



Self-assembling covalent organic framework functionalized poly (styrene-divinyl benzene-glycidylmethacrylate) composite for the rapid extraction of non-steroidal anti-inflammatory drugs in wastewater

Weixia Li^a, Lin Huang^b, Dandan Guo^a, Yonggang Zhao^a, Yan Zhu^{a,*}

^a Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou 310028, China

^b College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China



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ABSTRACT

The growing use of non-steroidal anti-inflammatory drugs (NSAIDs) has seriously affected human health and ecosystems, as a result, the World Health Organization (WHO) has regarded them as emerging contaminants. NSAID's polar nature and trace amount present in wastewater make their extraction and determination challenging in modern analytical science. Therefore, regarding the need, we herein report a rapid, sensitive and selective in-syringe solid-phase extraction (SPE) method coupled with ultra-high performance liquid chromatography and UV detector for the determination of seven NSAIDs in environmental water samples. Specifically, the NSAIDs in water samples were directly extracted by using synthesized porous covalent organic framework functionalized poly (styrene-divinyl benzene-glycidylmethacrylate) composite (COF@PS-GMA) without further cleanup procedures. The adsorption of NSAIDs on COF@PS-GMA sorbent was investigated by using adsorption isotherms and kinetic studies. Various parameters, including amount of sorbent, pH of the samples, the volume of desorption solvent, and desorption time that were involved in in-syringe SPE were optimized. Under the optimized conditions, good linearity was observed at 0.005–5.0 $\mu\text{g mL}^{-1}$ with method quantification limits (LOQs) estimated between 0.54–2.74 $\mu\text{g L}^{-1}$. The recoveries of the seven NSAIDs at the level of 0.5, 5.0 and 20.0 $\mu\text{g L}^{-1}$ were ranging from 84.3% to 99.6%.

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1. Introduction

Non-steroidal anti-inflammatory drugs (NSAIDs) is a group of compounds that has antipyretic, anti-inflammatory and analgesic effects for the treatment of rheumatic disorders, inflammation and soreness [1–3]. Because of their broad-spectrum application, NSAIDs are consumed by means of numerous human activities and discharged into the environment through urine, wastewater, and the discarding of expired drugs. NSAIDs are continually introduced into the aquatic environment; therefore, they have made elicit chronic effects in aquatic and terrestrial inhabitants [4,5]. Hence, NSAIDs are regarded as emerging contaminants by the World Health Organization (WHO) [6,7]. Accordingly, the development of reliable analytical method for determining NSAIDs in water samples is crucially important.

To date, various sample pretreatment methods, such as liquid-liquid extraction (HF-LPME), ultrasound-assisted liquid-phase microextraction (UA-LPME), solid-phase extraction (SPE), and solid-phase microextraction (SPME), have been used in determining NSAIDs [8–12]. Among these methods, SPE is the most frequently used method because of its relatively convenient operation and high extraction efficiency. Moreover, the diverse choices for sorbents materials provided ample space for SPE development. Recently, $\text{K}_2\text{Ti}_4\text{O}_9$, metal organic frameworks (MOF), and ionic liquid were applied as a modifier of the sorbent for extracting of NSAIDs [13–15]. Ting Wang et al. prepared a MOF-functionalized magnetic material for extracting NSAIDs in wastewater and environmental water samples [14]. Amiri et al. pretreated NSAIDs in biological fluids by using supercritical fluid extraction combined with SPE procedure ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{IL}$) [15]. All of the sorbents have their own merits, but because of their slow binding kinetics, they require long extraction times, which is an important limitation for high-throughput samples analysis.

* Corresponding author.

E-mail address: zhuyan@zju.edu.cn (Y. Zhu).

Covalent organic frameworks (COFs) are covalently bound crystalline porous material which were composed of lightweight elements such as C, H, O, N and B. COF have become noteworthy since being first reported in 2005 [16,17]. These materials possess considerable fascinating properties including high specific surface area, excellent thermal stability, high porosity, and low density. Moreover, COFs are more stable in water and acidic media than MOFs [18]. With these unique properties, COFs have been considered as a promising sorbent material with favorable capacity. However, the direct use of COF in the sample pretreatment of NSAIDs have several drawbacks, such as the relatively low affinity of bare COF for NSAIDs and the tedious centrifugal separation. Hence, the design of COF-functionalized composites with a strong NSAID affinity, and an operational convenient device are essential for the rapid and highly efficient extraction.

In this study, we prepared a novel COF-functionalized poly (styrene-divinyl benzene-glycidylmethacrylate) composite (COF@PS-GMA) by generating COF on the surface of the PS-GMA particles for NSAID extraction. The composite could be successfully synthesized via hydrothermal reaction because of the strong π - π interaction between monomers and PS-GMA particles, as well as the self-assembly nature of COF [19]. The π -electron system of the composite provided affinity sites for the interaction with NSAIDs. In addition, the mesopores of the COF layer could eliminate the large scale interferences from the complex matrix [20]. Moreover, we proposed a miniaturized in-syringe solid-phase extraction device by using filter holder [21]. Therefore, this study provides a COF-based composite couple with a miniaturized extraction device for the rapid and efficient extraction of NSAIDs in environmental water samples.

