



Facile synthesis of magnetic molecularly imprinted polymers and its application in magnetic solid phase extraction for fluoroquinolones in milk samples



Hao-Bo Zheng^a, Jie-Zhen Mo^a, Yu Zhang^a, Qiang Gao^{a,b}, Jun Ding^a,
Qiong-Wei Yu^a, Yu-Qi Feng^{a,*}

^a Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, PR China

^b Engineering Research Center of Nano-Geomaterials of Ministry of Education, Department of Material Science & Chemistry Engineering, China University of Geosciences, Wuhan 430074, PR China

ARTICLE INFO

Article history:

Received 11 October 2013

Received in revised form

27 December 2013

Accepted 29 December 2013

Available online 2 January 2014

Keywords:

Magnetic molecularly imprinted polymers

Magnetic solid phase extraction

Milk samples

High performance liquid chromatography

with ultraviolet detector

Fluoroquinolones

ABSTRACT

In this work, we proposed a simple co-mixing method to fabricate magnetic molecularly imprinted polymers (magnetic MIPs). MIPs were commercial products while magnetic nanoparticles (MNPs) were prepared by chemical oxidation and solvothermal methods. When MNPs and MIPs (with mass ratio 1:1) were co-mixed and vortexed evenly in methanol, they could assemble into magnetic composites spontaneously and thus be magnetically separable. To testify the feasibility of the magnetic composites in sample preparation, the resultant magnetic MIPs were applied as sorbents for magnetic solid-phase extraction (MSPE) of fluoroquinolones (FQs) in milk samples. Under optimized conditions, a rapid, convenient, and efficient method for the determination of three FQs in milk samples was established by magnetic MIPs based MSPE coupling with high performance liquid chromatography with ultraviolet detector (HPLC-UV). The limits of detection (LODs) for three FQs were found to be 1.8–3.2 ng/g. The intra- and inter-day relative standard deviations (RSDs) were less than 9.5% and 12.5%, respectively. The recoveries of FQs for two spiked milk samples were in the range from 94.0% to 124.4% with the RSDs less than 11.6%.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Molecularly imprinted polymers (MIPs) are tailor-made materials with high selectivity for target molecules [1,2], and most frequently utilized as affinity-based separation media for sample preconcentration and separation, via solid-phase extraction (SPE) and traditional solid-phase micro-extraction (SPME) [3]. In addition to these sample pretreatment methods, recently, MIPs are served as sorbents in another technology named magnetic solid-phase extraction (MSPE). In this mode, magnetic materials are first dispersed in a sample solution. After incubation for an appropriate time until the target analytes adsorb on the sorbents, the magnetic materials can be easily isolated from the solution by applying an external magnetic field. When removing the external magnetic field, the magnetic materials can re-disperse in solution, which is convenient for the following washing and desorption [4]. Compared with conventional solid support, magnetic materials have many superior characteristics, such as high surface-to-volume

ratio, fast and effective binding target analytes and high magnetic susceptibility [5]. In addition, high backpressure caused by tightly packed cartridges in SPE procedure does not exist, which expand their application in extracting analytes from environmental or biological samples. Furthermore, as MIPs immobilized on magnetic components, the resulting composite polymers will not only have magnetically susceptible characteristic, but also have selectivity for the guest molecules [6–9].

The magnetic MIPs have been synthesized by different methods. The most commonly used synthetic process is divided into the following four steps. The first step is the preparation of magnetic nanoparticles, such as Fe₃O₄. The second step is the surface modification or functionalization of the magnetic components. The third step is surface-imprinted polymerization using functionalized nanoparticle as magnetic core in the presence of the template molecule, functional monomer and cross-linker. And the fourth step is to remove the template molecules from the polymer [5]. Nevertheless, procedures involved in the chemical modification are relatively tedious. In another aspect, as the most popular and general method to prepare MIPs, bulk polymerization has many attractive properties, such as rapidity and simplicity in preparation with no requirement for sophisticated

* Corresponding author. Tel.: +86 27 68755595; fax: +86 27 68755595.
E-mail address: yqfeng@whu.edu.cn (Y.-Q. Feng).

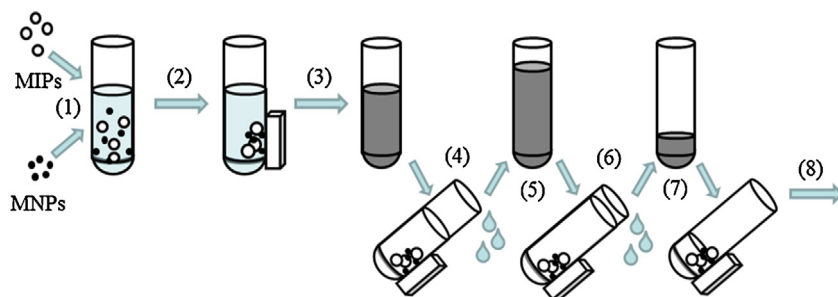


Fig. 1. Schematic of proposed MIMSPE method: (1) adding raw materials, (2) synthetic process of magnetic MIPs, (3) sample loading and vortexing, (4) decanting, (5) washing, (6) decanting, (7) eluting, (8) further analysis.

or expensive instrumentation [3]. However, to the best of our knowledge, MIPs obtained by bulk polymerization have not been served as sorbents in MSPE, which handicap their utilization in sample pretreatment. To overcome above-mentioned shortages, a new solution should be considered. In recent years, we reported a “aggregate warp” process for the fabrication of magnetic carbon nanotubes [10,11], magnetic graphene [12], magnetic 1D-conductive polymers [13] and magnetic graphitized carbon black and primary secondary amine [14]. When some materials are co-mixed with magnetic nanoparticles (MNPs) in proper solvent, the MNPs can be trapped spontaneously in the aggregates of the materials, leading to the formation of magnetic composites. Herein, we intended to expand this strategy by fabricating magnetic MIPs. With the aid of vortex, magnetic MIPs can successfully form by MNPs and a commercial molecularly imprinted solid-phase extraction (MISPE) packing material obtained by bulk polymerization.

