PVAm Nanofibers Fabricated by Rotary Jet Wet Spinning and Applied to Bisphenol A Recognition

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ABSTRACT: Poly(vinylamine) (PVAm) is an important polymer with the highest content of primary amine groups of any polymer. PVAm has a great potential in selective separation and smart materials. It is difficult to fabricate pure PVAm nanofibers by electrospinning and rotary jet spinning (RJS) without additional polymers. In this work, rotary jet wet spinning (RJWS) was applied to fabricate molecular imprinting nanofibers (MINFs) with polyelectrolyte for the first time. Initially, optimal parameters of spinning are investigated, including coagulation bath, solution viscosity, and rotation speed. The PVAm aqueous solution is sensitive to alcohol. To demonstrate RJWS application, PVAm-based MINFs for bisphenol A (an endocrine disruptor) recognition are prepared by adding dummy template, cross-linking, and template elution. The association constant (8.6 mg/L), equilibrium time (30 min), and binding sites utilization rate (80%) of MINFs are evaluated. Its adsorption amount and selectivity are little lower than those of MIPs prepared by bulk polymerization; however, its adsorption speed is faster than that of MIPs.

1. INTRODUCTION

Many important functional polymers with high content of amine groups, such as poly(vinylamine) (PVAm),1 poly(ethyleneimine) (PEI), poly(allylamine) (PAH), and chitosan, are widely applied in biomedical,2 toxic heavy metal removal,3 chemical sensors,4 and so on. Specially, PVAm polymer, with the highest content of primary amine groups of any polymers, possesses good polyelectrolyte effects.5 Its mixed membranes have been applied to CO2 filtration,5–7 water/ethanol separation,8,9 and so on. Engineering the functional polymers into nano fiber materials can further greatly enhance their selectivity of adsorption, separation, penetration efficiency, and filtration. In the literatures published during the last 13 years, nanofibers of these functional polymers were only fabricated by electrospinning (ES) with expensive volatile solvents and additional polymers.10–14 Only PVAm nanofibers have not been fabricated by ES or rotary jet spinning (RJS), which is high rate production spinning with centrifugal force.15,16

According to the newest reviews of rotary jet spinning reported by Rogalski et al.17 and Chen et al.,18 most rotary jet spinning methods reported can be categorized to rotary jet dry spinning or rotary jet melt spinning. This mechanism of fiber formation has been comprehensively demonstrated.15,19–25

The primary challenges of pure PVAm nanofiber fabrication include (1) the difficulty to find volatile solvents to fit ES and RJS; because of its high viscoelasticity and hydrophilicity of PVAm aqueous solution, water cannot evaporate rapidly to form nanofibers; (2) the limited choice of coagulation bath in wet spinning; and (3) specific viscosity regulation.

Kevin Kit Parker’s group in Harvard University recognized that the high reliance on volatile carrier solvents was the disadvantage of dry RJS; thus, they developed immersion rotary jet spinning (iRJS) in 2016.26 The iRJS increases uniformity of nanofiber’s diameter, but it may be difficult to draw thinner fiber when fibers immerse into precipitation bath too early and difficult to fabricate nanofiber membrane with bigger area. Conventional RJS, rotary jet wet spinning (RJWS), and iRJS are three important pieces of puzzle in functional polymeric nanofibers fabrication. To address these challenges, we developed rotary jet wet spinning (RJWS) for the fabrication of pure polyelectrolyte polymeric nanofiber membrane. The spinning technique was applied for Chinese...
patent in 2015, and issued patent certificate in 2019. RJWS will further promote the industrial application of rotary jet spinning.

