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Superhydrophilic molecularly imprinted polymers based on a water-soluble functional monomer for the recognition of gastrodin in water media

Wenhua Ji[a], Mingming Zhang[b], Daijie Wang[a], Xiao Wang[a,*], Jianhua Liu[a], Luqi Huang[c,*]

[a] Key Laboratory of TCM Quality Control Technology, Shandong Analysis and Test Center, Shandong Academy of Sciences, 19 Keyuan Street, Jinan 250014, China
[b] School of Life Sciences, Shandong Normal University, Jinan 250014, China
[c] National Resource Center for Chinese Materia Medica, State Key Laboratory Breeding Base of Dao-di Herbs, China Academy of Chinese Medical Sciences, Beijing 100700, China

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ABSTRACT

In this study, the first successfully developed superhydrophilic molecularly imprinted polymers (MIPs) for gastrodin recognition have been described. MIPs were prepared via the bulk polymerization process in an aqueous solution using alkenyl glycosides glucose (AGG) as the water-soluble functional monomer. The non-imprinted polymers (NIPs) were also synthesized using the same method without the use of the template. The dynamic water contact angles and photographs of the dispersion properties confirmed that the molecularly imprinted polymers displayed excellent superhydrophilicity. The results demonstrated that the MIPs exhibited high selectivity and an excellent imprinting effect. A molecularly imprinted solid phase extraction (MISPE) method was established. Optimization of various parameters affecting MISPE was investigated. Under the optimized conditions, a wide linear range (0.001–100.0 $\mu g\,mL^{-1}$) and low limits of detection (LOD) and quantification (LOQ) (0.03 and 0.09 $ng\,mL^{-1}$, respectively) were achieved. When compared with the NIPs, higher recoveries (90.5% to 97.6%) of gastrodin with lower relative standard deviations values (below 6.4%) using high performance liquid chromatography were obtained at three spiked levels in three blank samples. These results demonstrated one efficient, highly selective and environmentally-friendly MISPE technique with excellent reproducibility for the purification and pre-concentration of gastrodin from an aqueous extract of *Gastrodia elata* roots.

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1. Introduction

Solid phase extraction (SPE) is a well-established sample pre-treatment technique that can be used to integrate the isolation and enrichment of target analytes from complex matrices into a single step [1,2]. The technique is in high demand in the natural products research field due to its clear advantages which include efficiency, simplicity, sensitivity, lack of solvent consumption and fast operation [3]. The SPE technique aims to establish the extraction equilibrium of target analytes between the sample matrix and sorbents, therefore, the properties of the sorbents are particularly important and significantly impact extraction in SPE devices. Commercial sorbents, such as carboxen/poly(dimethylsiloxane), poly(dimethylsiloxane), poly(dimethylsiloxane)/divinylbenzene, poly(ethyleneglycol)/divinylbenzene, car-bowax/divinylbenzene and polyacrylate, have been successfully applied in many fields [4–7]. However, commercial sorbents lack specific adsorption properties which commonly cause co-extraction of interference components with the target components from natural products with complex matrices [3]. To address this problem, sorbents must be modified to enhance their sensitivity and selectivity.

The most powerful approach to achieve selectivity and high-enrichment efficiency in SPE is the application of molecular imprinted polymers (MIPs), commonly referred to as artificial materials, which can be tailored to specifically bind to a target molecule [8–10]. MIPs have been used as solid-phase extraction sorbents for the selective extraction of bioactive constituents from medicinal plants [11–17]. However, previously developed MIPs are normally prepared using hydrophobic functional monomers in organic, non-polar solvents. They mostly show high non-specific adsorption and a poor ability to recognize hydrophilic compounds in aqueous solution [18–22]. Hydrophilic MIPs have been

* Corresponding authors.
E-mail addresses: wangx@sdas.org (X. Wang), luqihuang@126.com (L. Huang).

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developed using the controlled or "living" radical precipitation polymerization technique (CRPP) [23–26], cold plasma-induced grafting polymerization [27] and modification [28]. Despite their excellent performance, the proposed methods refer to complicated synthesis processes. Bulk polymerization under mild reaction conditions is the most popular and general approach for synthesizing MIPs due to its simplicity and speed. Consequently, there is an urgent need to search for water-soluble monomers and to develop bulk polymerization for the preparation of hydrophilic MIPs in aqueous media.

Gastrodin (GAS) is one of the water-soluble bioactive constituents isolated from *Gastrodia elata* Blume (Tianma in Chinese) and has known anti-convulsant effects [29–31]. Due to the excellent pharmacological properties, GAS has been used as a quality control standard for original herbs and herbal preparations. Analysis of GAS has been developed using chromatographic techniques, which mainly include high performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector [32]. However, *G. elata* roots are complex biological samples containing a large number of hydrophobic compounds, such as 4-hydroxybenzaldehyde (PHBA), 4-hydroxybenzyl alcohol (PHA), 4-hydroxy-3-methoxybenzyl alcohol (PHMA), 4-hydroxy-3-methoxybenzaldehyde (PMA) and D-(+)-glucose (Fig. 1A). There is a need to enrich and isolate the target components before detection. In our previous work, a molecular imprinted solid phase extraction (MISPE) method using 2,3,4,6-tetra-*O*-acetyl-glucopyranoside (TAGL) and 1,2,3,4,5-pentafluoro-6-vinylbenzene (PFVB) as hydrophobic functional monomers was developed [33]. The MIPs/TAGL polymer possesses highly selective binding cavities for recognition of GAS in aqueous solution. However, the hydrophobic MIPs/TAGL-SPE has poor permeability and can be fouled easily, showing an obvious decline in its ability to specifically recognize when the sorbents are recycled.

