



Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma



Magnetic solid–phase extraction of tetracyclines using ferrous oxide coated magnetic silica microspheres from water samples

Lili Lian, Jinyi Lv, Xiyue Wang, Dawei Lou*

Department of Analytical Chemistry, Jilin Institute of Chemical Technology, No. 45 Chengde Street, Jilin 132022, PR China

ARTICLE INFO

Article history:

Received 17 September 2017
Received in revised form 9 December 2017
Accepted 15 December 2017
Available online xxx

Keywords:

Magnetic
Solid–phase extraction
Tetracyclines
Antibiotics
Core–shell

ABSTRACT

A novel magnetic solid–phase extraction approach was proposed for extraction of potential residues of tetracyclines (TCs) in tap and river water samples, based on $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeO}$ magnetic nanocomposite. Characterized results showed that the received $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeO}$ had distinguished magnetism and core–shell structure. Modified FeO nanoparticles with an ~ 5 nm size distribution were homogeneously dispersed on the surface of the silica shell. Owing to the strong surface affinity of Fe (II) toward TCs, the magnetic nanocomposite could be applied to efficiently extract three TCs antibiotics, namely, oxytetracycline, tetracycline and chlortetracycline from water samples. Several factors, such as sorbent amount, pH condition, adsorption and desorption time, desorption solvent, selectivity and sample volume, influencing the extraction performance of TCs were investigated and optimized. The developed method showed excellent linearity ($R > 0.9992$) in the range of $0.133\text{--}333 \mu\text{g L}^{-1}$, under optimized conditions. The limits of detection were between 0.027 and $0.107 \mu\text{g L}^{-1}$ for oxytetracycline, tetracycline and chlortetracycline, respectively. The feasibility of this method was evaluated by analysis of tap and river water samples. The recoveries at the spiked concentration levels ranged from 91.0% to 104.6% with favorable reproducibility ($\text{RSD} < 4\%$).

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Antibiotics are synthetic or semisynthetic drugs by a natural way. They have been widely used in human medicine and livestock animals for prophylactic, therapeutic and growth promoting purposes [1,2]. However, antibiotics residues in surface water sources can't be neglected, because it may pose many significant threats to human health, such as antimicrobial resistance, allergic reactions and gastrointestinal disturbance [3,4]. According to the recent studies, the excessive use of antibiotics in medical, intensive livestock farming, as well as the untreated pharmaceutical wastewater directly into river, have resulted in the pollution of several of surface water sources in China, which further affects the quality of subsequently drinking water [5–7]. Statistics showed that tetracyclines (TCs) are the second most used antibiotics, which total usage is 9.7×10^4 tons in China [8]. It accounted for the dominant proportion of total antibiotic residues in animal-producing food and water samples [9]. Consequently, it is necessary to develop a fast, sensitive and reliable method to detect and quantify TCs residues both in tap and environmental water samples.

High–performance liquid chromatography (HPLC) is widely used for determination the antibiotic residues in various samples given its high separation efficiency and accuracy in quantitative analysis. However, a pretreatment step is necessary for accurate determination of analytes by HPLC considering the trace level of target analytes in the majority of samples and high levels of matrix interferences [10–12]. Solid–phase extraction (SPE) is one of the most commonly used techniques for preconcentration of trace analytes before detection. SPE methods with different cartridges were developed for determination tetracyclines in honey, milk, and animal tissues. The commonly used C8 and C18 cartridges show a low recovery yield for TCs during sample pretreatment due to the irreversible forming of compounds of the silanol groups contained in silica-based materials and TCs ketone groups [13–16]. The SPE copolymer cartridges such as Oasis HLB, with favorable affinity to TCs, are successfully used in the pretreatment of TCs from various matrixes [17–19]. However, SPE methods are prone to interferences by impurities in the complex matrix, and require large volumes of organic solvents, which are unfriendly to the environment. Furthermore, the methods cost high, because the SPE cartridges can be used only once.

In recent years, considerable attention has been accorded to magnetic solid–phase extraction (MSPE). MSPE is a promising extraction approach on the basis of using magnetic or magnetiz-

* Corresponding author.

E-mail address: dwlou@hotmail.com (D. Lou).

able materials, which can be easily isolated from sample matrix with an external magnet [20,21]. Various functionalized magnetic materials have been fabricated and used as an appropriate sorbent in MSPE technique [22–26]. Magnetic materials are characterized by a high specific surface area and can achieve a balance between sorbent and test samples within a short time given the small particle size and good dispersibility. These features are very suitable for extraction trace level of analytes from a large volume of water samples [27]. Several magnetic materials are exploited and used to extract TCs in various kinds of matrixes. For example, Eu- and Tb-coated magnetic nanocomposites are prepared for the isolation and enrichment of TCs from animal muscle samples. The limits of detection (LOD) obtained are between 0.8 and 12.7 $\mu\text{g kg}^{-1}$ [28]. Specifically, magnetic graphene/carbon nanotube composites are synthesized by a simple and time-saving method and applied as a MSPE sorbent for rapid extraction and determination of oxytetracycline in sewage water. The LOD under the optimum conditions is 3.6 ng mL^{-1} , and the recoveries ranged from 95.5% to 112.5% with relative standard deviations (RSD) less than 5.8% [29].

