



Selective extraction and determination of chlorogenic acid in fruit juices using hydrophilic magnetic imprinted nanoparticles



Yi Hao^{a,b}, Ruixia Gao^{b,*}, Dechun Liu^c, Gaiyan He^{a,b}, Yuhai Tang^{a,b}, Zengjun Guo^{a,*}

^a School of Pharmacy, Xi'an Jiaotong University, Xi'an 710061, China

^b Institute of Analytical Science, School of Science, Xi'an Jiaotong University, Xi'an 710049, China

^c Department of Hepatobiliary Surgery, First Hospital of Xi'an Jiaotong University, Xi'an 710061, China

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ABSTRACT

In this paper, the novel hydrophilic magnetic molecularly imprinted nanoparticles were developed for selective separation and determination of chlorogenic acid in aqueous fruit juices. The polymers were prepared by using amino-functionalized magnetic nanoparticles as carriers, branched polyethyleneimine as functional monomer, and chlorogenic acid as template molecule. Branched polyethyleneimine with abundant active amino groups could react with template sufficiently, and its unique dendritic structure may amplify the number of the imprinted cavities. Meanwhile, it would improve the hydrophilicity of imprinted materials for attaining high extraction efficiency. The resulted polymers exhibit fast kinetics, high adsorption capacity, and favorable selectivity. In addition, the obtained nanoparticles were used as solid-phase extraction sorbents for selective isolation and determination of chlorogenic acid in peach, apple, and grape juices (0.92, 4.21, and 0.75 $\mu\text{g mL}^{-1}$, respectively).

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1. Introduction

Molecular imprinting, proposed by Wulff and Sarhan (1972), has become an attractive technique to create specific cavities complementary to the template molecule in shape, size, and chemical functionality. Molecularly imprinted polymers (MIPs) possess the advantages of predetermination, low cost, easy preparation, mechanical and chemical stability, applicability in harsh environment, and high specificity. Owing to their outstanding merits, MIPs have been widely used in the fields of chromatography (Santos, Tavares, Boralli, & Figueiredo, 2015; Shao et al., 2015), biosensor (Eren, Atar, Yola, & Karimi-Maleh, 2015; Lenain, Saeger, Mattiasson, & Hedström, 2015), drug delivery (Kempe, Pujolràs, & Kempe, 2015; Suksuwan et al., 2015), and solid-phase extraction (SPE) (Lata, Sharma, Naik, Rajput, & Mann, 2015; Yang et al., 2015). Among these applications, MIPs used as SPE adsorbents have exhibited a great prospect for the selective extraction or clean-up of target analytes from various complex matrices.

Traditionally, MIPs have to be packed into SPE cartridge or adopt centrifugation and filtration procedures when used in the process of SPE. The time-consuming and complicated course commonly yield low extraction efficiency. Therefore, magnetic Fe_3O_4

nanoparticles (NPs), because of their good biocompatibility, magnetic susceptibility, low toxicity, have been encapsulated into MIPs to solve the above problems. The resulting composites not only have magnetic characteristic for rapid separation but also possess high selectivity for recognition of the target molecule (Hao et al., 2015; Huang, Zhou, Chen, Wu, & Lu, 2015; Liu et al., 2015).

Chlorogenic acid (CGA), a bioactive phenolic acid, is extensively distributed in fruit, plant, and used in feed industry. It is reported that CGA has several beneficial biological properties including antibacterial, antiphlogistic, antiviral, mutant resistance, and even inhibitory effects on carcinogenesis in large intestine, liver, and tongue (Bagdas et al., 2015; Heyman et al., 2015; Naso et al., 2014; Wang et al., 2015). CGA is water-soluble and usually coexists with some compounds hold similar functional groups such as caffeic acid, gallic acid, and so on. Thus, selective extraction of CGA from complex matrices prior to its quantification is urgently required. However, CGA-imprinted polymers previously reported were usually prepared in organic media (Gu et al., 2010; Saad, Madbouly, Ayyoub, & Nashar, 2015), which could lead to poor recognition ability and high non-specific adsorption in aqueous matrices. Therefore, a facile and efficient approach to prepare hydrophilic CGA-imprinted polymers is highly desirable.

