



Development of magnetic molecularly imprinted polymers with double templates for the rapid and selective determination of amphenicol antibiotics in water, blood, and egg samples



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ABSTRACT

A magnetic mesoporous dual-template molecularly imprinted polymer ($\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{DMIP}$) with a specific recognition capability for chloramphenicol (CAP) and florfenicol (FF) was synthesised. CAP and FF were used as dual-template molecules, α -methacrylic acid and $\text{Fe}_3\text{O}_4@\text{mSiO}_2@-\text{CH}=\text{CH}_2$ as dual functional monomers, and ethylene glycol dimethyl methacrylate as a crosslinking agent. For comparison, a magnetic mesoporous non-molecularly imprinted polymer ($\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{NIP}$) was also prepared using the same synthesis procedure, but without the dual templates. The prepared polymers were characterised using scanning electron microscopy, Fourier-transform infrared spectroscopy and adsorption experiments. Results indicated that both the $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{DMIP}$ and the $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{NIP}$ were microspherical nanoparticles, and the surface of the $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{DMIP}$ was rougher than that of the $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{NIP}$. In addition, the prepared $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{DMIP}$ possessed a higher adsorption capacity and better selectivity for CAP and FF than the $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{NIP}$. The maximum static adsorption capacities of the $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{DMIP}$ for CAP and FF were 146.5 and 190.1 mg g^{-1} , respectively, whereas those of the $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{NIP}$ were 50.0 and 44.0 mg g^{-1} , respectively. The obtained $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{DMIP}$ particles were applied as a magnetic solid-phase extraction sorbent for the rapid and selective extraction of CAP, FF, and thiamphenicol (TAP) in water, chicken blood and egg samples. The method of magnetic molecularly imprinted solid-phase extraction (M-MISPE) coupled to high-performance liquid chromatography with UV detection (HPLC-UV) was conducted to detect CAP, FF, and TAP. The limits of detection for CAP, FF, and TAP were 0.16 , 0.08 , and 0.08 $\mu\text{g kg}^{-1}$, respectively. The average recovery and precision values for the spiked water, chicken blood, and egg samples ranged from 88.3% to 99.1% and 2.7% to 7.9% , respectively. Given its rapidity, selectivity, and sensitivity, the developed method of M-MISPE coupled to HPLC-UV detection has good application prospects in environmental, biological, and food samples.

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1. Introduction

Chloramphenicol (CAP), florfenicol (FF) and thiamphenicol (TAP) are broad-spectrum amphenicol antibiotics that exhibit good antibacterial activities. However, prolonged use of CAP may inhibit the medullary hematopoietic function of the human body and cause aplastic anaemia, bone marrow suppression, and 'Grey baby syndrome' (Johnson, 2003) [1]. Moreover, the toxic side effect of CAP is dosage independent. Hence, the use of CAP in food-producing animals has been banned in the European Union, the United States of

America, Japan, and China [2]. FF and TAP possess a similar stable structure and efficacy to CAP but do not cause aplastic anaemia in humans. These antibiotics have been applied mainly in the treatment and prophylaxis of animal diseases, particularly respiratory system diseases, as a substitute for CAP [3]. Nevertheless, FF and TAP may suppress the production of platelets and adversely affect the blood system. In addition, the extensive use and eventual accumulation of these antibiotics may harm the human body. Thus, a rapid, specific, and accurate method to detect these antibiotics should be developed to avoid their possible abuse and ensure the health of consumers.

Different methods have been developed to detect CAP, TAP, and FF; these methods include high-performance liquid chromatography (HPLC) [4,5], liquid chromatography–tandem mass

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spectrometry (LC–MS/MS) [6,7], gas chromatography–mass spectrometry [8], sensors [9,10], and immunological methods [11,12]. However, pre-treatment procedures are often necessary to apply these detection methods in complex samples, such as chicken blood and eggs. Various pre-treatment methods, including liquid–liquid extraction (LLE) [13], dispersive liquid–liquid microextraction (DLLME) [14], conventional solid-phase extraction (SPE) [15], matrix solid-phase dispersion extraction (MSPD) [7], and molecularly imprinted solid-phase extraction (MISPE) [11,16–23], have been explored to detect amphenicols in food and environmental samples. LLE requires large volumes of organic solvents and complex consequent operations. The defects of DLLME are low extraction rate, poor selectivity and stability. Conventional SPE and MSPD are typically time consuming and exhibit poor selectivity and weak anti-interference capability. Fortunately, MISPE with molecularly imprinted polymers (MIPs) as SPE sorbents shows a higher selectivity, recovery, and cleanliness of the final extract. MIPs are synthetic materials with recognition sites that specifically bind target molecules in mixtures with other compounds [24]. Single-template MIPs, which were prepared using CAP, FF, or TAP as a template molecule, were used in these studies. These MIPs are expected to exhibit group selectivity toward CAP, FF, and TAP, but they only display high affinity and selectivity to the template molecules [25]. To overcome this limitation, Dickert et al. [26] introduced ‘double molecular imprinting’, in which anthracene and chrysene are used as templates and simultaneously imprinted in a crosslinked polyurethane thin film that can recognise both templates. Compared with single-template imprinted polymers, double-template imprinted polymers demonstrate higher binding capacity, higher group selectivity and faster mass transfer. To the best of our knowledge, double-template MIPs for amphenicols are currently unavailable. Moreover, all the proposed single-template MIPs for amphenicols have been used in cartridge mode, which resulted in a tedious column packing procedure, high backpressure and long duration.

