Regular Article

Preparation of mixed-matrix membranes from metal organic framework (MIL-53) and poly (vinylidene fluoride) for use in determination of sulfonylurea herbicides in aqueous environments by high performance liquid chromatography

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ARTICLE INFO

Article history:
Received 16 April 2019
Revised 23 June 2019
Accepted 24 June 2019
Available online 25 June 2019

Keywords:
Sulfonylurea herbicides (SUs)
Dispersion membrane extraction (DME)
Metal-organic frameworks (MOFs)
Mixed-matrix membrane (MMM)
Aqueous environments

ABSTRACT

Novel mixed-matrix membranes (MMM) were prepared from metal-organic frameworks (MOF) (MIL-53) and poly (vinylidene fluoride) (PVDF), viz MIL-53–PVDF MMM, for the simultaneous dispersion membrane extraction (DME) of seven sulfonylurea herbicides (SUs) in aqueous environments followed by high performance liquid chromatography (HPLC) determination. The MIL-53–PVDF MMM was well characterized and major factors influencing DME performances were systematically investigated including membrane type, MOF dosage, eluent type, solution pH, extraction/elution time and salinity, etc. Under optimal conditions, the MIL-53–PVDF MMM based DME coupled with HPLC exhibited excellent linearity within 0.03–10 l gL −1 for chlorimuronethyl and 0.01–10 l gL −1 for other six SUs individual. High enrichment factor of 250 was obtained, as well as low detection limits and quantification limits ranged from 3.75 to 10.30 ng L −1 and 12.49–34.30 ng L −1, respectively. Furthermore, the method attained high recoveries of 77.20–111.00% at three spiking levels of SUs, with relative standard deviations of 1.28–14.67% in...
1. Introduction

Trace contaminants in aqueous environment are well known to be difficult to detect directly. Thus, it is necessary to develop sample pretreatment techniques for contaminants enrichment prior to related instrumental determination. The pretreatment techniques for contaminants in water mainly include liquid–liquid extraction (LLE) [1], solid phase extraction (SPE) [2–4], solid phase microextraction (SPME) [5,6], magnetic solid phase extraction (MSPE) [7,8], stir bar sorptive extraction (SBSE) [9] and dispersion membrane extraction (DME) [10–12]. As mature techniques, LLE and SPE have been widely implemented, however, they also have some limitations. For example, SPE is time-consuming and requires a large amount of solvents. The SPE requires additional operation equipment, and the SPE column is easily blocked. In addition, the enrichment materials used in the sample pretreatment are usually organic solvents, activated carbon, and multi-wall carbon, etc., which are difficult to be completely separate from solution, and the operation is complicated, which is not conducive to recycling and reuse. Fortunately, DME developed in recent years can overcome the above problems. Initially, Lee et al. used a polypropylene film-wrapped ZIF-8 as an adsorbent of DME for the extraction of polycyclic aromatic hydrocarbons (PAHs) from water samples [13], but the preparation of the polypropylene shell was sophisticated. Accordingly, it is highly expected to simplify the preparation process of adsorbent materials and to endow the materials with high enrichment ability, recyclability, and easy separation from water samples, for efficient DME of targeted pollutants in aqueous environments.

Metal-organic frameworks (MOFs) are a new class of functional materials first reported in 1995 by Yaghi et al. [14]. MOFs are porous materials comprised of metal centers and multifunctional organic ligands [15]. Because of their large porosity and specific surface area, adjustable pore size, diverse structure and function [16], unsaturated metal sites and excellent biocompatibility, MOFs have been widely used in gas storage [17], drug carriers [18], sensors [19,20], catalysis [21,22] and pollutant adsorption and separation [23–26]. Meanwhile, researchers have begun to pay attention to the preparation of MOFs membranes for removal of environmental pollutants [27,28]. However few researches focus on the enrichment of environmental pollutants in solution samples by functionalized MOF membranes [29].

