



ELSEVIER

Contents lists available at ScienceDirect

Talanta

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

A novel metal-organic framework composite MIL-101(Cr)@GO as an efficient sorbent in dispersive micro-solid phase extraction coupling with UHPLC-MS/MS for the determination of sulfonamides in milk samples

Xiuna Jia^a, Pan Zhao^a, Xiu Ye^a, Lianjun Zhang^a, Ting Wang^a, Qinyu Chen^b, Xiaohong Hou^{b,*}

^a School of Pharmacy, Shenyang Pharmaceutical University, Shenyang, Liaoning Province, PR China

^b School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang, Liaoning Province, PR China

ARTICLE INFO

Article history:

Received 4 August 2016

Received in revised form

26 August 2016

Accepted 31 August 2016

Keywords:

Metal-organic frameworks

MIL-101(Cr)@GO

Dispersive micro-solid phase extraction

Sulfonamides

Milk

ABSTRACT

As a novel material, metal-organic framework/graphite oxide (MIL-101(Cr)@GO) has great potential for the pretreatment of trace analytes. In the present study, MIL-101(Cr)@GO was synthesized using a solvothermal synthesis method at the nanoscale and was applied as sorbent in the dispersive micro-solid phase extraction (DMSPE) for the enrichment of the trace sulfonamides (SAs) from milk samples for the first time. Several experimental parameters including kinds of sorbents, the effect of pH, the amount of MIL-101(Cr)@GO, ionic strength, adsorption time, desorption solvent and desorption time were investigated. Under the optimal conditions, the linear ranges were from 0.1 to 10 µg/L, 0.2–20 µg/L or 0.5–50 µg/L for the analytes with regression coefficients (*r*) from 0.9942 to 0.9999. The limits of detection were between 0.012 and 0.145 µg/L. The recoveries ranged from 79.83% to 103.8% with relative standard deviations (RSDs) < 10% (*n* = 3). MIL-101(Cr)@GO exhibited remarkable advantages compared to MIL-101(Cr), MIL-100(Fe), activated carbon and other sorbent materials used in pretreatment methods. A simple, rapid, sensitive, inexpensive and less solvent consuming method of DMSPE-ultra-high performance liquid chromatography-tandem mass spectrometry (DMSPE-UHPLC-MS/MS) was successfully applied to the pre-concentration and determination of twelve SAs in milk samples.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Sulfonamides (SAs), an important class of antibacterial compounds, are widely used in veterinary practice to promote the growth of livestock and to prevent and treat the bacterial infections with lower cost [1,2]. However, the abuse and the unnecessary administration of SAs may result in the accumulation of chemical residues in cattle and then induce adverse effects on human beings by such veterinary products, such as hypersensitive allergic reactions, drug-resistant problems and even carcinogenic character [3,4]. Milk is a kind of nutritious wholesome food consumed globally since it is an inexpensive source of protein and calcium essential for promoting growth in human health. Therefore, the presence of SAs residues in milk is of great public concern. Accordingly, it is desirable to determine the contents of SAs in milk samples for milk safety and human health protection.

Sample pretreatment for both cleaning up samples and pre-concentrating prior to instrumental analysis is a crucial step in the whole analytical process, especially in the analysis of trace materials in complex matrices. In recent years, some typical methods have been applied in milk sample matrix, such as solid-phase extraction (SPE) [5], solid-phase micro-extraction (SPME) [6], dispersive solid phase extraction (DSPE) [7], matrix solid-phase dispersion (MSPD) [8], and so on. Although each of these methods has its advantages, shortcomings still exist in these procedures. For example, the MSPD is a simple and efficient pretreatment method, but time-consuming purification processes are usually required when it is used to pretreat high-fat samples. SPME performs with high enrichment ability and low organic solvent consumption, but it suffers from low recovery and reproducibility. Generally, SPE is one of the most widely used sample pretreatment techniques. However, it is time-consuming, expensive and more toxic organic solvent consuming in the conventional mode. In 2003, Anastasiades and coworkers introduced a novel sample pretreatment technique named dispersive solid phase extraction (DSPE) to simplify the SPE process [9]. In 2009, dispersive micro-solid phase

* Corresponding author.