Furthermore, we tested the feasibility of the magnetic MIPs in MSPE method for concentration and purification of fluoroquinolones (FQs) in milk samples. FQs are piperazinyl derivatives of quinolones, and are commonly used in human and veterinarian medicine as antibacterial agents against several diseases over the last decade [15,16]. The wide range of applications and possibility of abuse or misuse of FQs present potential hazards to human health, such as the emergence and spread of drug-resistant bacterial strains and possible induction of cancer [17,18]. Therefore, there is a need for development of efficient methods for determination of FQs in foodstuffs and drinks.

In this study, a simple method for preparation of magnetic MIPs was established, in which no chemical modification to the raw material was required, thus the pristine surface chemistries of materials remained. Therefore, the synthesis process should not affect the extraction selectivity of MIPs. In addition, a method for the analysis of FQs in milk samples was set up by combination of MSPE using the prepared magnetic MIPs as sorbents with high performance liquid chromatography (HPLC).

2. Experimental

2.1. Materials

Ethylene glycol (EG), ethylene diamine (ED), ferric trichloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ammonium acetate (NH_4Ac), sodium acetate (NaAc), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$), acetone, *n*-hexane and acetic acid (HAc) were purchased from Sinopharm Chemical Reagent (Shanghai, China). All these chemicals were used directly without further purification. HPLC grade acetonitrile (ACN) and methanol (MeOH) were purchased from Fisher Scientific Company (Fair Lawn, NJ, USA). Purified water was obtained with a Millipore Milli-Q apparatus (Bedford, MA, USA).

A water-compatible commercial MIPs material, SupelMIPTM SPE-Fluoroquinolones was purchased from Sigma-Aldrich (St. Louis, MO, USA).

Ofloxacin (OFL), ciprofloxacin hydrochloride (CIP), lomefloxacin (LOM) were purchased from laboratories of Dr. Ehrenstorfer (Augsburg, Germany). Individual stock solutions of three FQs were prepared in MeOH at a concentration of 1 mg/mL stored at 4 °C in darkness. Intermediate solutions that were used for spiking milk samples were prepared by serial dilution of the stock solution to desired concentrations.

2.2. Preparation of Fe_3O_4 magnetite nanoparticles

MNPs were synthesized via a solvothermal process according to our previously reported method [12]. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.0 g) was dissolved in EG (100 mL). NaAc (15.0 g) and ED (50 mL) were then added to the solution. After being vigorously stirred for 30 min, the homogeneous mixture was sealed in a teflon-lined stainless-steel autoclave (200 mL). The autoclave was heated to 200 °C and maintained for 8 h, and then allowed to cool to room temperature. The product was magnetically collected, and washed with water/ethanol for several times. The washed product was then vacuum-dried at 60 °C for 6 h.

2.3. Extraction of FQs from milk

Milk samples were purchased from supermarket in Wuhan (China). 10.0 g milk sample was weighted into an Eppendorf vial (50 mL), and appropriate volumes of FQs standards were added to the vial. Then the sample was dissolved in 10 mL 10 mM NH_4Ac (pH 5.0). After centrifugation (5000 rpm, 5 min), the supernatant was adjusted to pH 6.0 with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and HAc.

A schematic representation of proposed MIMSPE method is shown in Fig. 1. The procedure included the following steps: 1 mL methanol was added into an Eppendorf vial (5 mL) containing 20 mg MIPs and 20 mg MNPs. Then the mixture was vortexed vigorously for 1 min. On applying an external magnet, the magnetic MIPs were attracted toward the magnet rapidly. After discarding the supernatant, 2 mL ultra-pure water was added, and the mixture was vortexed vigorously for another 1 min. The supernatant was discarded with the aid of an external magnet. Then 2 mL milk sample solution was added. The mixture was vortexed for 1 min to form a homogeneous dispersion solution, and then FQs-absorbed magnetic MIPs were separated rapidly from the solution by an external magnet. After washing with 3 mL ultra-pure water, 1 mL ACN, 1 mL 15% ACN in ultra-pure water in sequence, FQs were eluted from the magnetic MIPs by 1.0 mL of MeOH containing 7.0% $\text{NH}_3 \cdot \text{H}_2\text{O}$ (v/v) with 2.0 min vortexing. The solution was separated from magnetic MIPs by a magnet, and evaporated to dryness under a mild nitrogen stream at 35 °C. The residue was dissolved in 100 μL of mobile phase, and 20 μL of the solution was analyzed by HPLC. To avoid

Download English Version:

<https://daneshyari.com/en/article/7613730>

Download Persian Version:

<https://daneshyari.com/article/7613730>

[Daneshyari.com](https://daneshyari.com)