



A green cyclodextrin metal–organic framework as solid–phase extraction medium for enrichment of sulfonamides before their HPLC determination

Yuanyuan Li^{a,b,*}, Nan Zhu^{a,b}, Tong Chen^c, Yulong Ma^{a,b}, Qiang Li^{a,b}

^a State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, Ningxia University, Yinchuan 750021, China

^b College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China

^c Zhenjiang Entry-exit Inspection and Quarantine Bureau, Zhenjiang 212008, China

ARTICLE INFO

Article history:

Received 4 January 2018

Received in revised form 22 January 2018

Accepted 22 January 2018

Available online xxxx

Keywords:

Cyclodextrin metal–organic framework

Sulfonamides

Solid-phase extraction

Pre-enrichment

ABSTRACT

A facile approach was used to prepare a cyclodextrin metal–organic framework (CD-MOF) based on γ -cyclodextrins (γ -CDs) and alkali metal cations. As a green, renewable framework material, the CD-MOF exhibits high selectivity and sorptive capacity toward sulfonamides (SAs). Therefore, five SAs including sulfathiazole (STZ), sulfamethoxymidine (SMD), sulfamerazine (SMR), sulfadimethoxine (SDM) and sulfaquinolaxine (SQX) were selected as target analytes to validate the extraction performance of CD-MOF as a solid-phase extraction (SPE) adsorbent, coupled with high-performance liquid chromatography (HPLC) and the adsorption mechanism was investigated. The results showed that the CD-MOF as adsorbent exhibited good enrichment capability for five SAs and obtained short adsorption equilibrium time (30 min). Under optimized conditions, the spiked recoveries into meat samples were satisfied (76%–102%) with relative standard deviation below 2.4%–6.5% ($n = 3$) which indicated that the method was suitable for the effective extraction of SAs from complicated matrices.

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1. Introduction

Sulfonamides (SAs) are the most commonly used antibacterial drugs in the process of livestock and poultry breeding, chiefly because of low cost and their relative efficacy in some common bacterial diseases [1,2]. Often improper use and treatment of sulfa antibiotics for treated animals can result in some SAs residues inside the animals when they are slaughtered for food, which can cause imbalance of microbial system in the body [3–5]. If the SAs are used for long-term and accumulation content is too high, it can also cause toxic effects such as emicton and hemopoiesis turbulence [6–9]. Many countries have adopted a maximum residue level for SAs in foodstuffs of animal origin. The concentration of SAs in water and animal-derived foods is usually low (ng L^{-1} – $\mu\text{g L}^{-1}$) [10–12], so it is of great importance to develop an effective method for trace-level SAs pre-enrichment before the analysis.

Current techniques for the pre-concentration of SAs include solvent extraction [13], solid phase extraction (SPE) [14–16], solid phase microextraction (MSPE) [17] and liquid phase microextraction (LPME) [18]. Among these methods, SPE as a mature technique, has been widely used because of its simplicity, rapidity, low cost, and ability to combine with different detection techniques in both on-line and off-line mode.

Nowadays, SPE techniques mainly focus on different types of adsorbents [19–21], as they have key roles in obtaining high enrichment efficiency in trace analysis in complex matrices. For example, Wu et al. developed a simple analytical method for analyzing SAs in pork using MWCNTs as a SPE material [22]. An adsorbent of the magnetic multiwalled carbon nanotubes (MMWCNTs) was used for the extraction of SAs from egg samples by Ding et al. [23]. Najafi et al. synthesized Fe_3O_4 magnetic nanoparticles and were modified by a molecularly imprinted polymer for extraction and determination of SAs in meat sample [24]. But it is still an important problem that SAs are isolated and preconcentrated due to their decreased hydrophobicity and the low degrees of extraction. Therefore, it is necessary to develop new adsorbents for the determination of SAs in environmental samples.

Recently, metal–organic frameworks (MOFs) with metal clusters and organic linkers are showing great promise for better adsorption/separation of various contaminants due to their unique characteristics, such as permanent nanoscale porosity, high surface area, uniformly structured cavities and the availability of in-pore functionality [25–29]. Church et al. developed an aluminium aminoterephthalate (amino-MIL-101(Al)) and it has been applied to the adsorptive removal of dyes [30]. It was proved that MIL-101 can give much higher affinity and bigger adsorption capacity. Liu et al. reported a MOF based on copper-benzenetricarboxylates and it was applied to the adsorption of methylene blue from aqueous solution [31]. Thus, MOFs have great potential as novel SPE adsorbents for the sample enrichment.

* Corresponding author at: State Key Laboratory of High-efficiency Coal Utilization and Green Chemical Engineering, Ningxia University, Yinchuan 750021, China.

E-mail address: liy@nxu.edu.cn (Y. Li).

Cyclodextrin (CD) from natural products derive displays the – OCCO– binding motif on both their primary and secondary faces auguring well for forming extended structures with Group IA and IIA metal and the host-guest complexes [32]. Here, a composed of green and readily available CD-MOF was prepared using a simple method in aqueous media under ambient conditions. CD-MOF was subsequently employed as adsorbent for the enrichment of trace amounts of five SAs because of its high adsorption capacity. Its adsorption behaviors were evaluated by static and kinetic adsorption experiments. To further evaluate the accuracy of the proposed method, the developed SPE method was also adopted to analyze the real samples.

