



Surface imprinted polymers based on amino-hyperbranched magnetic nanoparticles for selective extraction and detection of chlorogenic acid in Honeysuckle tea

Yayun Zhao^{a,b}, Yuhai Tang^a, Jun He^a, Yuan Xu^a, Ruixia Gao^{a,*}, Junjie Zhang^a, Tie Chong^b, Li Wang^b, Xiaoshuang Tang^{b,*}

^a School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

^b Department of Urology, The Second Affiliated Hospital of Xi'an Jiaotong University, Xi'an, Shaanxi 710061, China

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ABSTRACT

Novel water-compatible magnetic molecularly imprinted polymers were developed. The magnetic core was firstly grafted by methyl acrylate and ethanediamine to increase the number of amino groups, which could immobilize more templates and form high-density recognition sites. Dopamine was adopted as functional monomer and crosslinker to retighten templates and prepare hydrophilic polymers. The characterization, adsorption capability, selectivity, and reusability were investigated in detail. The limit of detection and quantification of the method were $0.01 \mu\text{g mL}^{-1}$ and $0.038 \mu\text{g mL}^{-1}$. The experimental results exhibited that the resultant nanomaterials had high crystallinity, satisfactory magnetic property, fast kinetics, favorable adsorption capacity, excellent specificity, and pleasing recovery after a mild elution. In addition, the recoveries of the proposed method at four spiked levels analysis were between 98.4% to 101.3%. The obtained imprinted nanoparticles were used as sorbents for selective separation and determination of chlorogenic acid in Honeysuckle tea.

1. Introduction

Chlorogenic acid (CHA) extensively exists in higher plants including fruits, vegetables, berries, and some traditional Chinese medicines [1,2]. CHA is a raw material of drug, food, and health care products, which has pharmacological properties containing anti-inflammatory, analgesic, antipyretic [3], antioxidants [4], neuroprotective [5], and antihyperalgesic activities [6]. Actually, CHA usually coexists with some structurally related compounds: caffeic acid, gallic acid, for example. Because of the difficulty in purifying these substances, CHA has yet to be obtained in the crystalline form whether by synthesis or isolation [7]. Therefore, prior to quantification, it is necessary to selective extraction of CHA from complex matrices. Up to now, molecularly imprinted technique, microwave-assisted extraction, and pH gradient counter current chromatography have been employed in the separation and purification of CHA [8–10]. Among these methods, molecularly imprinted polymers (MIPs) used as solid phase extraction (SPE)

adsorbents have revealed good prospects [11].

MIPs have attracted growing attention due to their advantages of predetermination, easy preparation, low cost, physical and chemical stability, tolerance to harsh circumstances, and great specificity. All these make MIPs very promising separation tools for SPE and sample preconcentration. So far, MIPs have been used for selective separation of proteins [12], metal ions [13,14], and drugs [15] from complicated samples. Surface MIPs is currently the most popular type of MIPs on account of their improved binding capacity, enhanced mass transfer rate, and high densities of recognition sites. Surface imprinting is based on nano/micro solids (e.g., SiO_2 , quantum dot, carbon nanotube, and magnetic nanoparticle), which is expected to form MIPs with large surface-to-volume ratio and well defined shape [16–19]. Among these solid carriers, magnetic nanoparticles with rapid separation by the aid of an external magnet is the favorite [20]. Magnetic surface MIPs might be hopeful for efficient extraction of CHA from higher plants by virtue of specificity and easy isolation.

Abbreviations: CHA, chlorogenic acid; GA, gallic acid; CA, caffeic acid; PCA, protocatechuic acid, DA, dopamine; IF, imprinting factor; SC, selectivity coefficient; RM, room temperature; $\text{Fe}_3\text{O}_4@NH_2$, amino-functionalized Fe_3O_4 nanoparticles; $H\text{-Fe}_3\text{O}_4@NH_2$, amino-hyperbranched magnetic nanoparticles; $H\text{-Fe}_3\text{O}_4@CHA\text{-MIPs}$, imprinted magnetic nanomaterials for CHA; $H\text{-Fe}_3\text{O}_4@NIPs$, non-imprinted magnetic nanomaterials; SPE, solid phase extraction; VSM, vibrating sample magnetometry; XRD, X-ray diffraction; TEM, transmission electron microscope; SEM, scanning electron microscope; FT-IR, fourier transform infrared; HPLC, high performance liquid chromatography

* Corresponding authors.