In this work, the optimal parameters of pure PVAm nanofibers fabrication are investigated. Then, to demonstrate the practical application, the optimal process is applied to spin molecular imprinting nanofibers (MINFs) for bisphenol A (BPA) recognition, one of the endocrine disruptors and acutely toxic to aquatic organisms.27 Molecular imprinting material was first developed by Wulff and Sarhan.28 Now the technique becomes one of the most versatile methods for the fabrication of molecular recognition materials29 and is applied to the development of material nanoarchitectonics.30 In this work, cross-linking between PVAm and glutaraldehyde (GA) is carried out after assembling between dummy template and PVAm. Following that, the specific binding sites are generated after dummy template is eluted. The leakage of toxic template can be avoided by using dummy template to take palace of the BPA template. Because phenol red possesses two flexible phenol structures similar to BPA and possesses very high aqueous solubility, it may be a good dummy template for BPA in aqueous preparation systems. The adsorption properties and selectivity of the resulted MINFs for BPA against its analogues are evaluated in spiked standard water and real river water with high-performance liquid chromatography (HPLC) system. Rotary jet spinning technique was first applied to the fabrication of molecular imprinting nanofibers. In comparison with other works of molecular imprinting nanofibers fabricated by ES and molecular imprinting particles (MIPs) prepared by bulk polymerization, the adsorption equilibrium of MINFs for BPA solution at low concentration was reached in 30 min, similar to other nanofiber material fabricated by ES;31 in addition, in this work, it is not necessary to synthesize uniform nanosize molecular imprinting particles prior to spinning molecular imprinting nanofibers, choose a volatile solvent, and worry about the leakage of residual template32,33 with the combination of RJS and dummy molecular imprinting (DMI).

2. RESULTS AND DISCUSSION

2.1. Optimizing PVAm Nanofiber Fabrication.

2.1.1. Morphology of PVAm Nanofiber. Figure 1 shows that the smallest diameter of PVAm nanofibers vary as spun speed increases from 6000, 8000 to 12 000 rpm with 8 wt % concentration. They are about 500 nm (Figure 1a), 260 nm (Figure 1b), and 320 nm (Figure 1c), respectively. With different rotation speeds, their median diameters are 1673 ± 345, 1273 ± 212, and 734 ±276 nm, respectively (see Supporting Information Figures S4–S6). From 6000 to 8000 rpm, the uniformity of PVAm nanofibers diameter becomes better; but from 8000 to 12 000 rpm, it turns bad. The best uniformity of PVAm nanofibers diameter is achieved at 8000 rpm with 8 wt % concentration. Other parameters are as follows: orifice distance and diameter are 1.0 and 0.4 mm, respectively, and coagulation bath is ethanol. In comparison with other works, the uniformity of the resulted superfine fibers fabricated by rotary jet wet spinning is lower than that of those fabricated by rotary jet dry spinning.

A very interesting phenomenon is observed that regularly spaced large and small section stay in a line along the fiber direction, forming a L−M−L−M structure (Figure 2d). The special phenomenon, named capillary wavelength, is discussed in detail by Wang et al.34 In this work, capillary wavelength is 6–10 times the fiber diameter, larger than their results (3.15 times); the dominant mode may be the long-wave mode. Figure 1d shows the critical balance status of the interaction between the centrifugal force and the surface tension of the viscoelastic PVAm solution is frozen. It is obvious that the smallest diameter of PVAm nanofiber with capillary wavelength is about 50 nm (Figure 1e), confirming the generation of smallest nanofibers reported by Badrossamay et al.15 It may indicate the low limit of the nanofiber diameter fabricated by rotary jet spinning. In addition, to prevent the superfine fibers from shrinking, a metal filter (200–300 mesh) is laid on the coagulation bath to adhere the ultrafine fibers firmly and keep their diameter stable during the spinning process, resulting in gaining real nanometric size dimension at various fabricated parameters.

The crystallinity of PVAm nanofibers is very low, and there are no obvious crystallization peaks in their X-ray diffraction (XRD) spectra, indicating that most of PVAm molecules exist in amorphous form (see Supporting Information Figure S7).

