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Fabrication and characterization of metal organic frameworks/polyvinyl alcohol cryogel and their application in extraction of non-steroidal anti-inflammatory drugs in water samples

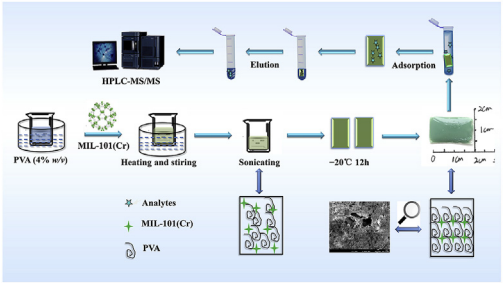
Yudan Wang [a], Yang Zhang [a], Jianan Cui [b], Shuo Li [a], Ming Yuan [a], Ting Wang [b], Qi Hu [b, **], Xiaohong Hou [b, *]

[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

HIGHLIGHTS

- A variety of monolithic MOFs/PVA cryogel were fabricated for the first time.
- A more suitable preparation process for MOFs/PVA cryogel was obtained.
- MIL-101(Cr)/PVA cryogel was chosen to validate the applicability in the extraction of NSAIDs in water samples.
- Easy operation and high enrichment efficiency were achieved by using MIL-101(Cr)/PVA cryogel as the sorbent.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of novel MOFs/PVA composite cryogel (MIL-101(Cr)/PVA, MIL-100(Fe)/PVA, ZIF-8(Zn)/PVA, MOF-199(Cu)/PVA and MIL-53(Al)/PVA) were fabricated by using a facile and green freeze-thaw approach for the first time. MIL-101(Cr)/PVA cryogel was selected as a VA-SPE sorbent for extraction of four NSAIDs in environmental water samples. The procedures of condition investigation (synthesis and extraction optimization) and characterization were also performed. And a satisfactory result of methodology validation was obtained by making use of HPLC-MS/MS. Under the optimum conditions, good sensitivity levels were achieved with the limits of detection between 0.007 and 0.037 $\mu g\,L^{-1}$, a linearity of 0.10 $-10\,\mu g\,L^{-1}$ for phenylbutazone, indomethacin, nimesulide and 0.020–2.0 $\mu g\,L^{-1}$ for benorilate ($r^2 \geq$ 0.9934). The relative recoveries of the target analytes were in the range from 78.44% to 105.7% with relative standard deviation (RSD) from 1.33% to 9.85%. In the extraction process, MIL-101(Cr)/PVA cryogel as a whole sheet outperformed the pristine dispersive MIL-101(Cr) in separation from solvent, and the application of cryogel also simplified the operation procedure. Additionally, the combination of PVA with MOFs might strengthen the interaction ability between the sorbent and analytes. This novel pretreatment method had a variety of merits, such as easy operation, high enrichment efficiency and low matrix

* Corresponding author. School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang, 110016, PR China.
** Corresponding author.
E-mail addresses: huqiguyue@126.com (Q. Hu), syphu_houxiaohong@163.com (X. Hou).

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effect. It looks forward to further optimization or functionalization and application of these MOFs/PVA cryogel in various disciplines.

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1. Introduction

Recently, a considerable number of novel materials with attractive features have been developed for their use of analytical pretreatment. Among them, metal organic frameworks (MOFs) have gained widespread recognition and been considered a promising platform for sample pretreatment as an efficient enrichment material [1]. Herein, MOFs have appeared as highly valuable sorbents for solid phase extraction (SPE) due to their ultrahigh porosity, high surface area and adjustable specific host-guest interactions via the chemical modifications [2]. Initially, MOFs are often employed as the sorbent for dispersive solid phase extraction, because MOFs material can sufficiently disperse in the sample solution, and this makes the analytes can be efficiently captured in the structure of MOFs by hydrogen bond, π–π interaction and so on [3]. However, small particle size, excellent dispersive ability and light texture of MOFs makes the material difficult to be wholly retrieved from sample solvent, and this may cause quantitation loss. To overcome these drawbacks, a vast number of efficient and convenient pretreatment methods basing on MOFs have been explored, such as typical SPE packed column [4,5], solid phase micro extraction (SPME) [6,7], membrane protected micro solid phase extraction [8,9], magnetic solid phase extraction (MSPE) [10], stir-bar sorptive extraction (SBSE) [11] and mixed-matrix membranes (MMMs) [12]. The design idea of these novel methods is to encapsulate the powdery MOFs material in a container or attach the material to a carrier, thus a monolithic device is eventually required. Overall, these studies, while encouraging, it's a hard task to prepare these attractive extraction devices. Therefore, constant efforts are still being made to design some easy preparation and convenient application extraction technologies. Herein, we embarked on exploring the possibility of MOFs shaping, from unorganized powder to a whole composite gel. It speculates that MOFs material would be loaded into the porous of the macro porous gel, and then the powdery MOFs material would be immobilized on the colloid. Finally, synergies between highly porous MOFs and colloid could be exploited to develop high performance sorbent for adsorption extraction.