MOF membranes can be prepared by in-situ growth method, seed growth method, post-synthesis modification method and mixed-matrix membrane (MMM) method [30]. Among them, the MOF mixed matrix membranes (MOF MMMs) were prepared by combining the MOF material with polymer. So the MOF MMMs not only retain the advantages of MOFs, such as high specific surface area, high permeability and good selectivity, but also overcome the disadvantages of traditional membranes, e.g. poor mechanical strength and reproducibility, and complicated process [31]. Common MOF MMMs include UiO-66, ZIF-8, HKUST-1, MIL-101 and MIL-53 types MMMs, and most of them had been applied to separate and purify gases [32–34]. There are only few reports to enrich organic compounds in liquid samples by using MIL-53 MMM [29,35]. MIL-53 MMM is synthesized by combining MIL-53 with polymers, in which MIL-53 is constructed of transition metal elements Al, Fe and dicarboxylic acid ligands with strong thermal stability and reversible structural transformation. MIL-53 MMM can be applied to the enrichment of pollutants such as estrogen in solution [29]. Therefore, it is of great significance to expand the applications of MIL-53 MMM in the field of sample pretreatment.

In the analytical detection of various pollutants in aqueous environments, pesticides have received increasing concerns. Sulfonylurea herbicides (SUs) have become one of the fastest growing pesticides and have been widely used to control broadleaf weeds and herbaceous crops, owing to their multiple types, high herbicidal activity, low toxicity to mammals, and low dose but high efficiency [36]. However, SUs have an inevitable shortcoming of high phytotoxicity which can affect the cell division of susceptible plants and reduce yield [37]. Due to the good water solubility, excessively used SUs easily enter the surface and ground water through washing and irrigation processes, which has a potential impact on the aquatic ecosystem. Currently, nicosulfuron in SUs has been found in most rivers of mid-western United States [38]. So it is imperative and important to detect the SUs in environmental waters.

In view of the advantages of MOF materials and membranes in extraction, we synthesized a novel MMM by MIL-53 and poly(vinylidene fluoride) (PVDF), namely MIL-53–PVDF MMM, and it was used to determine SUs in aqueous environments by high performance liquid chromatography (HPLC). The as-prepared MIL-53–PVDF MMM was well characterized and then used as an extractant material in DME. To the best of our knowledge, this is the first report that MIL-53–PVDF MMM was used for the enrichment of SUs in water. The influence factors of DME were investigated in detail, including membrane type, MOF dosage, eluent type/volume, solution pH, extraction time, salinity, and elution time. The MMM based DME coupled with HPLC method was validated and successfully applied to tap water, surface water and seawater samples.

2. Experimental

2.1. Reagents and materials

All chemicals were of at least analytical grade. Aluminum nitrate nonahydrate (Al(NO3)3·9H2O) was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Benzene-1,4-dicarboxylic acid (H2BDC) was procured from Tianjin Guanfu Fine Chemical Research Institute (Tianjin, China). Poly(vinylidene fluoride) (PVDF) was obtained from American Arkema Company (USA). Chromatographic grade methanol (CH3OH), acetone (CH3COCH3) and acetonitrile (CH3CN) were purchased from Shanghai Anpu Reagent Co., Ltd. (Shanghai, China). Sodium chloride (NaCl), N,N-dimethylformamide (DMF), dichloromethane (CH2Cl2) and ethanol (EtOH) were supplied by Shanghai Ebene Chemical Reagent Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl) and nitric acid (HNO3) were purchased from Shanghai City Kant Chemical Co., Ltd. (Qingdao, China). Sodium hydroxide (NaOH) was supplied by Tianjin Hongyan Chemical Reagent Factory (Tianjin, China). Phosphoric acid (H3PO4) was purchased from Tianjin Kaixin Chemical Co., Ltd.
Ultra-pure water (18.2 MΩ) was obtained by a model Mingche D-24UV ultra-pure water system (Millipore, France).

Nicosulfuron, thifensulfuronmethyl, metsulfuronmethyl, benzisulfuronmethyl, pyrazosulfuronethyl and chlorimuronethyl were purchased from Shanghai Pesticide Testing Research Center (Shanghai, China). Sulfometuronmethyl was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The structural formula and pKa values of the seven tested SUs were shown in Fig. S1. 10 mg of nicosulfuron, thifensulfuronmethyl, metsulfuronmethyl, benzisulfuronmethyl, pyrazosulfuronethyl, sulfometuronmethyl and chlorimuronethyl powders were respectively dissolved into 10 mL acetone to prepare 1000 mg L⁻¹ stock solutions. Then, the stock solutions were put at 4 °C in the dark.