2.1.2. Coagulation Bath. Coagulation bath characteristics are very crucial to the formation of nanofiber in wet spinning. PVAm’s strong hydrophilicity hinders water to evaporate rapidly from the solution and fiber to generate during dry spinning. Several polar solvents are investigated as coagulation baths. Their spinning performance follows the ranking.
methanol ≥ ethanol > N-propanol > isopropanol > dimethyl sulfoxide (DMSO). If isopropanol is chosen as a coagulation bath, all fibers will stick together and separating each fiber is difficult (see Supporting Information Figure S8). The solidifying performance of the coagulation bath for fiber formation may have relationship with the functional groups of polymeric chains, the polarity and surface tension of coagulation bath. Specially, we found that the PVAm aqueous solution will become solid rapidly in methanol or ethanol and return to be highly viscoelastic status after it has evaporated, indicating that PVAm aqueous solution or PVAm gel can be used as smart material and selective filtration material for water/ethanol mixed solution. During fiber formation, water uses in ethanol coagulation bath; however, ethanol could not enter the PVAm aqueous solution. Meanwhile, ethanol or methanol compels the primary amine groups to only vibrate inside the fiber. That phenomenon was observed in our previous work when the fibers grafted with PEI were immersed into ethanol.35−37

2.1.3. Specific Viscosity of Solution on PVAm Nanofiber Formation. 2.1.3.1. Effect of Concentration on Specific Viscosity of solution. Figure 2 shows that the specific viscosity increases from 10 to 2500 mPa.s with the concentration of the PVAm solution increasing from 1 to 12 wt % (rotation speed was 8000 rpm; coagulation liquid is ethanol; orifice distance and diameter are 1.0 and 0.4 mm). Changes in the slope of the curve indicate the generation of unentangle and entangle between the PVAm polymer chains. Obviously, the critical concentration \( c^* \) of PVAm is found to be 5.5 wt %. At low concentration value (2 wt %), beads and very short fibers are obtained frequently. When the PVAm solution concentration increases to and above the critical concentration (5.5 wt %), more PVAm molecular chains overlap; uniform and continuous fibers are fabricated. Meanwhile, fewer solution beads are generated. Compared with newest reported works,13,15 the viscoelastic PVAm aqueous solution may be the highest spinning solution, up to 2500 mPa.s (almost 10 times of other spinning solutions).

2.1.3.2. pH Value and Temperature on Specific Viscosity of Solution. Figure 3a shows that using sodium hydroxide as the pH regulator, the solution viscosity decreases rapidly with the pH value increasing from 7 to 11. The result is consistent with the result reported by Kobayashi et al.38 PVAm is a cationic polyelectrolyte, and its primary amine groups are protonated under acidic conditions.1 Under strong basic conditions, at pH 11 and higher, there are almost no protonated groups and the conformation of the polymer chain changes from extended to mainly coiled. Thus, the
electrostatic interaction between PVAm molecular chains becomes weaker and weaker. Macroscopically, the intrinsic viscosity decreases. When ethylenediamine (EDA) aqueous is used as a pH regulator, the viscosity is higher than that when NaOH aqueous is used as a pH regulator. The reason may be because ethylenediamine (EDA) is ionized to protect PVAm polymer chains to coil rapidly.

The effect of temperature on the viscosity is indicated in Figure 3b. The higher the solution concentration, the viscosity decreases faster as the temperature increases, especially when the temperature is higher than 25 °C. Therefore, the solution viscosity can be regulated conveniently by changing the concentration, pH value, and temperature.

2.1.4. Rotation Speed on PVAm Nanofiber Formation.

With the same parameters: ethanol as coagulation bath; orifice concentration, pH value, and temperature, viscosity can be regulated conveniently by changing the concentration, pH value, and temperature.

2.1.4. Rotation Speed on PVAm Nanofiber Formation.

With the same parameters: ethanol as coagulation bath; orifice distance and diameters 1.0 and 0.4 mm, concentration 8 wt %; when the rotation speed is 4000 rpm or less, the centrifugal force is less than the surface tension of spinning solution, resulting in beads and very short fibers, and they are dispersed along a wide ring with diameter between 3 and 11 cm (Figure 4a). As the rotation speed increases from 6000 to 8000 rpm, continuous fibers spread on a narrow ring with diameter between 4 and 8 cm (Figure 4b), between 5 and 9 cm (Figure 4c), respectively. However, when spun at 12,000 rpm, continuous fibers are spread on a wider ring with diameter between 4 and 10 cm than other rotation speed; meanwhile, resulting in nanofibers with smaller diameter and higher alignment (Figure 4d).