Polyethyleneimine (PEI), a water-soluble and non-toxic polycation (Bahulekar, Ayyangar, & Ponrathnam, 1991), consists of high content of functional groups (primary, secondary, and tertiary amine groups). What is more, PEI could assemble layer-by-layer

* Corresponding authors.

E-mail addresses: ruixiagao@mail.xjtu.edu.cn (R. Gao), guozj@mail.xjtu.edu.cn (Z. Guo).

with glutaraldehyde as cross-linking agent (Zhao et al., 2015). Based on these distinctive features, PEI has been widely applied in gas adsorption (Lee, Lee, & Park, 2015; Sabri, Guillemette, Guermoune, Sijaj, & Szkopek, 2012), drug/gene delivery (Ambattu & Rekha, 2015; Jung, Kim, Lee, & Mok, 2015), enzyme immobilization (Khoobi et al., 2015), and heavy metals removal (Chen et al., 2014; Lindén, Larsson, Coad, Skinner, & Nydén, 2014).

Herein, we attempt to prepare novel hydrophilic MIPs adopting branched PEI as functional monomer and CGA as template molecule. The abundant functional groups on PEI can react with CGA through multiple hydrogen bonds and electronic interactions. Meanwhile, its unique dendritic structure and water solubility could greatly improve the density of recognition sites and hydrophilicity of MIPs. The characteristics and binding properties of the obtained MIPs were investigated. In addition, the resulted polymers were used as SPE sorbents and coupled with HPLC to selective extraction and determination of CGA in fruit juices. The developed approach would exhibit great potential for preparation of hydrophilic MIPs with satisfactory imprinting performance.

2. Experimental

2.1. Chemicals and reagents

Ferricchloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 1,6-hexadiazine (HDM), glutaraldehyde, sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), ethylene glycol (EG), anhydrous sodium acetate (NaOAc), phosphoric acid (H_3PO_4), ethanol, acetonitrile, and acetic acid were provided by Xi'an Chemicals Ltd. CGA, caffeic acid (CA), cichoric acid (CCA), caftaric acid (CFA), protocatechuic acid (PCA), and polyethyleneimine (PEI) ($MW = 10,000$, Purity $\geq 99.0\%$) were obtained from Aladdin Industrial Corporation. All reagents used were of at least analytical grade. The ultrapure water ($18.25 \text{ M}\Omega \text{ cm}^{-1}$) was obtained from a WaterPro water system (Axlwater Corporation, TY10AXLC1805-2, China) and used throughout the experiments.

2.2. Instrumentation and analytical conditions

JEM-2100 transmission electron microscope (TEM) (JEOL Co., Japan) was used to observe morphology of as-synthesized magnetic nanoparticles. Fourier transform infrared (FT-IR) spectra ($4000\text{--}400 \text{ cm}^{-1}$) were obtained via a Nicolet AVATAR-330 FT-IR spectrometer (Thermo Electron Co., U.S.A.). The magnetic properties were measured at room temperature using an LDJ 9600-1 vibrating sample magnetometer (VSM) (LDJ Co., U.S.A.). The identification of the crystalline phase was carried out by a Rigaku D/max/2500v/pcX-ray diffractometer (Rigaku Co., Japan) with $\text{Cu K}\alpha$ radiation. The HPLC profiles were recorded using a Shimadzu HPLC system equipped with LC-10AT pump, SPD-M 10A detector, CTO-10AS column oven, and Shimadzu VP-ODS C18 column ($5 \mu\text{m}$, $150 \text{ mm} \times 4.6 \text{ mm}$). The column temperature was $30 \text{ }^\circ\text{C}$. The optimized mobile phase was acetonitrile-0.05% phosphoric acid solution (85:15, v/v) delivered at a flow rate of 1.0 mL min^{-1} , the injection volume was $20 \mu\text{L}$, and the column effluent was monitored at 323 nm . Sample solutions were filtered through a nylon $0.22 \mu\text{m}$ filter before determination.