E-mail addresses: ruixiagao@mail.xjtu.edu.cn (R. Gao), tangxiaos@sina.com (X. Tang).

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Dopamine (DA) is a small-molecule mimic of the adhesive proteins of mussels. It can self-polymerize to generate polydopamine (PDA) at alkaline pH values, and spontaneously deposit on different kinds of materials to form a conformal layer [21]. PDA is stable, convenient, eco-friendly, and more importantly, with abundant functional groups (such as phenyl, amino, and hydroxyl groups). Owing to these above advantages, DA can be simultaneously served as functional monomer and crosslinker for improving imprinted effect and facilitating synthesis process of MIPs.

In this work, we fabricated Fe₃O₄@PDA core-shell nanomaterials which can be utilized for selective extraction and detection of CHA by combining the merits of magnetic separation, surface MIPs, and two-step immobilized template strategy. The magnetic core was firstly grafted by methyl acrylate and ethanediamine to increase the number of amino functional groups, which could immobilize more templates and form high-density recognition cavities. DA was adopted as functional monomer and crosslinker to retighten template CHA and prepare novel water-compatible MIPs. The characterization, adsorption isotherms/kinetics, competitive binding, and reusability were investigated. The experimental results indicated that the synthetic nanomaterials exhibited high crystallinity, satisfactory magnetic property, fast kinetics, favorable selectivity, and good recovery after a proper elution. Furthermore, the resultant polymers were used as SPE sorbents and accompanied with HPLC for real sample analysis.

2. Experimental

2.1. Chemicals and reagents

Ferricchloride hexahydrate (FeCl₃·6H₂O), 1,6-hexadiazine (HDM), methyl acrylate (MA), ethanediamine, ethylene glycol, anhydrous sodium acetate (NaOAc), phosphoric acid, ethanol, acetonitrile, acetic acid (HAc), hydrochloric acid (HCl), and trihydroxymethyl aminomethane (Tris) were provided by Xi'an Chemicals Ltd. Chlorogenic acid (CHA), caffeic acid (CA), gallic acid (GA), protocatechuic acid (PCA), dopamine (DA), cynaroside, and palmitic acid were obtained from Aladdin Industrial Corporation. The ultrapure water (18.25 MΩ cm) was obtained from a WaterPro water system (Axlwater Corporation, TY10AXLC1805-2, China) and used throughout the experiments. All reagents used were of at least analytical grade.

2.2. Preparation of the magnetic nanomaterials

The amino-functionalized Fe₃O₄ nanoparticles (denoted as Fe₃O₄@NH₂) were synthesized as our previous work [22]. The amino-hyperbranched magnetic nanoparticles (designated as H-Fe₃O₄@NH₂) were prepared as follows: MA (10 mL) and Fe₃O₄@NH₂ (500 mg) were dissolved in 30 mL of ethanol in a three-necked flask. The mixture was controlled to react for 7 h. The products were gathered by an external magnetic field and then 30 mL of ethanol-ethanediamine solution (1:1, v/v) was added. The mixture was stirred for 5 h at 50 °C to prepare H-Fe₃O₄@NH₂. Then, the H-Fe₃O₄@NH₂ were washed with ultrapure water and dried in a vacuum for further use.

H-Fe₃O₄@NH₂ (150 mg) and CHA (30 mg) were added in 30 mL of Tris-HCl buffered solution (pH = 8.5) in a three-necked flask and carried out to react for 30 min. Then the mixture was stirred for 8 h at RT after DA (40, 50, 60, 70, or 80 mg) was added. The obtained polymers were gathered through an external magnetic field and washed with ethanol-HAc (95:5, v/v) to remove the embedded templates until no adsorption was detected by HPLC at 324 nm. And the imprinted magnetic nanomaterials for CHA (designated as H-Fe₃O₄@CHA-MIPs) were synthesized. For comparison, the non-imprinted magnetic nanoparticles (denoted as H-Fe₃O₄@NIPs) were prepared following the same procedures as those of H-Fe₃O₄@CHA-MIPs in the absence of the template molecules.