The environmental water samples were collected from our laboratory, Dagu River and Huanghai Sea, and Fig. S2 schematically shows the sampling points. All samples were filtered through the 0.45 μm filter membrane, and then placed in the refrigerator at 4 °C for further analysis.

### 2.2. Apparatus

Agilent 1100 series HPLC device was used to detect the concentration of SUs. The HPLC contained a quaternary delivery pump, an auto-sampler, a diode array UV detector and a thermostatted column compartment. A personal computer equipped with Agilent ChemStation for HPLC was used to process the data. A ZORBAX SB-C₁₈ column (4.6 × 250 mm, 5 μm) was used as separation column of seven SUs at 30 °C. The sample injection volume was 20 μL. The test wavelength was set at 230 nm, and the reference wavelength was 360 nm. The mobile phase consisted of acetonitrile and water (pH = 3.0, adjusted by phosphoric acid). The gradient elution procedure was as following: 20% acetonitrile (0 min); 35% acetonitrile (10 min, hold 15 min); 40% acetonitrile (30 min, hold 10 min); 50% acetonitrile (40 min). The flow rate was 1 mL min⁻¹.

### 2.3. Synthesis of MIL-53–PVDF MMM

The synthesis process of MIL-53–PVDF MMM was schematically shown in Fig. 1. Firstly, the solvothermal synthesis of MIL-53 was according to that reported [39]. 3.38 g aluminum nitrate nonahydrate and 1.00 g terephthalic acid were dispersed in a mixture solution of 44 mL DMF and 16 mL ultrapure water, and mechanically stirred in a water bath at 40 °C for 2 h. The mixture was transferred to an autoclave with a volume of 100 mL, and then reacted in an oven at 130 °C for 48 h. After cooling, the mixture was soaked in DMF for 24 h, and placed in an oven at 150 °C for 12 h. Finally, the white powder obtained was MIL-53.

Then, the synthesis of MIL-53–PVDF MMM was prepared by referring to the reported method [29]. 120 mg MIL-53 powder was dispersed in 5 mL acetone for 30 min in an ultrasonic bath. Then 2 mL PVDF solution (100 mg PVDF powder dissolved in 4 mL DMF) was added dropwise to the above mixture, and sonicated for 30 min. The acetone was then removed by rotary evaporation, and the obtained mixture was uniformly coated on the glass substrate to form membrane. The membrane was placed in a isothermal oven at 70 °C for 1 h to remove the solvent. After completely dried, the membrane was layered by dipping the self-standing membrane from the glass substrate into methanol, and then dried in the air.

### 2.4. Characterization

The microscopic morphology of MIL-53–PVDF MMM was determined by Hitachi S-4800 scanning electron microscope (Hitachi, Japan). The X-ray diffractometer (XRD) patterns of MIL-53 and MIL-53–PVDF MMM were measured by D8 Advance X-ray diffractometer (Bruker, USA). The Fourier transform infrared spectrum (FT-IR) of MIL-53 and MIL-53–PVDF MMM were recorded in the wave number range of 4000–700 cm⁻¹ using a PerkinElmer Frontier spectrometer and Frontier Nicolet iN10 infrared spectrometer (Thermo Fisher, USA), respectively. The water contact angle (CA) of MIL-53–PVDF MMM was determined by an acid-base titration method [40]. 0.1 g membrane was shaken with 100 mL CO₂ free aqueous solution. A recorded volume of 0.1 mol L⁻¹ HNO₃ or NaOH was added into the mixture.