In summary, the optimal parameters can be listed as follows: better rotation speed of 8000 rpm; better specific viscosity between 800 and 2500 mPas (corresponding concentrations are 8−12 wt %); and viscosity can be controlled conveniently by concentration and EDA aqueous solution. Ethanol is the best coagulation bath. According to the existing literatures, the PVAm superfine fibers can be applicable to selective separation and filtration for some chemicals and smart materials. In this work, the RJWS technique is applied to prepare PVAm-based MINFs for enhancing the BPA detection accuracy.

2.2. Analysis of PVAm-Based MINF for BPA Recognition. 2.2.1. Morphology of PVAm-Based MINF.

With rotary jet wet spinning technique, PVAm molecular imprinting nanofibers (MINFs) for BPA recognition are prepared by adding phenol red as a dummy template into the PVAm spinning solution and removing the template after nanofibers are cross-linked with GA. Phenol red template amount affects the binding sites amount positively. It means that more template will lead to more binding sites. So, the better choice is that more phenol red will be added to the spinning solution; however, excessive phenol red template (more than 0.04 mM) will lead to a much insoluble template, which will seriously block the spinning orifice.25 In this work, phenol red template amount was selected to be 0.03 mM in the following preparation of MINFs for BPA (see Supporting Information Figure S9).

The color of PVAm nanofibers with phenol red template is dark yellow (Figure 5a). After cross-linking and removing phenol red template, the PVAm nanofibers turned light yellow; the resulted superfine fibers were named PVAm molecular imprinting nanofibers (MINFs). The color of the original PVAm nanofibers was white (Figure 5b). After cross-linking, the PVAm nanofibers turned light yellow (Figure 5c). Adding phenol red template affects the viscoelasticity of the PVAm spinning solution; in addition, after cross-linking and removing phenol red template, the resulting MINFs (Figure 5d,f) presented a little rougher surface than that of NMINF (Figure 5e,g). Because the size of specific binding sites is about several nanometers, it is difficult to catch the changes after removing phenol red template on the resulted SEM images in this work. In addition, MIPs prepared by bulk polymerization possess an irregular shape (Figure 5h) and an obviously higher porosity (Figure 5i). The main reason of the higher porosity in MIPs may be the existence of porogen (methanol). So, to increase the porosity of MINFs, one suitable porogen should be added to the spinning solution.

The chemical structure changes in original PVAm fibers, transitional PVAm fibers, and resulted MINFs are characterized by using infrared (IR), and the spectra are presented in Figure 6. The strong bands at about 3400, 3000, and 1654 cm⁻¹ are characteristic of the N−H stretching, C−H stretching, and C=O stretching in pure PVAm fibers, respectively. After adding phenol red into the spinning solution, spinning onto the coagulation bath, and cross-linking with glutaraldehyde, the absorption signals of N−H stretching become weaker. Five new bands obviously display at 1508, 1170, 1132 cm⁻¹, 1015, and 738 cm⁻¹, which are characteristic of C=O stretching, S=O stretching, and benzene-ring stretching in transitional PVAm fibers, respectively. Furthermore, the existence of C=N stretching demonstrates Schiff base is formed by primary amine group reacting with glutaraldehyde. The existence of S=O stretching and benzene-ring stretching demonstrates the existence of phenol red template in PVAm fibers. Finally, phenol red template is eluted from transitional PVAm fibers. In comparison with the IR spectra of the original PVAm fibers, the only difference is a band at 1508 cm⁻¹ in the IR spectra of the resulting MINFs, which indicates the existence of Schiff base. Meanwhile, phenol...
red is proved to be removed completely from transitional PVAm fibers.