2. Experimental

2.1. Reagents and instrumentation

Flurbiprofen, ketoprofen, aspirin, naproxen, diclofenac, indomethacin, and ibuprofen were supplied by Sigma-Aldrich (MO, USA). The standard stock solution (1000 mg L^{-1}) of the seven NSAIDs was prepared by dissolving the compounds in HPLC-grade

methanol. A series of working solution was obtained daily by diluting the stock solution with deionized water.

PS-GMA particles (55% cross-linking degree) were prepared in our laboratory following a method from a previous work [22]. Methanol of HPLC-grade were purchased from Tedia Company, Inc (OH, USA). 1,3,5-Triformylbenzene and 4,4'-Diaminobiphenyl were obtained from Sigma-Aldrich, USA. Furthermore, purified water was produced by using GenPure Pro system (Thermo Fisher Scientific, USA).

The morphology images of COF@PS-GMA were studied by scanning electron microscope (SU8010, Japan). Elemental analysis and Fourier transform infrared (FT-IR) spectroscopy was studied on Flash EA1112 analyzer (Thermo Finnigan, USA) and Bruker Vector 22 spectrometer, respectively. Thermo-gravimetric analysis (TGA) was conducted with a TA DSCQ1000 (TA, New Castle, Delaware, USA). Brunauer–Emmett–Teller (BET) was performed by N_2 adsorption and desorption isotherms to evaluate the pore properties of COF@PS-GMA.

2.2. Sample collection and pretreatment

The river water, hospital wastewater and tap water samples were collected from different place in Hangzhou, Zhejiang, China. The water samples were filtered by $0.22 \mu\text{m}$ membrane and stored at -20°C .

2.3. Preparation of COF@PS-GMA particles

The scheme of the synthesis of COF@PS-GMA composites is demonstrated in Fig. 1. 300 mg of PS-GMA particles was dispersed in 30 mL of 1,4-dioxane in a hydrothermal reaction vessel, and sonicated for 5 min. Then, 1,3,5-triformylbenzene (48.6 mg) and 4,4'-diaminobiphenyl (82.8 mg) were added sequentially. After stirring for 20 min, $60 \mu\text{L}$ of acetic acid (6 mol L^{-1}) was dropwise added into the mixture. Thereafter, the mixture was maintained at 120°C for 72 h, and the yellow precipitate (COF@PS-GMA) took shape in the hydrothermal reaction vessel [23,24]. The collected yellow precipitates were washed thrice with anhydrous methanol and tetrahydrofuran, and then dried under vacuum at 30°C .

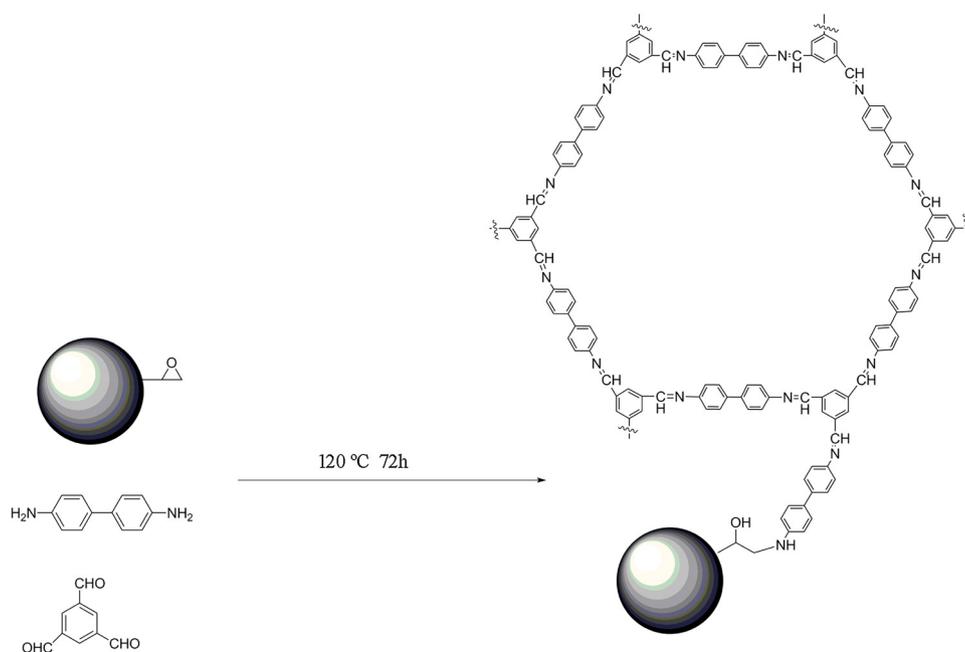


Fig. 1. Scheme of the fabrication of COF@PS-GMA.

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