![Fig. 1. Schematic illustration of the preparation process for the MIL-53–PVDF MMM.](image-url)
Time interval between each addition was maintained around 20 min to stabilize the solution pH and the pH value of the mixture was then recorded. The surface charge of membrane (σ) was determined by the potentiometric titration experiments, and calculated by the following equation.

$$\sigma = \frac{(C_A + C_B + [OH^-] + [H^+]) F}{m}$$

where \(C_A\) and \(C_B\) are the concentration of acid and base added to reach a certain pH, \([H^+]\) and \([OH^-]\) are the concentrations of \(H^+\) and \(OH^-\), \(F\) is the faraday's constant \((96,490 \, \text{C mol}^{-1})\), and \(m\) is the membrane dosage (g).

### 2.5. DME procedure

Fig. 2 illustrates the DME process. The MIL-53–PVDF MMM activated with methanol was placed in 100 mL concentration of 5 lμg L\(^{-1}\) SUs solution with certain pH and salinity. After shaken in a constant temperature water bath shaker for 25 min, the MIL-53–PVDF MMM was taken out and eluted twice with methanol by shaking for 30 min each time, and then the eluate was placed in a gentle stream of nitrogen blower and blown to near dryness. After reconstitution with a mixture of 0.4 mL of 20% acetonitrile and 80% phosphoric acid water, the solution was passed through a 0.45 \(\mu\)m filter and detected by HPLC. In order to obtain the best extraction performance of MIL-53–PVDF MMM for SUs, the DME conditions were optimized, including the type of extraction membranes, the MOF dosage in the MMM, the type and volume of eluent, the pH of the sample solution, the extraction time, the salinity and the elution time. Specific experimental parameters are listed in Table S1.

### 3. Results and discussion

#### 3.1. Characterization of MIL-53–PVDF MMM

MIL-53 and MIL-53–PVDF MMM were characterized by SEM, XRD and FT-IR. Fig. 3a and b show the SEM images with different magnifications of MIL-53–PVDF MMM. The cubic crystal of MIL-53 can be seen on the MIL-53–PVDF MMM with a size of about 100 nm. MIL-53 particles were uniformly dispersed on the membrane. The microscopic morphology of MIL-53 on MIL-53–PVDF MMM was consistent with that reported [41].

Fig. 4 shows the XRD patterns. As seen from Fig. 4a, the characteristic peaks of MIL-53 were located at 2θ = 9.3°, 17.8°, 21.8°, and 27.2°, which were corresponding to (0 0 1), (1 0 3), (0 0 2), and (0 5 1), respectively, and consistent with that reported [42]. The XRD pattern of MIL-53–PVDF MMM (Fig. 4b) was almost the same as that of MIL-53, indicating that its preparation into membrane did not have much influence on the crystal structure of MOFs.

Fig. 5 shows the FT-IR of MIL-53, MIL-53–PVDF MMM and PVDF over the wavenumber range of 4000–700 cm\(^{-1}\). As can be seen from Fig. 5a, the absorption band at 3425 cm\(^{-1}\) belonged to the –OH characteristic peak, and the characteristic peak absorption band of C=O was at 1696 cm\(^{-1}\). The two absorption bands at 1600 cm\(^{-1}\) and 1500 cm\(^{-1}\) in Fig. 5a and b could be attributed to the stretching vibration of C=C in the benzene ring. These FT-IR
results were consistent with those reported in the literature [43]. The peak of 1450 cm\(^{-1}\) in Fig. 5 corresponded to the deformation of –CH\(_2\). In addition, in Fig. 5b and c, there was C–F stretching vibration absorption band at 1200 cm\(^{-1}\). Consequently, the MIL-53–PVDF MMM was proved to be successfully synthesized.

The contact angle measurement provides the information on the surface hydrophilicity of the membrane. Fig. 6 shows that the water contact angle of the original PVDF membrane and MIL-53–PVDF MMM largely decreased from 119° to 89.5°. This indicated that the incorporation of the raw material MIL-53 did improve the hydrophilicity of the membrane, thereby improving the permeability of the MIL-53–PVDF MMM [44].