2.2.2. Adsorption Properties and Selectivity of PVAm-Based MINFs. 2.2.2.1. Adsorption Properties. The adsorption property of molecular imprinting nanofibers spun at various speeds (6000, 8000, and 12,000 rpm) is investigated. All these MINFs fabricated with 0.03 mM phenol red template and 8 wt % PVAm concentration. The isotherm curves show the adsorption amount of MINFs for BPA is higher than that of NMINFs (Figure 7a). It is proved that MINFs spun at a higher spun speed, leading to a thinner diameter, has a higher surface area. The binding affinity of MINFs to BPA template is evaluated by Scatchard plot analysis (Figure 7b) (spun at 12,000 rpm). The number of fitting lines represents the class of binding sites, and the values of association constants indicate the strength of the binding affinity.39,40

Figure 7b shows two straight lines fitting the Scatchard equation \( \frac{Q_e}{C_e} = -\frac{1}{K_a} + \frac{Q_{max}}{K_a} \), indicating that there are two classes of binding sites in MINFs. From the Scatchard plot, a low association constant \( K_a \) (8.6 mg/L, Line 1) is obtained, meaning a strong binding interaction between MINFs and BPA. The maximum binding capacity of MINFs is 5.6 mg/g (0.024 mmol/g, Line 2), which is lower than the MIPs prepared by bulk polymerization in the comparative experiments and other reported work.40 However, considering the phenol red dummy template amount is 0.03 mmol per gram PVAm polymer in the MINF preparation system, it can be calculated that about 80% selective binding sites are efficiently utilized to binding BPA templates. In addition, the amount of template to that of cross-linker and monomer is only about 1% in this work, which is lower than that of MIPs prepared by bulk polymerization (about 8.8%) and other reported work (about 6.2%).40 It indicates that more very expensive templates can be saved or reduce the risk of highly toxic templates to scientists and environment.

The adsorption equilibrium of MINFs in BPA solution at low concentration is reached in 30 min (Figure 7c); it is similar to other nanofiber materials fabricated by ES.31 However, the adsorption equilibrium time of MIPs prepared by bulk polymerization for BPA at low concentration is about 80
template imprinting technique, the resulted MINFs show an obviously higher selective affinity than NMINFs. At the concentration of 25 mg/L, the imprinted factor was 2.4 and the competitive coefficient of MINFs for BPA against BPS or BP reaches up to 5.3 or 6.5, respectively. These results indicate that MINFs possess good imprinting effect and high selectivity for BPA, named high recognition for BPA.

From Figure 7d and Table 1, the selective coefficient ($K_a$) of MIPs prepared by bulk polymerization is higher than MINF, against BPS or BP, is up to 6.5 and 9.2. The main reason may be that BPA template is used during the preparation of molecular imprinting polymers (MIPs). After removing the BPA template, the obtained three-dimensional binding sites are more precise than that obtained using phenol red as a dummy template. Because the molecular structure of BP and BPS are more rigid than that of BPA, it is more difficult for them to interact with the binding sites rapidly.

After seven cycles of adsorption–desorption experiments, the adsorption capacity of MINFs in BPA remain stable (see Supporting Information Figure S10).

### Table 1. Imprinted Factor and Selectivity Coefficients of Four Materials: MINFs, NMINFs, MIPs, and Nonmolecular Imprinting Polymer Particles (NMIPs)

| adsorbent fibers | adsorption amount (mg/g) | s.d. (mg/g) | imprinting factor (IF) | selectivity coefficients ($K_a$) |
|------------------|--------------------------|-------------|------------------------|------------------------------|
| MINF             | 5.3                      | 0.23        | 2.4                    | 6.5                          |
| NMINF            | 2.2                      | 0.25        | 2.6                    | 2.1                          |
| MIPs             | 8.4                      | 0.45        | 2.63                   | 9.2                          |
| NMIPs            | 3.2                      | 0.28        | 1.4                    | 1.8                          |

2.2.2.2. Selectivity. The selectivity coefficients ($K_a$) of the two adsorbents for BPA against BP or bis(4-hydroxyphenyl) sulfone (BPS) in their mixed solution are shown in Figure 7d and Table 1. It can be found that after adopting the dummy template imprinting technique, the resulted MINFs show an obviously higher selective affinity than NMINFs. At the concentration of 25 mg/L, the imprinted factor was 2.4 and the competitive coefficient of MINFs for BPA against BPS or BP reaches up to 5.3 or 6.5, respectively. These results indicate that MINFs possess good imprinting effect and high selectivity for BPA.