These methods still undergo problems, such as high cost, time-consuming synthesis procedures, low selectivity, and unsatisfactory sensitivity, although they have achieved significant progress in the convenient enrichment of TCs from different matrixes. The new extraction and clean-up techniques with the advantages of low cost, simplicity of operation, high selectivity, satisfactory enrichment factors, and favorable repeatability are still necessary. Considering the trace level of TCs and existence of other interfering substances in water matrixes, we fabricated the multifunctional magnetic nanocomposite $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeO}$ though a simple method to effectively extract TCs from tap and river water samples. In general, TCs contain several ionizable groups such as diketone, tricarbonylmethane, and dimethylammonium [30]. These electron-donor groups in the TCs promote interaction with divalent cation Fe (II) by forming stable metal-tetracycline complexes [31,32]. Therefore, integrating FeO and magnetic silica into a hybrid material has virtues of Fe (II) and magnetic silica. FeO embedded around the magnetic silica can significantly increase the extraction efficiency of TCs from water samples and maintain a high magnetism. Furthermore, a novel MSPE method combined with ultra-high-performance liquid chromatography (UPLC) for determining trace amounts of TCs in water samples was developed.

2. Experimental

2.1. Chemicals and reagents

HPLC grade acetonitrile (ACN) and methanol (MeOH) were obtained from TEDIA (USA). Analytical grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and tetraethoxysilane (TEOS), ammonia solution (25%), and oxalic acid dihydrate were obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). Sodium hydroxide (NaOH), hydrochloric acid (HCl) and ethanol absolute were purchased from Tianjin chemical reagent Technology Co., Ltd. (Tianjin, China). Ultrapure water was prepared using a Milli-Q system from Millipore (Bedford, MA, USA). Tetracycline hydrochloride (TC), chloramphenicol (CAP), and enrofloxacin (ENR) ($\geq 95\%$ by HPLC) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Oxytetracycline hydrochloride (OTC), and chlortetracycline hydrochloride (CTC) ($\geq 95\%$ by HPLC) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). And the chemical structures of the three tetracyclines are shown in Fig. 1. The standard stock solutions (1000 mg L^{-1}) were prepared by dissolving the required amount of the mentioned tetracyclines in methanol and stored at 4 °C. The trace tetracyclines (TC, OTC, CTC)

in water samples were extraction by the magnetic microspheres simultaneously, and detected with UPLC.

2.2. Instrumentation and conditions

The morphological evaluation of the sorbent was performed by field-emission transmission electron microscope (TEM, JEOL, JEM-2100F, Japan) and scanning electron microscope (SEM, JEOL, JSM-7500F, Japan). The surface charges were carried out by a zeta-potential analyzer (Malvern, Zetasizer Nano ZS90, UK). Magnetic properties were evaluated on a superconducting quantum interference device (SQUID) magnetometer (MPMS XL-5, Quantum Design, USA) at room temperature with fields up to 10,000 Oe. The functional groups of the magnetic microspheres were confirmed by a FT-IR spectrometer (Vertex 80V, Bruker, Germany).

The concentrations of TCs were determined at 314 nm by using UPLC (Waters, U.S.A.) with a tunable ultraviolet detector (TUV) detector, and a C18 analytical column (BEH C18, 50 mm \times 2.1 mm I.D., 1.7 μm particle size, Waters) working at 30 °C. Mobile phase flow rate was 0.1 mL min^{-1} and was constituted of the aqueous solution C (0.02 mol L^{-1} oxalic acid), organic phase B (methanol) and D (acetonitrile), (C/B/D = 7:1:2, v/v).

2.3. Procedures

2.3.1. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$

Firstly, Fe_3O_4 magnetic nanoparticles with narrow size distribution were synthesized using a solvothermal method [33]. The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell magnetic microspheres were then prepared according to our previous method with some modification [34]. Briefly, 0.2 g Fe_3O_4 was dispersed in 40 mL HCl (0.1 M) solution and sonicated for 10 min. After being washed by deionized water several times, the received magnetic nanocomposites were then dissolved into the solution consisted of 160 mL ethanol, 40 mL deionized water and 4.0 mL ammonia solution. Subsequently, TEOS (2.0 mL) was added into the solution slowly under vigorous stirring. Reaction was continued for 6 h at room temperature. Finally, the resultant $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres were separated by an external magnetic field, washed with ethanol and water several times, and then dried in vacuum at 60 °C.

2.3.2. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeO}$ magnetic microspheres

In order to improve the extraction efficiency and the selectivity towards TCs, FeO nanoparticles were modified on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ by a hydrothermal method. First, 0.2 g $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was homogeneous mixed with the solution consisted of 1 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 1 mL ammonia solution, 10 mmol $\text{NH}_4\text{-Cl}$ and 40 mL deionized water. Then the mixture was heated at 140 °C for 10 h in an autoclave. After cooling, the precipitate was recovered with the aid of a magnet and washed with deionized water and ethanol several times. Finally, the obtained $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeO}$ magnetic microspheres were dried in vacuum at 60 °C for 6 h.

2.4. Binding property investigation

Static adsorption and selective binding experiments were conducted to investigate the binding properties of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeO}$ for TCs.

The adsorption experiments were conducted as follows: 2 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeO}$ was dispersed in a flask containing 10.0 mL TCs solutions of various concentrations (10–50 mg L^{-1}). $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{FeO}$ was separated from the samples through a magnet after 6 h of shaking at 25 °C. The residual concentration of TCs in aqueous solution was measured with UPLC-TUV. The adsorption capacity (q_e , mg g^{-1}) at any concentrations was evaluated by the difference between the initial and remaining concentrations

Download English Version:

<https://daneshyari.com/en/article/7608985>

Download Persian Version:

<https://daneshyari.com/article/7608985>

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