



Aluminum based metal-organic framework-polymer monolith in solid-phase microextraction of penicillins in river water and milk samples



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ABSTRACT

In this study, aluminum based metal-organic framework (Al-MOF)-organic polymer monoliths were prepared via microwave-assisted polymerization of ethylene dimethacrylate (EDMA), butyl methacrylate (BMA) with different weight percentages of Al-MOF (MIL-53; 37.5–62.5%) and subsequently utilized as sorbent in solid-phase microextraction (SPME) of penicillins (penicillin G, penicillin V, oxacillin, cloxacillin, dicloxacillin, nafcillin). The Al-MOF-polymer was characterized using Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and SEM-energy-dispersive X-ray spectroscopy (SEM-EDS) to clarify the retained crystalline structure well as the homogeneous dispersion of Al-MOF (MIL-53) in polymer monolith. The developed Al-MOF-polymer (MIL-53) monolithic column was evaluated according to its extraction recovery of penicillins. Several parameters affecting the extraction recoveries of penicillins using fabricated Al-MOF-polymer (MIL-53) monolithic column including different MIL-53 weight percentages, column length, pH, desorption solvent, and mobile phase flow rate were investigated. For comparison, different Al-based MOFs (MIL-68, CYCU-4 and DUT-5) were fabricated using the optimized condition for MIL-53-polymer (sample matrix at pH 3, 200 μ L desorption volume using methanol, 37.5% of MOF, 4-cm column length at 0.100 mL min⁻¹ flow rate). Among all the Al-MOF-polymers, MIL-53(Al)-polymer still afforded the best extraction recovery for penicillins ranging from 90.5 to 95.7% for intra-day with less than 3.5% relative standard deviations (RSDs) and inter-day precision were in the range of 90.7–97.6% with less than 4.2% RSDs. Meanwhile, the recoveries for column-to-column were in the range of 89.5–93.5% (<3.4% RSDs) while 88.5–90.5% (<5.8% RSDs) for batch-to-batch ($n = 3$). Under the optimal conditions, the limit of detections were in the range of 0.06–0.26 μ g L⁻¹ and limit of quantifications between 0.20 and 0.87 μ g L⁻¹. Finally, the MIL-53-polymer was applied for the extraction of penicillin in river water and milk by spiking trace-level penicillin for as low as 50 μ g L⁻¹ and 100 μ g L⁻¹ with recoveries ranging from 80.8% to 90.9% (<6.7% RSDs) in river water and 81.1% to 100.7% (<7.1% RSDs) in milk sample, respectively.

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1. Introduction

Penicillin has long been used effectively to prevent and treat numerous bacterial infections in human and livestock, and generally can be added to feedstuff to promote animal growth [1]. Conversely, traces of penicillin in animal origin such as milk can cause human health problems like allergic reactions and development of drug resistant microorganisms [2]. For this reason, maximum residue limit (MRL) values were established in Taiwan

and European Economic Community (EEC) regulation to monitor the present substances. For instance, in milk, these values range from 4 μ g L⁻¹ to 300 μ g L⁻¹, depending on the present β -lactam antibiotics [3]. In most cases, analytical methods to monitor the antibiotic residues have focused on using liquid chromatography (LC) coupled with mass spectrometry (MS) or with UV detection [4,5]. However, even using LC-MS or LC-UV method, a common drawback involved in the analysis of real sample is the extraction procedure for antibiotic due to the complexity of the matrix. Also, because of their low exposure levels, pre-concentration to a detectable level is often required prior to the detection of penicillin in milk.

Solid-phase microextraction (SPME) has long been known to be an effective technique for pre-concentration and clean-up step

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in complex samples. SPME, which was developed by Arthur and Pawliszyn in 1996 [6], has gained tremendous attention because of simplicity in operation, reduction of analysis time, and solvent-free technique for sample pre-treatment prior to analysis [6]. This technique is based on the interaction and distribution of analytes between the sample solution and the stationary phase. SPME has been widely accepted to be useful in the analysis of food, environmental and biological sample, pharmaceutical, forensic analysis and so on [7,8]. In SPME, various sorbents and techniques have been developed which includes the use of organic polymer monolithic materials extraction as PMME mode. For PMME, an organic polymer monolith is utilized, which is prepared via *in situ* polymerization in “mold”, has been effective as stationary phase and gained numerous research interests [9], which has been reviewed in the past few years [7,8,10]. Developing the monolithic materials generally requires a single-step polymerization wherein the porous structure and surface properties of the polymer are usually tunable. Because of its simplicity, organic polymer materials have been useful for separation science and SPME [8].