2. Materials and methods

2.1. Chemicals and materials

γ -Cyclodextrin (γ -CD, 98%) was purchased from Yuanye Bio-Technology Co., Ltd. (Shanghai, China). Potassium hydroxide (KOH) and cetyltrimethylammonium bromide (CTAB) were obtained from Green Analytical Chemical Technology Co., Ltd. (Shanghai, China). Sulfathiazole (STZ), sulfamethoxymidine (SMD), sulfamerazine (SMR), sulfadimethoxine (SDM) and sulfaquinolaxaline (SQX) were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), and their structures are shown in Fig. 1. All other chemicals used in this work were of analytical reagent (Tianjin Chemicals, China). Ultrapure water ($>18 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout the experiments.

2.2. Instrumentation and chromatographic conditions

Field emission scanning electron microscopy (FE-SEM) images were obtained on a Hitachi S-4800. X-ray diffraction (XRD) pattern was recorded on a D8 Advance X-ray diffractometer that used graphite-

monochromated Cu K radiation. IR spectra were obtained on a Nicolet 20 NEXUS 670 FT-IR (Madison, USA).

Determination of SAs was performed using FL2200 system (Wenling, China). The separation was performed on an Ultimate AQ-C₁₈ column (250 × 4.6 mm, 5 μm) from Phenomenex (USA). The chromatographic conditions were as follows: the column temperature was 25 °C, the flow rate was 1.0 mL/min and the injection volume was 20 μL . The mobile phase was acetonitrile/water (30/70, V/V) and ultraviolet detection wavelength was monitored at 270 nm.

2.3. Synthesis of CD-MOF

CD-MOF was prepared using a modified literature procedure [32]. In the preparation process, the crystal-growth time was altered. Firstly, γ -CD (0.489 g) was dissolved in 15 mL KOH ($200 \text{ mmol}\cdot\text{L}^{-1}$) aqueous solution. The solution was filtered through a 0.45 μm PTFE membrane into medium beaker, and the medium beaker was placed in a large beaker 19 mL methanol. Methanol was allowed to vapor-diffuse into the solution of the first crystal-growth time at 25 °C for 36 h. Then, CTAB (0.04 g) and 5 mL of methanol were added to the above solution. The solution was incubated for 3 h of the second crystal-growth time. The CD-MOF formed was collected by centrifugation, repeated washing with ethanol, dried at room temperature.

2.4. Adsorption capacity of CD-MOF

2.4.1. Static adsorption experiments

Static adsorption experiments were carried out by follow process: a stock solution of 10–1000 ng mL^{-1} STZ, SMD, SMR, SDM and SQX was prepared by dissolving a known quantity of SAs in methanol. Batch adsorption capacity was performed by mixing 0.04 g CD-MOF and 5 mL

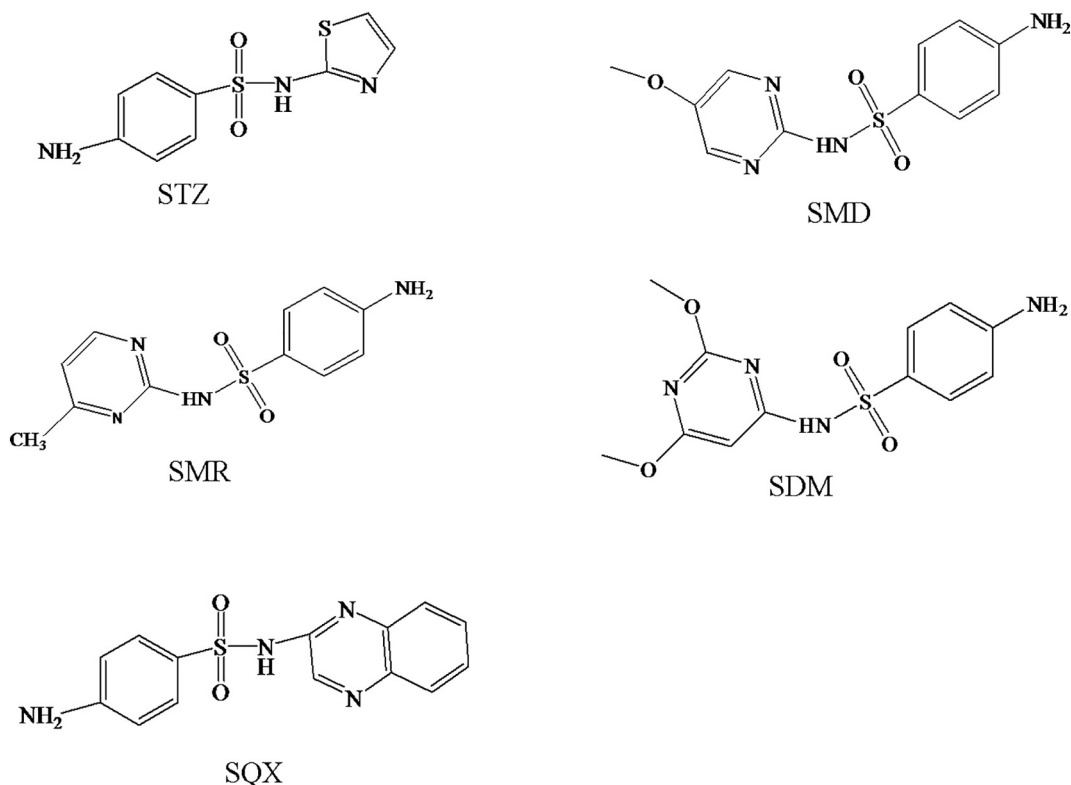


Fig. 1. Structures of STZ, SMD, SMR, SDM and SQX.

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