Magnetic molecularly imprinted solid-phase extraction (M-MISPE) is a new sample pre-treatment method that uses magnetic MIPs as adsorbents. M-MISPE does not need to be packed into an SPE cartridge. This method displays the advantages of both MIPs (i.e. high selectivity and stability) and magnetic separation (i.e. easy separation by an external magnet). Thus, M-MISPE has attracted considerable attention as a pre-treatment method for food, herbal medicine, environmental and biological samples [27–33].

At present, CAP is illegally used in the treatment and prophylaxis of animal diseases. Accordingly, this study synthesised a double-template MIP on the surface of magnetic mesoporous silica nanoparticles ($\text{Fe}_3\text{O}_4@\text{mSiO}_2$) by using CAP and FF as template molecules via a multi-step procedure. Firstly, $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ was prepared through co-precipitation and tetraethoxysilane (TEOS) hydrolysis under an alkaline medium at 80 °C, with hexadecyl trimethyl ammonium bromide (CTAB) as the template. Subsequently, polymerisable vinyl end-groups were modified onto $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ through vinyltrimethoxysilane (VTMOS) hydrolysis under an alkaline medium at room temperature. Finally, the MIP was copolymerized onto the surface of $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ particles through the vinyl end-groups of $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ surface, the preassembled solution of methacrylic acid (MAA) with CAP and FF by using ethylene glycol dimethacrylate (EGDMA) and $\text{K}_2\text{S}_2\text{O}_8$ as a crosslinking agent and initiator, respectively. The prepared $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{DMIP}$ particles were characterised via Fourier-transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM), as well as static, dynamic, and selective adsorption experiments. Coupled with LC analysis, the obtained $\text{Fe}_3\text{O}_4@\text{mSiO}_2@\text{DMIP}$ particles were applied as a magnetic SPE sorbent to extract and remove the amphenicols in food and

environmental samples. The parameters affecting M-MISPE were investigated. The M-MISPE–HPLC method was also evaluated.

2. Materials and methods

2.1. Materials and apparatus

CAP, FF, and TAP were purchased from Zhangjiagang Hengsheng Pharmaceutical Co., Ltd. (Zhangjiagang, China). HPLC grade acetonitrile and methanol used for the mobile phase were bought from Tianjin Chemical Reagent Co., Ltd. (Tianjin, China). Analytical grade ammonium ferrous sulfate ($\text{NH}_4\text{FeSO}_4 \cdot 12\text{H}_2\text{O}$), ferric trichloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ammonium hydroxide (25–30 wt%), and cetyltrimethylammonium bromide (CTAB) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Analytical grade sodium hydroxide (NaOH), toluene, 4-nitro phenol (NP), polyvinyl alcohol (PVA), potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$), methanol, ethanol, acetone, trichloromethane, and acetic acid were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). Tetraethoxysilane (TEOS), Vinyltrimethoxysilane (VTMOS), Methacrylic acid (MAA), ethylene glycol dimethylacrylate (EGDMA), azobisisobutyronitrile (AIBN) was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Distilled water was purchased from Guangzhou Watson’s Food & Beverage Co., Ltd. (Guangzhou, China). Eggs and the chicken blood were bought from a local market in Zhaoqing.

A UV–vis spectrophotometer (GBC 916, Scientific Equipment Pty Ltd., Australia) was used to measure absorbance. A Fourier transform infrared spectroscopy system (FTIR-8400S, Shimadzu, Japan) was used to characterise polymers. The surface morphology and structure of the materials were identified using a SEM system (NGB4-DXS-10AC). An AGKC21CR4 electric-heated thermostatic water bath (Shanghai, China) was used to control the reaction temperature. An AJJ-1 electric timing stirrer (Chongqing, China) was used to synthesise magnetic polymers. An AHZS-HA thermostatic water bath oscillator (Haerbin, China) was adopted for pre-polymerization and full interaction between the magnetic polymers and solutions. An SB 1200 ultrasonic cleaner (Zhejiang, China) was used to remove the template of CAP and FF. pH was measured using a PHS-3CpH meter (Dapu Instrumentation Corp., Ltd. Shanghai, China). The specific surface area and average pore size of the polymers were calculated from nitrogen adsorption data according to the Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods, respectively, by using an ASAP 2020 M + C system (Micromeritics, USA).

2.2. $\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-CH=CH}_2$ preparation

$\text{Fe}_3\text{O}_4@\text{mSiO}_2\text{-CH=CH}_2$ was prepared according to Xie’s work with some modifications [34]. First, Fe_3O_4 MNPs were synthesised via chemical co-precipitation. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (11.2 mmol) and $\text{NH}_4\text{FeSO}_4 \cdot 12\text{H}_2\text{O}$ (5.6 mmol) were dissolved in 150 mL of distilled water and then heated to 85 °C under a nitrogen atmosphere and stirred mechanically. Approximately 10 mL of ammonium hydroxide solution (25%) was added into the solution until the pH reached 10. After 30 min, the reaction solution was naturally cooled to room temperature. The obtained black precipitate was separated with a permanent magnet and then washed several times successively with ethanol and distilled water. The products were dried in a vacuum oven at 50 °C for 24 h.

Next, CTAB (0.5 g), 1 mol L⁻¹ NaOH (3.5 mL), and water (480 mL) were mixed via mechanical stirring for 15 min and then heated to 80 °C. Approximately 0.5 g of the synthesised Fe_3O_4 MNPs were added into the solution and then stirred for 2 min. Finally, about 2.0 mL of TEOS was added dropwise to the mixture and stirred

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