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Hydrophilic gallic acid–imprinted polymers over magnetic mesoporous silica microspheres with excellent molecular recognition ability in aqueous fruit juices

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ABSTRACT

Hydrophilic molecularly imprinted polymers (MIPs) for gallic acid (GA) were prepared with excellent recognition ability in an aqueous solution. The proposed MIPs were designed by self-polymerization of dopamine (DA) on magnetic mesoporous silica (Fe_3O_4@SiO_2@mSiO_2, MMS) using GA as template. Resulting Fe_3O_4@SiO_2@mSiO_2@MIPs (MMS–MIPs) were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TGA), Brunauer–Emmett–Teller (BET), vibrating sample magnetometer (VSM), and evaluated by adsorption isotherms/kinetics and competitive adsorption. The adsorption behavior between GA and MMS–MIPs followed Langmuir and Sips adsorption isotherms with a maximum adsorption capacity at 88.7 mg/g and pseudo-second-order reaction kinetics with fast binding (equilibrium time at 100 min). In addition, MMS–MIPs showed rapid magnetic separation (10 s) and stability (retained 95.2% after six cycles). Subsequently, MMS–MIPs were applied for the selective extraction and determination of GA from grape, apple, peach and orange juices (4.02, 3.91, 5.97, and 0.67 μg/g, respectively). Generally, the described method may pave the way towards rationally designing more advanced hydrophilic MIPs.

1. Introduction

Sample preparation generally involves selective isolation and/or enrichment of target components from complex matrices (Zhang, Liu, Hu, & Li, 2009), which plays an important role in analytical procedures for higher sensitivity and better specificity (Berendsen, Stolker, & Nielen, 2013; Zhao, Qin, Wu, & Zou, 2012). Up to now, a variety of sample preparation methods (e.g. liquid–liquid extraction (Moret et al., 2014), solid-phase extraction (Mashhadizadeh, Amoli-Diva, Shapouri, & Afruzi, 2014)) have been developed. Each method has its advantages and disadvantages. However, selective methods are expected for the rid of matrix effects (Li, Zhu, Luo, Yuan, & Feng, 2013). Molecularly imprinted polymers (MIPs) are promising selective candidates with specific recognition sites, mechanical/chemical stability and reversible adsorption/release procedure (Shi, Guo, You, Chen, & Zhang, 2014; You et al., 2014), which has attracted wide attention for the selective extraction of small organic components or macromolecules from complex matrices (e.g. food, natural product, environmental and biological samples) (Pardeshi, Dhodapkar, & Kumar, 2014; Su et al., 2015).

In most cases, MIPs showed specific adsorption of components at very low concentrations (Yan, Qiao, & Row, 2007; You et al., 2014). However, previously developed MIPs are normally prepared in organic, non-polar solvents, and they mostly show poor recognition ability and high non-specific adsorption in aqueous solution (Guo, Liang, Wang, & Gui, 2013; Ji, Chen, Ma, Wang, & Huang, 2014). Therefore, efforts are being made to design hydrophilic MIPs, which involve the use of a hydrophilic co-monomer, functional monomer and crosslinker (Dirion, Cobb, Schillinger, & Sellergren, 2013; Ma, Pan, Zhang, & Zhang, 2013; Zhang, 2014). However, the design/preparation of hydrophilic comonomer, functional monomer and/or crosslinker is complicated and reagent-consuming processes. Therefore, the development of facile and efficient approaches for preparation of hydrophilic MIPs is highly desirable.

Dopamine (DA) can be self-polymerized in basic solution to form thin and surface-adherent polydopamine (PDA) coating with excellent environmental stability and especially hydrophilic property (Lee, Dellatore, & Miller, 2007). Inspired by this breakthrough, several studies have been reported on the preparation of hydrophilic MIPs for biomacromolecules (Chen, Shao, Xu, Zhou, & Lee, 2012;

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Ouyang, Lei, & Ju, 2010; Yao, Liang, Huang, Wang, & Qiu, 2013). Imprinting MIPs on the surface of nano/micro solid support (e.g. silica particles (Xie, Guo, Zhang, & Shi, 2014), carbon nanotubes (Xiao, Dromou, Xiong, & Li, 2013), polymer supports (Pan, Yao, Guan, Zou, & Li, 2011) and magnetic nanoparticles (You et al., 2014)) can increase the binding capacity and shorten the equilibrium time (Shi et al., 2014). Also, mesoporous materials with absolute high surface to volume ratio have gained more attention (Deng, Qi, Deng, & Zhao, 2008; Liu, He, Jin, & Zhao, 2014). The preparation of PDA-coated MIPs on magnetic mesoporous silica microspheres (MMS) exert simultaneously advantages of magnetic microparticles, mesoporous silica, hydrophilic PDA and surface MIPs. However, relating works have not been reported as far as we know.

Gallic acid (GA), a strong natural antioxidant (Zheng & Wang, 2001), is widely present in fruit, plant and usually used in feed industry (Geerkens et al., 2013). GA has high polarity, and is usually co-eluted with some interferences during high-performance liquid chromatography (HPLC) analysis (Zuo & Deng, 2002). Then, pretreatment and clean-up steps prior to its quantification are required. GA imprinted MIPs have been previously prepared by bulk polymerization and precipitation polymerization in organic solvents (Pardeshi et al., 2014; Zhu et al., 2009), which are hydrophobic and have limited binding capacity in an aqueous solution.