After being injected directly, BPA in real river water cannot be detected by HPLC (Figure 8c), indicating the concentrations of BPA below the limit of detection (LOD) of the HPLC analysis system. However, after being extracted with PVAm-based MINFs, the peak signals of BPA, BP, and BPS are captured (Figure 8d). The detection accuracy for BPA increases with highest times against its analogues, and the concentration of BPA is detected to be 60 ng/L. The high recognition performance of PVAm-based MINFs indicates that the resulted PVAm-based MINFs meet well the requirement of industrial application.

### 3. CONCLUSIONS

In this work, rotary jet spinning technique (RJS) was applied to the fabrication of molecular imprinting nanofibers for the first time. Rotary jet wet spinning (RJWS) has been developed for pure polyelectrolyte nanofiber membrane with a strong charge density. Pure PVAm nanofibers are fabricated from their highly viscoelastic aqueous solution without additional polymers by RJWS. It is found that PVAm aqueous solution possesses reversible sensitivity to alcohol, and the smallest diameter of PVAm nanofiber with capillary wavelength is 50 nm, confirming the dimension limit of rotary jet spinning. Finally, the association constant (8.6 mg/L), equilibrium time (30 min), and binding sites utilization rate (80%) of MINFs are evaluated, indicating that MINFs meet well the requirement of industrial application. In comparison with other MINF materials fabricated by ES, it is not necessary to synthesize uniform nanosize particles prior to spinning, choose a volatile solvent, and worry about the leakage of residual template with the combination of RJS and DMI in this work. The adsorption amount and selectivity of MINFs are little lower than those of MIPs prepared by bulk polymerization. Adding one suitable porogen will increase the specific binding amount of MINFs in future. RJWS will further promote the industrial application of RJS.

![Figure 8. Chromatograms of the spiked standard water (1) and river water (2): curves a and c, samples are directly injected for HPLC analysis; curves b and d, samples are pretreated by MINF microextraction prior to be injected for HPLC analysis; in all curves, peak 1, peak 2, and peak 3 represent BPS, BP, and BPA, respectively.](https://example.com/figure8.png)
4. EXPERIMENTAL SECTION

4.1. Reagents. Poly(vinylamine) (PVAm powder, KP8040, molecular weight was about 3 million) was purchased from Dia-Nitrix Co., Ltd. (Japan). Methanol, ethanol, N-propanol, isopropanol, dimethyl sulfoxide (DMSO), sodium hydroxide, ethylenediamine (EDA), methacrylic acid (MAA), and glutaraldehyde (GA) were purchased from Guangzhou Reagent Factory (Guangzhou, China). Bisphenol A (BPA), 4,4′-dihydroxybiphenyl (BP), bis(4-hydroxyphenyl) sulfone (BPS) (Figure 9), ethylene glycol dimethacrylate (EGDMA), benzoin ethyl ether (BEE), and phenol red were purchased from Aldrich Chemical Co., Ltd. (Shanghai, China). All reagents and solvents were used without further purification.

4.2. Instruments. A rotary jet wet spinning machine was made by our group and used to fabricate PVAm nano fibers (see Supporting Information Figure S1). UV light (LUYOR-2010AUV, LUYOR Corporation) and high-energy ball mill (8000D Mixer/Mill, SPEX Co., Ltd.) were used to prepare molecular imprinting polymeric particles. A spectrophotometer (UV-5100, Shanghai Metash instruments Co., Ltd.) was used to measure the concentration of BPA, BP, and BPS in adsorption and selectivity experiments. A Fourier transform infrared (FT-IR) analyzer (Nicolet/Nexus 670), equipped with an ATR objective, was employed to test the chemical structure of materials (at the range of 400 to 4000 cm⁻¹). A field-emission scanning electron microscope (JSM-6330F, Japan) was used to observe the surface morphology of nano fibers. Powder X-ray diffraction (XRD, D8 ADVANCE, BRUKER Textile Technologies GmbH & Co., KG, Germany) was employed to analyze PVAm nanofibers. A HPLC system (LCQ, Thermo Fisher) was used to demonstrate selective recognition and solid-phase microextraction (SPME) performance of the resulting molecular imprinting nanofibers.