2.3. Adsorption evaluation

To evaluate the binding kinetics of the obtained nanomaterials, 20 mg of H-Fe₃O₄@CHA-MIPs or H-Fe₃O₄@NIPs were added to 10 mL of CHA solution with a concentration of 35 µg mL⁻¹, and shaken on a reciprocating shaking-table from 2 min to 20 min. Then the supernatants and polymers were separated by a magnet. The concentrations of CHA in the supernatants were measured after filtration through 0.22 µm nylon membrane filters. The adsorption amounts (*Q*, mg g⁻¹) of H-Fe₃O₄@CHA-MIPs or H-Fe₃O₄@NIPs to CHA were calculated on the basis of Eq. (1). The kinetic data were used to fit the pseudo-second-order kinetic model based on Eq. (2).

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

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} = \frac{1}{v_0} + \frac{t}{Q_e} \quad (2)$$

Where *C*₀ and *C*_e (mg mL⁻¹) represent the initial and equilibrium concentration of CHA. *V* (mL) and *W* (g) are the volume of the CHA solution and the mass of the polymers, respectively. *Q*_e and *Q*_t are the amount of adsorbate onto sorbent at the equilibrium and time *t* (min). *K* (g mg⁻¹ min⁻¹) is the rate constant of the pseudo-second-order adsorption and *v*₀ (mg g⁻¹ min⁻¹) is the initial adsorption rate.

To investigate the binding capacity of polymers towards CHA, 20 mg of H-Fe₃O₄@CHA-MIPs or H-Fe₃O₄@NIPs were added to 10 mL of CHA solutions with different concentrations (2–50 µg mL⁻¹), and incubated for 10 min at RT. The separation and detection procedures are the same as those of kinetic adsorption test. The equilibrium adsorption was described by Langmuir and Freundlich isothermal models. They are defined as Eqs. (3) and (4).

$$\frac{C_e}{Q} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \quad (3)$$

$$\log Q = m \log C_e + \log K_F \quad (4)$$

Where *Q*_{max} (mg g⁻¹) is the maximum adsorption capacity of H-Fe₃O₄@CHA-MIPs or H-Fe₃O₄@NIPs, *K*_L (mL mg⁻¹) is the Langmuir constant and *K*_F (mg g⁻¹) is the Freundlich constant. *m* is the Freundlich exponent which represents the system's heterogeneity.

The selectivity of the obtained nanomaterials was testified by applying three structural analogs (GA, CA, and PCA) and other two possible co-existing compounds (cynaroside and palmitic acid) as the competitors, respectively. Briefly, 10 mL of the mixed standard solution (CHA and its analogs or possible co-existing compounds, 35 µg mL⁻¹) was incubated with 20 mg of H-Fe₃O₄@CHA-MIPs or H-Fe₃O₄@NIPs for 10 min. The following operating steps were the similar as those of kinetic adsorption test. The capacity of specific recognition of H-Fe₃O₄@CHA-MIPs was assessed by imprinting factor (*IF*) and selectivity coefficient (*SC*) which were expressed in Eqs. (5) and (6).

$$IF = \frac{Q_{MIP}}{Q_{NIP}} \quad (5)$$

$$SC = \frac{IF_t}{IF_c} \quad (6)$$

Where *Q*_{MIP} and *Q*_{NIP} (mg g⁻¹) represent the adsorption capacity of template molecule or competitors on H-Fe₃O₄@CHA-MIPs and H-Fe₃O₄@NIPs. *IF*_t and *IF*_c are the imprinting factors for template molecule and competitors.

2.4. Reusability

Six circles of adsorption-desorption procedure were carried out by employing the same polymers to estimate the regeneration of H-Fe₃O₄@CHA-MIPs. 20 mg of H-Fe₃O₄@CHA-MIPs were mixed with

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