Herein, we attempt to prepare novel hydrophilic MIPs (Fe_3O_4@SiO_2@mSiO_2@MIPs, MMS–MIPs) for GA, investigate the adsorption isotherms/kinetics, competitive adsorption, reproducibility, and then apply these for the selective extraction of GA from fruit juices. The results suggested that prepared MMS–MIPs exerted high binding capacity, fast binding kinetics, excellent selectivity, and quick separation ability in aqueous solution. This finding may open the door for preparation of hydrophilic MIPs with outstanding performance.

2. Experimental

2.1. Chemicals and reagents

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), polyethylene glycol 6000 (PEG 6000), cetyltrimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), ammonium persulfate (APS), DA, $NH_3{\cdot}H_2O$ (28 wt%), and HPLC grade methanol were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received. Benzoic acid (BA), salicylic acid (SA), 4-hydroxybenzoic acid (4-HBA), protocatechuic acid (PCA), caffeic acid (CA) and GA with purities over 99% were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Ultrapure water (18.2 MΩ) was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). The other reagents were of analytical grade and purchased from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). All solutions used for HPLC analysis were filtered through a 0.45 μm filter.

2.2. Instrumentation

TEM (JEM–2100F, JEOL, Japan) was used to observe morphology of microspheres. FT-IR spectra (4000–400 cm^{-1}) were obtained via a Nicolet 6700 FT-IR spectrometer (Thermo Nicolet Co., Waltham, MA, USA). The encapsulation efficiency of microspheres was carried out by TGA (SDTQ600, TA, USA). The magnetic property was measured at room temperature using VSM (VSM7407, Lakeshore, USA). Nitrogen sorption isotherms were carried out at 77 K by a Monosorb Autosorb (Monosorb Autosorb, Quantachrome, USA).

Chromatographic separation was performed on an analytical ZORBAX SB-C_{18} column (150 mm × 4.6 mm, 5 μm, Agilent, Santa Clara, CA). The sample was analyzed by an Agilent 1260 HPLC system and a diode array detector system. The mobile phase was consisted of A (0.4% acetic acid in water) and B (0.4% acetic acid in methanol) with the linear gradient elution, 0–30 min for 20–30% B at a flow rate of 0.8 ml/min at 25 °C. Spectra were monitored at 260 nm.

2.3. Procedures for preparation of MMS–MIPs

The procedure to obtain MMS–MIPs was shown in Fig. 1. At first, Fe_3O_4@SiO_2 microspheres were synthesized according to our previous work (Zhang et al., 2014). Then, Fe_3O_4@SiO_2 microspheres were coated with mSiO_2 layer through a surfactant based sol–gel approach according to reported method with minor modifications (Deng et al., 2008). Typically, prepared Fe_3O_4@SiO_2 microspheres (50.0 mg) were mixed with CTAB (500.0 mg) in deionized water (50.0 ml) and ultrasonicated for 30 min. Then, the resultant homogenous solution was diluted with 1.0 mM NaOH aqueous solution (450.0 ml) and ultrasonically treated for another 5 min. Subsequently, the obtained basic dispersion was mechanically stirred with a motor-driven Teflon paddle at 170 rpm for 30 min at 60 °C, followed by the addition of TEOS/ethanol (1/4, V/V) solution (2.5 ml). The mixture obtained was mechanically stirred with a motor-driven Teflon paddle at 170 rpm for 1 min at 60 °C, and then let stand for 12 h. The Fe_3O_4@SiO_2@CTAB/SiO_2 microspheres were collected magnetically and then re-dispersed in acetone for refluxing at 80 °C twice of 24 h each to remove CTAB. Finally, MMS microspheres were collected, repeatedly washed by de-ionized water, and dried in vacuum at 50 °C for 12 h. At last, MMS–MIPs were prepared using DA as functional monomer (Ouyang et al., 2010; Yao et al., 2013). Generally, equal molar of GA and DA (0.16 mmol) was dissolved in phosphate buffer (20.0 ml, pH = 7.6) and mechanically stirred with a motor-driven Teflon paddle at 170 rpm for 1 h at room temperature to prepare preassembly solution, then MMS (80.0 mg) suspended in phosphate buffer (20.0 ml) were added to the above solution. After adding APS (0.02 mmol), chemical polymerization was allowed to proceed for 12.0 h at room temperature. After polymerization, the resulting polymers were collected magnetically, rinsed with water until the supernatant was clear, and then eluted with water–acetic acid (7/3, V/V) in a soxhlet apparatus to remove GA absolutely. Finally, the MMS–MIPs were washed with water to neutral pH and dried under vacuum at 50 °C for 12 h.

As a control, the same procedures were applied for the preparation of MMS–NIPs without GA in the self-polymerization stage.

2.4. Adsorption experiment and selectivity evaluation

MMS–MIPs/MMS–NIPs (10.0 mg) were suspended in 3.0 ml of various concentrations of GA aqueous solutions (0.05–2.0 mg/ml)

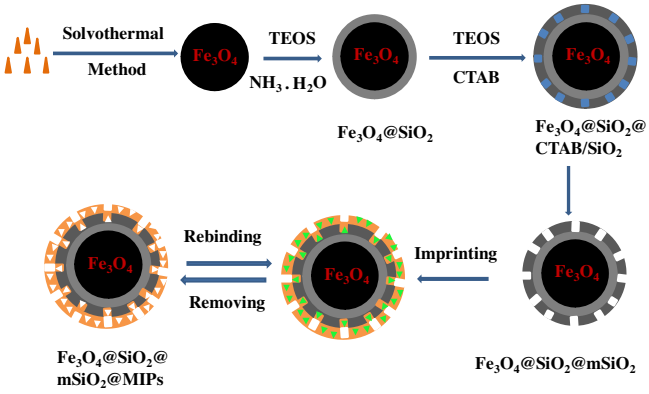

Fig. 1. Schematic preparation process of MMS–MIPs.