2.3. Preparation of Fe_3O_4 @CGA-MIPs and Fe_3O_4 @NIPs

The amino-functionalized Fe_3O_4 nanoparticles (denoted as Fe_3O_4 @NH₂) were synthesized as our previous work (Gao, Zhang, Hao, Cui, & Tang, 2014). The magnetic molecularly imprinted nanoparticles of CGA (designed as Fe_3O_4 @CGA-MIPs) were prepared as follows: CGA (40 mg) was dissolved in 20 mL of phosphate

buffered solution (PBS, pH = 7.4) in a three-necked flask, and combined with Fe_3O_4 @NH₂ (200 mg). The mixture was allowed to react for 1 h. Then 5 mL of PBS containing 30 mg of PEI (6.0 mg mL^{-1}) and $30 \mu\text{L}$ of glutaraldehyde were added, the mixture was stirred for 6 h at room temperature. The obtained imprinted polymers were collected by an external magnetic field and washed with ethanol-HAc (95:5, v/v) to remove the embedded template until no adsorption was detected by HPLC. Then, the Fe_3O_4 @CGA-MIPs were washed with ultrapure water and ethanol repeatedly, and dried under vacuum. For comparison, non-imprinted magnetic nanoparticles (designed as Fe_3O_4 @NIPs) were prepared following the same procedure in the absence of the template molecule CGA.

2.4. Adsorption experiment and selectivity evaluation

In kinetic adsorption test, 20 mg of Fe_3O_4 @CGA-MIPs or Fe_3O_4 @NIPs were suspended in 10 mL of PBS with CGA at a concentration of 0.40 mg mL^{-1} , and shaken on a reciprocating shaking-table at regular times from 5 min to 50 min. Then the supernatants and polymers were separated by an external magnetic field and the concentration of CGA in the filtrate was measured by HPLC. The adsorption amounts (Q , mg g^{-1}) of Fe_3O_4 @CGA-MIPs or Fe_3O_4 @NIPs to CGA were calculated according to Eq. (1), and the pseudo-first-order and pseudo-second-order rate kinetic models were applied to fit the kinetic data according to Eqs. (2) and (3).

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

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} = \frac{1}{v_0} + \frac{t}{Q_e} \quad (3)$$

where C_0 and C_e (mg mL^{-1}) are the initial and equilibrium concentration of CGA, respectively. V (mL) and m (g) represent the volume of the CGA solution and the mass of the polymers. Q_e and Q_t are the amount of adsorbate onto sorbent at the equilibrium and time t (min). v_0 ($\text{mg g}^{-1} \text{ min}^{-1}$) is the initial adsorption rate. k_1 and k_2 are the equilibrium rate constants of pseudo-first-order and pseudo-second-order equation, respectively.

In equilibrium binding test, 20 mg of Fe_3O_4 @CGA-MIPs or Fe_3O_4 @NIPs were dispersed into 10 mL of PBS with various CGA concentrations ($0.050\text{--}0.80 \text{ mg mL}^{-1}$), and incubated for 30 min at room temperature. The separation and detection procedures were conducted as described in kinetic adsorption test. For further evaluating the equilibrium adsorption, Langmuir and Freundlich isotherm models were selected to fit the experimental data. They are described as Eqs. (4) and (5).

$$\frac{C_e}{Q} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \quad (4)$$

$$\log Q = m \log C_e + \log K_F \quad (5)$$

where C_e (mg mL^{-1}) is equilibrium concentration of adsorbate, Q (mg g^{-1}) is the amount of CGA bound to Fe_3O_4 @CGA-MIPs or Fe_3O_4 @NIPs at equilibrium, Q_{\max} (mg g^{-1}) is the maximum adsorption capacity of the sorbent, K_L (mL mg^{-1}) and K_F (mg g^{-1}) are the Langmuir and Freundlich constant respectively, and m is the Freundlich exponent which represents the heterogeneity of the system.

The selectivity of Fe_3O_4 @CGA-MIPs was measured using the structure analogs CCA, CFA, CA, and PCA. 10 mL of the mixed standard solution of CGA and analogs at initial concentration of 0.40 mg mL^{-1} was incubated with 20 mg of Fe_3O_4 @CGA-MIPs or Fe_3O_4 @NIPs for 30 min, and then the operating sequence was the same as kinetic adsorption test. The specific recognition property of Fe_3O_4 @CGA-MIPs was evaluated by imprinting factor (IF), which

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