The mechanical strength of membranes is a key factor to evaluate their practical application potential [45]. Thus, the mechanical strength of MIL-53–PVDF MMM was examined by testing tensile strength and elongation at break. The mechanical properties of MIL-53–PVDF MMM and PVDF membrane were listed in Table S2. Overall, the tensile strength and elongation at break of MIL-53–PVDF MMM showed a decrease through the combination and cross-linking with PVDF. This explained that cross-linking does cause the MIL-53–PVDF MMM to become more brittle [46]. On the other hand, the addition of MIL-53 particles resulted in a decrease in the mechanical strength of the membrane. According to the literature [47], the addition of overloaded nanoparticles to such a cross-linking solution can result in reduced film elasticity, reduced impact strength and associated mechanical properties, and thereby producing a more fragile membrane. This phenomenon has also been observed in other studies [45]. Although the MIL-53–PVDF MMM exhibited relatively poor mechanical strength, the prepared membrane still exhibits a complete sheet film morphology of 0.065 mm thick. The DME process of the target compounds in water sample wouldn’t be affected by the application of a similar application force to cause membrane breakage.

Fig. 7 demonstrates the surface charge of MIL-53–PVDF MMM as a function of solution pH. The surface charge decreased with the increases in solution pH. The PZC of MIL-53–PVDF MMM was 4.0 according to the figure. This means that when the pH was lower than the 4.0, the surface charge of MIL-53–PVDF MMM was positive; at pH higher than 4.0, the surface charge of MIL-53–PVDF MMM was negative.

### 3.2. Optimization of MIL-53–PVDF MMM based DME conditions

The as-synthesized MIL-53–PVDF MMM was used for DME. The DME performance of contaminants in water was affected by many factors, including the type of extraction membranes, the MOF
dosage in the MMM, the type and volume of eluent, the pH of the sample solution, the extraction time, the salinity and the elution time. The extraction performance toward seven SUs were investigated under different conditions, and each optimization factor was parallel to three experiments. All results were shown in Fig. 8.

3.2.1. Effect of type of membrane

In order to select a suitable MOF MMM for the extraction of SUs in water, four common MOF MMMs namely MIL-53–PVDF MMM, UiO-66–PVDF MMM, ZIF-8–PVDF MMM and PVDF MMM, were prepared in this experiment. Their preparation details and BET parameters were given in Experimental S1 and Table S3, respectively. Among them, MIL-53 and UiO-66 were porous materials, which were formed by coordination of the coordination metal centers Al and Zr with the organic ligand terephthalic acid, respectively [48,49]. Since the aromatic ring in their ligand formed a π–π interaction with aromatic contaminants [9], UiO-66 and MIL-53 were applied to the adsorption of the contaminants containing benzene rings [50–52]. ZIF-8 in the ZIF series has permanent pore characteristics, high thermal stability and very good chemical stability [53]. In its applications, the imino group in its ligand 2-methylimidazole can form a hydrogen bond with a group such as hydrogen bonding, and crystallinity of the film, thereby lowering the separation performance of the membrane. When the amount of MIL-53 powder was 120 mg, the enrichment ability of the seven SUs was the best. Therefore, 120 mg MIL-53 powder was used to synthesize the MIL-53–PVDF MMM.

3.2.2. Effect of MOF dosage

In order to find out the optimized dosage of MIL-53 in the synthesis of MIL-53–PVDF MMM, the amount of PVDF remained 120 mg while the amount of MIL-53 varied from 40 to 140 mg. Then the extraction ability of above membranes for SUs in water was investigated. As shown in Fig. 8B, the extraction performance gradually increased as the amount of MIL-53 increased from 40 to 120 mg, but the extraction performance decreased significantly from 120 to 140 mg. This could be attributed to the fact that excess MOF would be stacked on top of each other in the membrane to form non-selective interface defects and then reduce the separation performance of the membrane [58]. In addition, excessive MOF also led to the increases in the thickness of the membrane, hydrogen bonding, and crystallinity of the film, thereby lowering the separation performance of the membrane. When the amount...
Fig. 8. Effects of (A) type of membranes, (B) amount of MOF, (C) type of eluent, (D) volume of eluent, (E) solution pH, (F) extraction time, (G) salinity, and (H) elution time on the DME efficiency for seven SUs.
compounds, indicating the longer extraction time did not benefit the extraction. This is most likely owing to that SUs are easily hydrolyzed in dilute solutions and acidic solutions [61], and are difficult to stabilize, so that loss of analytes and degradation will reduce the final extraction efficiency [60]. Therefore, the extraction time of the latter experiment was 25 min.