The aim of the current study was to develop an alternative sample pre-treatment method which targets natural active constituents by exploring MIP-based GAS capture. In contrast to MIPs targeting hydrophobic compounds, the imprinting of GAS should be compatible with an aqueous media. In the present study, alkenyl glycosides glucose (AGG) was synthesized as a water-soluble functional monomer. Superhydrophilic MIPs were prepared using bulk polymerization in aqueous solution. Based on the MIPs, molecularly imprinted polymer-assisted solid phase extraction (MISPE) was successfully used for the targeted extraction of GAS from a complex sample matrix. To our knowledge, we report for the first time the successful synthesis of a functional monomer that can be used directly in bulk polymerization for the efficient and specific recognition of hydrophilic molecules. This finding is a major breakthrough for molecular imprinting technology as it opens the opportunity for the rapid and simple preparation of MIPs with outstanding performance in real aqueous samples.

2. Experimental

2.1. Materials

GAS (≥98%, template) was obtained by Xi′an Guanyu Bio-tech Co., Ltd. *G. elata* roots were supplied from Yunnan, China. D-(+)-Glucose, allyl alcohol, acetyl chloride, *N*,*N*′-methylene diacrylamide (MBA, cross linker), methacrylic acid (MAA, functional monomer) and azoisobutyronitrile (AIBN, initiator) were purchased from Sigma–Aldrich (Steinheim, Germany). PHBA, PHA, PHMA and PMA were purchased from Alfa Aesar (Massachusetts, USA). HPLC-grade methanol and acetonitrile were sourced from Fisher Scientific (Fair Lawn, NJ, USA). Standard solutions of GAS, PHBA, PHA, PHMA, PMA and D-(+)-glucose were prepared in water.

2.2. Synthesis of alkenyl glycosides glucose (AGG, functional monomer)

The synthesis route of AGG was illustrated in Fig. 1B. Acetyl chloride (11.77 g, 150 mmol) was added to allyl alcohol (102.48 g, 1.76 mol) at −5 °C. After stirring for 1 h at −5 °C, D-(+)-glucose (10.00 g, 55.6 mmol) was added and the reaction mixture was stirred for 2 h at 90 °C. The mixture was quenched with $NaHCO_3$, filtered and co-concentrated with toluene. The residue was purified by using column chromatography on silica gel (ethyl acetate/methanol, 8:1) to afford alkenyl glycosides glucose as a colourless solid. Yield: 3.32 g (15.1 mmol, 55%). R_F-value: 0.34 (ethyl acetate/methanol, 8:1). ^{1}H NMR (D_2O, 400 MHz) δ 5.82–5.90 (m, 1H), 5.26 (d, 1H, J = 17.2 Hz), 5.15 (d, 1H, J = 10.4 Hz), 4.85 (d, 1H, J = 3.6 Hz), 4.09–4.15 (m, 1H), 3.93–3.98 (m, 1H), 3.71–3.81 (m, 1H), 3.61–3.66 (m, 2H), 3.44 (dd, 1H, J = 9.8 and 3.6 Hz), 3.26–3.36 (m, 1H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz) δ 135.4, 116.8, 98.3, 73.9, 72.4, 70.8, 69.2, 67.5, 61.5 ppm; ESI-MS m/z (%) = 243 (100) [M+Na$^+$].

2.3. Preparation and packing of MIPs and NIPs materials

The MIPs were prepared by bulk polymerization by using AGG and MAA as the hydrophilic functional monomers (see supporting information). Nonimprinted polymers (NIPs) were also tested so as to assess MIPs imprinting efficiency. To prepare MIPs and NIPs cartridges, 100 mg of both MIPs and NIPs were slurry-packed under vacuum into empty SPE cartridges (1 mL) and capped between two polyethylene disks.

2.4. Characterization of the MIPs and NIPs

Nitrogen adsorption–desorption isotherms were determined using Rise-1010 surface area measurement (Jinan, China). Before recording the sorption measurements, polymers were outgassed for 12 h at 120 °C. The specific surface area and total pore volume were calculated by the Brunauer–Emmett–Teller (BET) method.

2.5. Measurement of the dynamic water contact angles

Polymers were dispersed ultrasonically in DMF (10 mg mL^{-1}) and the films were carried out by casting the suspension solutions onto the glass surfaces. The resulting films were dried at 25 °C for 12 h after the evaporation of the solvent [22]. An OCA40 video optical contact angle equipment (Dataphysics, Germany) was used to determine the dynamic water contact angles.

2.6. HPLC analysis

An Agilent Series 1120 system (Santa Clara, CA, USA), controlled by *Chemstation B0403 Chromatographic Software*, was used to analyze the samples. Chromatographic separations were performed on an YMC-Pack ODS-A (5 μm, 4.6 × 250 mm) analytical column. The mobile phase was acetonitrile:H_2O (85:15, v/v) with the flow rate of 1.0 mL min^{-1} at 24 °C. The injection volume was 20 μL and the UV detector wavelength was set at 270 nm. The retention times of GAS, PHA, PHMA, PHBA and PMA were 4.09, 5.71, 6.62, 14.03 and 17.39 min, respectively. D-Glucose was obtained to separate as the library [33].

2.7. Sorption experiments

10 mg polymers were equilibrated with 2.5 mL various concentrations of GAS (0.05–0.5 mmol L^{-1}). The sorbents were shaken for 150 min at 25 °C. After being filtered through a 0.22 μm membrane, the free concentrations of GAS in the filtrates were analyzed by

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