The recent discovery of metal-organic frameworks (MOFs) has fascinated and opened up various applications for gas storage and separation [11], catalysis [12], chromatography [13], and drug delivery [14]. MOFs are described as crystalline structure consisting of clusters of metal ions and connected by organic ligands [15]. Owing to its high surface area (up to thousands $\text{m}^2 \text{g}^{-1}$), unique structure and pore size diversity, and good adsorption affinity, some MOFs such as MIL-53 (Al, Cr, Fe) [16], polydimethylsiloxane/MOF (PDMS/MOF) (MOF-5 (Zn), MIL-101 (Cr), MOF-199 (Cu), IRMOF-3 (Zn), Al-MIL-53-NH₂) [17–19], graphene oxide/MOF (GO/MOF) (MOF-199 (Cu)) [20], ZIF-7 (Zn), ZIF-8 (Zn) [21], MOF-199 (Cu, Zn) [21,22], MIL-88B (Fe) [23], Cd(II)-MOF [24], Fe₃O₄/MIL-101(Cr) [25] and UiO-66 (Zr) [26], have been applied successfully as sorbent for SPME in the analysis of organic compounds such as polyaromatic hydrocarbons (PAHs) [16,18,19], estrogens [17], pesticides [20,25,27,28], *n*-alkanes [21], gaseous benzene homologues [13,22], polychlorinated biphenyls (PCBs) [23], chemical warfare agents [29], benzene, toluene, *o*-, *m*-, *p*-xylene, and ethylbenzene (BTEX) [24] and phenols [26]. Despite the remarkable advances in MOFs as sorbent in SPME, however, majority of them are limited only to fiber SPME, which analyzes volatile organic compounds (VOCs). Similarly, the preparation of MOF on fiber and conditioning of SPME fiber is time consuming. In order to address and exploit the potential use of MOF in SPME application, our previous studies have demonstrated an efficient strategy of developing a monolithic column via room temperature ionic liquids (RTIL) as reaction media coupled with microwave-assisted heating [30–33]. In particular, a rapid (~5 min) synthetic strategy of novel hybrid MOF-polymer monolith columns as stationary phase in capillary electrochromatography (CEC) system and SPME were developed [30,31]. The successful fabrication of MOF-polymer monolithic columns provided a small mesopore (originated from MOF) as well as large through-pores (macropores) (originated from polymer) on its structure; in which the small mesopore provided adequate surface area required for solute retention, while large through-pores allow the mobile phase to flow through the stationary phase [30,31,34,35]. In particular, a cage-type MOF, which contains mesocages surrounded by windows either sharing faces or separated by spacers [36], such as MIL-101 (Cr), MIL-100 (Cr), MIL-100 (Fe), MIL-100 (Al), UiO-66 (Zr) and MIL-88B (Cr) copolymerized with butyl methacrylate-co-ethylene dimethacrylate (BMA-EDMA) were investigated as sorbent in SPME of penicillins, in which the MIL-101 (Cr)-polymer exhibited satisfactory extraction recovery and can be reused for at least 50 multiple extraction times [31]. With the results obtained from the hybrid material (MOF-polymer), it is noteworthy to take advantage its potential application for SPME system.

Aluminum based MOFs, which has mesopores nearby in the form of channels in at least one dimension [36], such as MIL-53 and MIL-68 have been reported to be interesting because of its flexible structure and breathing effect [37,38], and some studies have also demonstrated their adsorption capacity for hydrogen sulfide, bisphenol A, aniline, nitrobenzene and phenols [39–43] in aqueous solution as well as PAHs in fiber SPME mode [16]. Our previous work has demonstrated a cage-typed MOF-polymer composite (especially with MIL-101(Cr) as model MOF) used for in-tube SPME at the same time overcome the drawbacks in time consuming preparation and fragility of fiber SPME [31]. Owing to some of these advantages of aluminum based MOFs, further investigation is needed to maximize its capacity as adsorbent for SPME application. Therefore, this study attempts to further explore the different channel typed aluminum based MOF-polymer as sorbent for in-tube SPME.

In this work, we report the potential application of several channel-type aluminum based MOF-poly(butyl methacrylate-co-ethylene dimethacrylate) monolithic column (referred to as Al-MOF polymer) in SPME of penicillin in river water and milk samples. Different Al-MOF-polymers, which includes MIL-53, MIL-68, DUT-5 or CYCU-4, as MOF source, and BMA-EDMA, as polymeric monomer source, were prepared via RTIL as reaction medium using microwave-assisted heating. Despite the low adsorption ability of poly(BMA-EDMA) polymer for the test analytes as shown in Section 3.2, the reason of using this as model polymer from our previous and present works is due to the ease of preparation and can also be used as binder to fully accommodate the incorporation of MOF, which simplifies the fabrication of in-tube SPME extraction column. Structural characterizations were conducted on MOF-polymer using Fourier transform infrared (FTIR), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and SEM-energy dispersive X-ray spectroscopy (SEM-EDS). The characteristics of Al-MOF-polymer as SPME adsorbent such as stability, reproducibility and extraction recoveries of penicillins were investigated. Finally, using the optimized condition, the fabricated Al-MOF-polymer was applied in SPME of river water and milk samples spiked with or without six (6) penicillin antibiotics followed by ultra performance liquid chromatography with ultraviolet detection (UPLC-UV).

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were at least of analytical grade. Oxacillin (OXA) (pK_{a1} = 2.61) was obtained from Fluka (Buchs, Switzerland). Penicillin V (PENV) (pK_{a1} = 2.62) was purchased from ICN (Ohio, USA). Penicillin G (PENG) (pK_{a1} = 2.62), cloxacillin (CLOX) (pK_{a1} = 2.44) and dicloxacillin (DICLO) (pK_{a1} = 2.44) were purchased from Sigma (St. Louis, MO, USA). Nafcillin (NAFC) (pK_{a1} = 2.61) was purchased from MP (Eschwege, Germany). BMA (Lancaster, Ward Hill, MA, USA), EDMA (Acros, New Jersey, USA), and azobisisobutyronitrile (AIBN) (Showa, Tokyo, Japan) were used for the polymerization while 3-trimethoxysilylpropyl methacrylate (MSMA, 98%) were purchased from ACROS (Geel, Belgium) for pretreatment of column. The six penicillin standards were used as test analytes and dissolved in methanol (MeOH) at a stock concentration of 1 $\mu\text{g}/\text{mL}$. The ionic liquid 1-hexyl-3-methylimidazolium tetrafluoroborate ([C₆ mim][BF₄]) was synthesized in our laboratory and the identity was confirmed by ¹H NMR spectroscopy. The uncoated fused-silica capillary with 0.8 mm I.D. and 1.1 mm O.D. was purchased from Kimble Chase (Mexico).

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