4.3. Preparation of PVAm Nanofibers and PVAm-Based MINFs. First, optimal parameters of spinning process are investigated. The PVAm powder is dissolved in pure water with stirring. After degassing, the mixed solution is injected into the rotatable reservoir slowly. The fiber spinning process is composed of (1) the PVAm solution jetted through the orifice at high rotating speed and extruded into one continuous ultrafine stream and (2) the ultrafine stream dropped on one metal filter (with 200−300 mesh) and immersed into a coagulation bath, forming nanofibers rapidly. Several important optimal parameters of PVAm nanofiber fabrication are investigated, such as coagulation bath, specific viscosity of solution (three main factors affect viscosity, such as concentration, pH value, and temperature), and spinning speed.

To demonstrate the practical application, PVAm-based molecular imprinting nanofibers (MINFs) of bisphenol A (one endocrine disruptor) recognition are prepared as follows. Phenol red is dissolved in basic aqueous solution (its pH value is regulated to 11 with NaOH or EDA); then, the PVAm polymer powder is dissolved in a mixed solution. The primary amine groups of PVAm interact with the hydroxyl group of phenol red with a noncovalent bond. After cross-linking between PVAm nanofiber and glutaraldehyde, phenol red dummy template is removed by dynamic elution with basic aqueous/ethanol mixed solution until no phenol red is detected by a UV−vis spectrophotometer (360 nm). Many selective binding sites for BPA molecular in MINFs are obtained. The preparation principle of MINFs is illustrated in Scheme 1. The nonmolecular imprinted nanofibers (NMINFs)}
is prepared using the same procedure but without adding phenol red.

4.4. Preparation of MIPs by Bulk Polymerization. Similar to the work of Pérez-Moral and Mayes,41 in this work, bulk imprinted polymeric particles were synthesized using BPA (2 mmol), MAA (14 mmol), EGDMA (20 mmol), methanol (8 mL), and BEE (0.02 g) as template, functional monomer, cross-linking agent, solvent, and photoinitiator, respectively, through optimized experiments. The bulk polymerization was carried out under UV light for 15 min at room temperature. The resulting molecular imprinting particles were prepared after grinding with ball mill, screening with stainless steel screen (300 mesh) and template elution (see Supporting Information Figures S2 and S3). (1) Nonimprinted polymeric particles were synthesized following the same procedure but without the BPA template.

4.5. Batch Adsorption and Competitive Adsorption. The batch adsorptions are carried out as follows: the resulted MINFs, MIPs (0.25 g), or NMINFs (0.25 g) are dispersed in 25 mL of BPA aqueous solution with concentrations from 5 to 100 mg/L. The residual BPA concentration is determined by a UV−vis spectrophotometer by resolving the simultaneous equations of detailed experimental operation and results processing of batch previous work.35 After equilibrium adsorption, the concentrations of BPA, BP, or BPS in the mixed solutions are measured with a UV

4.6. SPME Performance for BPA Detection. The selective recognition for BPA of the resulting MINFs can be demonstrated by solid-phase microextraction (SPME) performance in spiked standard samples and real river water. The initial concentrations of spiked standard solutions, containing BPA and its analogue, are 1, 5, and 20 ng/mL, respectively. The river water samples are drawn from three locations of the TianSha River (around Wuyi University, China). All of the samples are filtered with mixed cellulose filters (0.45 and 0.25 μm) two times and purified by centrifugal force for 10 min at 8000 rpm. Fifty milliliters of the supernatant flows through a glass tube (Φ10 × 100 mm²) packed with 0.25 g of MINFs at a flow rate of 6 BV/h to extract trace chemicals. After extraction, 4 mL of ethanol is used to elute BPA from the MINFs at a flow rate of 2 BV/h, and their BPA concentration are determined with HPLC. Finally, the concentration of BPA in the spiked standard solutions and river water samples are calculated.
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