E-mail address: houxiaohong_syphu@163.com (X. Hou).

extraction (DMSPE) was reported by Tsai and his coworker as alternative miniaturization model of DSPE or SPE [10].

The whole DMSPE process only needs a smaller quantity of organic solvent and sorbent. It allows the analytes in aqueous sample to interact equally with all the sorbent particles to achieve greater capacity per mass of sorbent used. Moreover, This method avoids the channeling or blocking that easily occurs in the conventional SPE column or disks [11]. Based on all mentioned above, DMSPE technique has been successfully applied to the separation and the pre-concentration of pesticides [12], water contaminants [11,13] and pharmaceuticals [10,14] in different types of matrices including water, foods and biological samples by using different sorbents. It is worthy to mention that Yahaya used mesoporous carbon as the sorbent in DMSPE to extract penicillins in milk [15]. And, Iron oxide functionalized graphene oxide was also used as the sorbent in DMSPE to extract SAs in milk samples [16]. To our knowledge, the core of DMSPE is the sorbent materials that would remarkably impact the selectivity and the enrichment efficiency for the targets. Therefore, it is of great significance to prepare an excellent sorbent for the DMSPE technique.

Recently, Metal-organic frameworks (MOFs) have drawn a growing interest in the fields of adsorption and separation due to their ultrahigh porosity, enormous surface areas and tunable poresizes [17–22]. However, poor stability in humid conditions of MOFs restricted their applications in liquid phase. Encouragingly, MIL-101(Cr), reported by Férey [23], is one of the most prominent sorbents among thousands of MOFs owing to its attractive features such as large surface area, numerous unsaturated metal sites, high porosity, excellent chemical stability and inexpensiveness. What's more, if its dispersive forces are enhanced by combining MOF materials with other substrates, the adsorption performance of MOFs would be further improved due to their low density of atoms in the framework structure. In this sense, graphite oxide (GO) would be a great candidate as the hybrid substrates, since it has many epoxy and hydroxyl functional groups in the plane surface of each sheet accompanied by carboxyl groups in the edges [24,25]. These functional groups not only make it easier to disperse in water and other solvents with long-term stability [26], but also offer possibility to form hydrogen bonding and electrostatic interactions with organic compounds or metal ions. Badosz group have developed MOFs@GO composites [24–27] by unifying the favorable properties of carbonaceous graphite surfaces and tunable MOFs apart. It was found that the addition of GO would extremely enhance the adsorption capacity and the stability in water solution of the prepared composite [28]. MIL-101(Cr)@GO has been successfully used to adsorb azo dyes from water samples [29], nitrogen-containing compounds (NCCs) and sulfur-containing compounds (SCCs) from model fuels [30], a series of linear long chain alkanes from *n*-pentane to *n*-octane [31]. According to literature survey, MIL-101(Cr)@GO has not so far been used for the DMSPE of simultaneous or individual sulfonamide compounds. Consequently, MIL-101(Cr)@GO composite would have a potential to be adsorbent material to extract alternative analytes.

Herein, the preparation of MIL-101(Cr)@GO employed a modified simple hydrothermal method, a rapid, simple, and effective dispersive micro-solid-phase extraction (DMSPE) based on the novel MIL-101(Cr)@GO sorbent was developed to extract twelve SAs coupling with UHPLC-MS/MS detection in milk for the first time. The unique advantage of this method as well as the fact that there is no other report about the utilization of MIL-101(Cr)@GO in DMSPE motivated us to investigate its capability for the extraction and separation of sulfonamides. The present work focuses on the synthesis of MIL-101(Cr)@GO as a newly designed material for DMSPE and the optimization of the extraction and the detection conditions. This study would provide a new strategy for the pretreatment of SAs in milk as well as an important insight for the

applications of the MOFs@GO composite material for the extraction of other analytes in different matrixes.

