and ofloxacin than sildenafil, which may be due to the contribution of the piperazine moiety of these analytes and the relatively smaller shape size of ofloxacin than sildenafil.

**Recyclability of HP-MIPs.** To evaluate the recyclability of HP-MIP, the adsorption experiments of sildenafil on HP-MIP...
were conducted using the fresh HP-MIP and recycled HP-MIP. First, the adsorption of sildenafil was carried out on the fresh HP-MIP, and the equilibrium adsorption capacity of HP-MIP was 17.8 mg g\(^{-1}\). After the adsorption experiment, the used HP-MIP was collected, washed with methanol, and dried in an oven. Subsequently, a new and same adsorption process was conducted on the used HP-MIP, and this process was executed for five consecutive adsorption cycles using the recycled HP-MIP after each cycle. As shown in Figure 8, HP-MIP maintained its adsorption performance without loss, confirming the excellent recyclability of HP-MIP.

![Figure 7](image1)

**Figure 7.** (a) Selective adsorption of sildenafil and its interferences on HP-MIP and HP-NIP in single systems (containing only one substance in an aqueous solution) and (b) chemical structures of sildenafil and its interferences. Conditions: absorbents (5 mg mL\(^{-1}\)) and the tested compounds (0.21 mmol L\(^{-1}\)).

**Figure 8.** Recyclability of HP-MIP for the adsorption of sildenafil. Conditions: HP-MIP (5 mg mL\(^{-1}\)) and sildenafil (100 mg L\(^{-1}\)).

### CONCLUSIONS

A water-compatible HP-MIP was successfully synthesized using MOG as a structural modulator. It was found that the formation and elution of MOG during the synthesis process played an important role in the creation of additional structural defects in HP-MIP, resulting in a better adsorption capability for sildenafil in pure aqueous solution. Batch adsorption experiments demonstrated that HP-MIP exhibited much higher adsorption capacity for sildenafil than HP-NIP, and the presence of imprinted cavities in HP-MIP provided high specific binding affinity for sildenafil. Such an approach is feasible and versatile in preparing water-compatible HP-MIPs with porous structures without using hydrophilic monomers or grafting hydrophilic brushes. These water-compatible HP-MIPs find promising applications in environmental remediation, including adsorption, separation, and catalysis.

### EXPERIMENTAL SECTION

**Chemicals Reagents.** Sildenafil (98%) was purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Vardenafil hydrochloride and tadalafil were obtained from Shanghai ZZBIO Co., Ltd. (Shanghai, China). Sulfamethazine (99%), ofloxacin (98%), bisphenol A (99%), MAA (98%), EGDMA (98%), azobisobutyronitrile (AIBN, 98%), trimesic acid (H\(_3\)BTC, 98%), and iron nitrate nonahydrate (Fe(NO\(_3\))\(_3\), 9H\(_2\)O) were obtained from Aladdin Chemical Reagent Co. (Shanghai, China). Chromatographic grade methanol and formic acid were obtained from ANPEL Laboratory Technologies Incorporation (Shanghai, China). Ethanol, acetonitrile, and acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

**Characterization.** The morphologies of adsorbents were observed by scanning electron microscopy (SEM) (MERLIN Compact, ZEISS, Germany). Fourier transform infrared (FT-IR) spectroscopy of adsorbents was measured using a Thermo Scientific Nicolet 10 spectrometer. The Brunauer–Emmett–Teller (BET) surface areas of adsorbents were measured by the nitrogen adsorption–desorption isotherm at 77 K on a MICROMETERS ASAP 2400 analyzer, and the pore sizes of adsorbents were calculated based on density functional theory (DFT) analysis. The crystalline structures of adsorbents were characterized by Bruker D8 powder X-ray diffraction (XRD) using Cu K\(_\alpha\) radiation.