With the above notion, an expected gel with large enough aperture and convenient to preparation is desirable. Polyvinyl alcohol (PVA) is a water-soluble polymer containing many polar hydroxyl groups on the molecular chain. As the molecular chains can easily form hydrogen bonds, then can form a symmetrical and regular structure, it exhibits good film forming ability, water solubility, emulsification and adhesion [13]. In 1975, PVA hydrogel was prepared through the repeated freeze-thaw method reported by Peppas et al. [14], therefore the PVA hydrogel is also called PVA cryogel. The process of cryogelation is ideally thought to take place via the following steps: phase separation with ice-crystal formation, cross-linking and polymerization followed by thawing of ice-crystals to form an interconnected porous cryogel network. However, it was not until 2010 that this theoretical concept had been revealed in practical terms [15]. Since these pioneering reports, the freeze–thaw method for fabricating PVA cryogel has been extensively applied in different fields, such as bioseparation, immobilization of biopolymers, cell immobilization and other biological fields [16], in addition, cryogel has also been widely used for topical drug delivery [17]. All these applications are attributed to the better biocompatible, nontoxic and minimal cell adhesion of PVA cryogel [18]. Subsequently, PVA cryogel was introduced into the field of adsorption and extraction [19,20]. Unsatisfactorily, PVA cryogel has a low surface area and low adsorption capacity for target analytes. However, cryogel typically has interconnected macropores (or supermacropores), allowing unhindered diffusion of solutes of nearly any size, as well as mass transport of nano- and even microparticles. Thus, entrapment of adsorbent particles within the cryogel and high affinity coatings would increase its specific surface area and obtain a higher extraction efficiency [21]. Several literatures have reported that graphene oxide [22], graphene [23], multi-walled carbon nanotubes [24], and active carbon [25] have been fabricated with PVA by freeze-thaw method to form a whole cryogel, and they were used for adsorption extraction. Based on the aforementioned details, the view that PVA is employed to immobilize porous MOFs material may be feasible.

In this work, several highly elastic MOFs/PVA cryogel were synthesized after investigating a series of synthetic conditions for the first time. In order to validate the adsorption practicality of these synthesized cryogel, MIL-101(Cr) (Matérial Institute Lavoisier-101(Cr))/PVA cryogel was used to extract four non-steroidal anti-inflammatory drugs (NSAIDs) (phenylbutazone, indometacin, benorilate and nimesulide) in environmental water samples by combining with vortex assisted solid phase extraction (VA-SPE). We hope that the daringly designed MOFs/PVA cryogel would become a new classic of adsorption materials which can be applied in the field of sample pretreatment.

2. Experimental

2.1. Reagents and materials

Analytical grade terephthalic acid, chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$) and hydrofluoric acid (HF) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH) and concentrated hydrochloric acid (HCl) were obtained from Damao Chemical reagent factory (Tianjin, China). Dimethyl sulfoxide (DMSO) was acquired from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Ultrapure water was obtained with a Milli-Q Reagent Water system (Millipore, Bedford, MA). All other reagents were of analytical-reagent grade. HPLC-grade methanol, acetonitrile and acetone were acquired from Yuwang Group (Shandong, China).

PVA (average M.W. 57000-66000, 98–99% hydrolyzed) was obtained from Alfa Aesar (Waltham, USA). The standards of four NSAIDs, including phenylbutazone (99%), indometacin (98%), benorilate (98%) and nimesulide (99%) were purchased from J&K Scientific Ltd. (Beijing, China), and the chemical structures are shown in Fig. S1.

2.2. Instrumentation

The separation and quantification of the target NSAIDs was performed on an Agilent 1260 HPLC system (Agilent, USA) coupled to an Applied Biosystem API 4000 triple quadrupole mass spectrometer (Applied Biosystems-Sciex, USA) equipped with an

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