2. Experimental

2.1. Reagents and materials

Chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), trimesic acid (1, 3, 5-BTC), terephthalic acid (H_2BDC), and hydrofluoric acid (HF) were purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphite powder was purchased from Shanghai Aladdin Chemistry Co., Ltd. (Shanghai, China). Potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), and H_2O_2 (30%) were purchased from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Concentrated nitric acid (HNO_3), concentrated hydrochloric acid (HCl), concentrated sulfuric acid (H_2SO_4), ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$), sodium chloride (NaCl), sodium hydroxide (NaOH), and activated carbon were purchased from Damao Chemical Reagent Factory (Tianjin, China). All of the reagents above were of analytical grade. Double-deionized water was purified using a Milli-Q Reagent Water system (Millipore, Bedford, MA, USA). HPLC-grade methanol, acetonitrile, acetone, ethyl acetate, ethanol and *N,N*-dimethylformamide were purchased from Yuwang Group (Shandong, China). The MIL-101(Cr) and MIL-100(Fe) materials employed in the experiment have been previously synthesized and characterized in our laboratory and the procedure was described in the [Supplementary material](#).

The standards of twelve SAs, including sulfadiazine (SDZ, 99.88%), sulfapyridine (SPD, 99.66%), sulfamerazine (SMR, 99.74%), sulfamethazine (SMZ, 99.60%), sulfamethizole (SMT, 98.86%), sulfamethoxypridazine (SMP, 99.80%), sulfamonomethoxine (SMM, 99.86%), sulfachloropyridazine (SCP, 99.29%), sulfadoxine (SDX, 99.08%), sulfamethoxazole (SMX, 99.87%), sulfaquinoxaline (SQX, 99.99%) and sulfadimethoxine (SDMX, 99.87%) were obtained from Shanghai Aladdin Chemistry Co., Ltd. (Shanghai, China). The chemical structures and the pKa values of the target SAs are shown in [Fig. 1](#). Stock solutions were prepared by dissolving each substance in chromatographic grade methanol or acetonitrile at a concentration of 1 mg/mL and stored at 4 °C in darkness.

2.2. Instrumentation and analytical conditions

The separation and the quantification of SAs were performed on an ACQUITY Ultra High Performance LC system (Waters, Milford, MA, USA) coupled to a Waters Xevo TQ tandem quadrupole mass spectrometer (Waters, Milford, MA, USA) equipped with an electrospray ionization (ESI) interface.

The chromatographic separation was achieved on an ACQUITY UHPLC BEH[®] C₁₈ column (2.1 mm × 100 mm, 1.7 μm) protected by an in-line prefilter in front of the column. The column temperature was held at 30 °C. The mobile phase consisted of aqueous formic acid (0.1%, *v/v*) (A) and acetonitrile (B) with a gradient elution as follows: 10–85% B at 0–4 min, 85–10% B at 4–4.3 min, 10% B at 4.3–6 min and the flow rate was set at 0.3 mL/min. The sample manager was controlled at 4 °C and injection volume was 5 μL.

The mass spectrometry was operated in the multiple-reaction monitoring (MRM) mode and the electrospray ionization (ESI) in positive ion mode with the following parameters: cone voltage, 30 V; capillary voltage, 3.0 kV; desolvation temperature and source temperature, 350 and 120 °C, respectively; desolvation gas flow, 450 L/h. Argon was used as the collision gas in all cases and nitrogen as the auxiliary and sheath gas in the ESI source. The optimal MS parameters for the analysis are shown in [Table 1](#).

Other main equipments used for the sample preparation process are as follows: ALC-210.4 electronic balance (0.00001 g

Download English Version:

<https://daneshyari.com/en/article/5140963>

Download Persian Version:

<https://daneshyari.com/article/5140963>

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