**Synthesis of Water-Compatible HP-MIPs.** A water-compatible HP-MIP was synthesized using MOG as a structural modulator. First, 190 mg of sildenafil (0.4 mmol) and 100 mg of H\(_3\)BTC (0.5 mmol) were dissolved into 12 mL of a mixture solution of methanol and ethanol (2:1, v/v). Subsequently, 69 μL of MAA (0.8 mmol), 634 μL of EGDMA (3.2 mmol), 300 mg of Fe(NO\(_3\))\(_3\), 9H\(_2\)O (0.75 mmol), and 20 mg of AIBN (0.12 mmol) were added to obtain a clear preassemble solution by ultrasonication. After purging with nitrogen for 10 min to remove oxygen, polymerization was performed at 60 °C for 24 h. The obtained polymer (sildenafil@MOG@HP-MIP) with encapsulated sildenafil and MOG was first crushed and ground into fine particles, then washed thoroughly with a mixture solution of methanol and acetic acid (9:1, v/v) to remove the sildenafil template and MOG, afterward washed with methanol three times, and finally dried overnight in an oven at 60 °C to provide the desired HP-MIP. The water-compatible HP-NIP was synthesized by the same method as HP-MIP without the addition of sildenafil. During the preparation of HP-NIP, the obtained polymer before the elution of MOG was named MOG@HP-NIP. To compare the performance of imprinted polymers prepared in different conditions, a conventional MIP was prepared in the same way as HP-MIP, but without H\(_3\)BTC and Fe(NO\(_3\))\(_3\), 9H\(_2\)O. The conventional NIP was prepared according to a...
similar process as MIP but in the absence of sildenafil. The yields of HP-MIP, HP-NIP, MIP, and NIP were 21, 28, 79, and 75%, respectively.

**Equilibrium Binding Experiments.** To investigate the adsorption capacity of adsorbents, 5 mg of HP-MIP or HP-NIP was mixed into 1 mL of an aqueous solution with various concentrations (10–500 mg L\(^{-1}\)) of sildenafil. After incubation at room temperature for 12 h, the polymers were isolated by centrifugation, and the equilibrium concentration of sildenafil in the supernatants was determined by high-performance liquid chromatography (HPLC). The equilibrium adsorption capacity \(Q_e\) (mg g\(^{-1}\)) was calculated using the following equation

\[
Q_e = \frac{C_0 - C_e}{m} \times V
\]

where \(m\) (mg) is the amount of polymers, \(V\) (mL) is the volume of the adsorption solution, and \(C_0\) (mg L\(^{-1}\)) and \(C_e\) (mg L\(^{-1}\)) are the initial and equilibrium concentrations of sildenafil, respectively.

**Kinetic Binding Experiments.** In adsorption kinetics experiments, 5 mg of HP-MIP or HP-NIP was dispersed in 1 mL of a sildenafil aqueous solution at 100 mg L\(^{-1}\), and the mixture was stirred at room temperature and incubated at a regular time from 5 s to 250 min. After the incubation, the supernatant was immediately collected for measurement.

**Selectivity Study.** The selectivity of HP-MIP or HP-NIP was studied using vardenafil and tadalafl as the structural analogues to sildenafil, and using ofloxacin, sulfadimidine, and bisphenol A as coexisting organic pollutants. The selectivity experiments were performed by dispersing 5 mg of HP-MIP or HP-NIP in 1 mL of aqueous solutions containing only one analyte with each concentration of 0.2 mmol L\(^{-1}\). After incubation at room temperature for 12 h, the concentrations of sildenafil, vardenafil, tadalafl, ofloxacin, sulfadimidine, and bisphenol A in the supernatants were measured by HPLC on an Agilent 1290 HPLC system (Agilent Technologies, CA). Chromatographic separation was performed with a Thermo Hypersil GOLD C18 column (100 mm × 2.1 mm, 3.5 μm). For sildenafil, vardenafil, and tadalafl, the mobile phase was 60% acetonitrile and 40% H\(_2\)O containing 0.1% formic acid at a flow rate of 0.3 mL min\(^{-1}\), and the detection wavelength was 294 nm. For ofloxacin and sulfadimidine, the mobile phase was 10% methanol and 90% H\(_2\)O containing 0.1% formic acid at a flow rate of 0.3 mL min\(^{-1}\), and the detection wavelength was 266 nm. For bisphenol A, the mobile phase was 70% methanol and 30% H\(_2\)O containing 0.1% formic acid at a flow rate of 0.3 mL min\(^{-1}\), and the detection wavelength was 276 nm.

**Recyclability Study.** The recyclability of HP-MIP was also investigated. After sildenafil was first completely adsorbed, the used HP-MIP was collected by vacuum filtration, washed with methanol, and dried at 70 °C overnight. The recycled HP-MIP was redispersed into a fresh aqueous solution of sildenafil, and the second cycle of the adsorption experiment was conducted. In this way, the adsorption experiment was repeated several times.

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**Notes**

The authors declare no competing financial interest.

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