3.2.6. Effect of salinity
Salinity can promote or inhibit the interaction between adsorbate and adsorbent by compressing the two-electron layer, so the effect of salinity (0, 0.5, 1, 10, 20 and 26.5% (saturated)) on the membrane extraction of SUs in water were investigated and experimental results were shown in Fig. 8G. The extraction performance of the seven SUs increased with the increase of salinity from 0 to 0.5%, while decreased when the salinity was greater than 1%. This can be ascribed to that NaCl may reduce mass transfer by increasing the thickness of the Nernst diffusion layer [62]. Proper salinity would cause high ionic strength leading to the reduction of solubility of SUs in water and the increase of extraction on the membranes; however, the higher salinity would increase the viscosity of the solution resulting in the decrease of molecular mass transfer efficiency and extraction efficiency [63]. This phenomenon can be explained by that high concentrations of salt may block the pore passage, which hinders further mass transfer between the two phases [50]. Therefore, 0.5% salinity was chosen for the tested solution.

3.2.7. Effect of elution time
The extraction performances of SUs in water after eluted for 15, 20, 25, 30, 35 and 40 min for two times were investigated. As see from Fig. 8H, the extraction efficiencies were slightly improved with prolonged elution time. This is because as the elution time increased, the amount of exchange of methanol with the SUs on the MIL-53–PVDF MMM gradually increased, and the SUs to be tested was thus completely eluted. However, the increase was small and stabilized after $2 \times 30$ min. By considering the seven SUs, the elution time of $2 \times 30$ min were selected for the following experiments.

3.3. Analytical performance of the DME–HPLC method
Under the above optimized DME conditions, 100 mL water samples containing seven SUs at 0.01, 0.05, 0.1, 0.5, 1, 2, 5, and 10 $\mu$g L$^{-1}$ individual, respectively, were subjected to extraction

![HPLC-UV chromatograms of seven SUs in three real water samples](Fig. 9). HPLC-UV chromatograms of seven SUs in three real water samples of (A) tap water, (B) seawater and (C) surface water, after DME without spiking (a) and spiked with all the SUs individual at 8.00 $\mu$g L$^{-1}$ (b). Peak identification: (1) nicosulfuron; (2) thifensulfuronmethyl, (3) metsulfuronmethyl, (4) sulfometuronmethyl, (5) bensulfuronmethyl, (6) pyrazosulfuronethyl and (7) chlorimuronethyl. Extraction conditions were the optimal conditions.
and enrichment, followed by HPLC determination. Table S4 lists the regression equations, correlation coefficients (r), linear ranges, limits of detection (LOD), and limits of quantitation (LOQ). As seen, a good linearity in the range of 0.03–10 μgL⁻¹ for chlorimuronethyl was attained with r of 0.9915; a wide linear range was exhibited between 0.01 and 10 μgL⁻¹ for other six SUs, with r between 0.9900 and 0.9980. High enrichment ability was obtained with an enrichment factor of 250, and thereby presented low LODs and LOQs within 3.75–10.30 ng L⁻¹ and 12.49–34.30 ng L⁻¹, respectively, based on signal-to-noise ratio (S/N) of 3 and 10, respectively. This obtained LOQ is much lower than the permitted maximum residue level (MRL) of 1–5 μgL⁻¹ in European Union’s Water Law (75/440/EEC) and 0.1 μgL⁻¹ in European Drinking-water Quality Directive (80/778/EC). So, the MIL-53–PVDF MMM owned high enrichment ability and the MIL-53–PVDF MMM based DME coupled with HPLC-UV could highly sensitively detect trace SUs.

Furthermore, three water samples were prepared with SUs concentrations of 0.10, 1.00 and 8.00 μgL⁻¹ individual, respectively. According to the DME process, each concentration point was measured six times a day to examine the intra-day precision; the three concentrations were measured once a day, and the inter-day precision was measured for six days. As listed in Table S5, the relative standard deviations (RSDs) for intra-day and inter-day recoveries of the seven SUs were in a range of 4.20–13.71% and 4.35–14.25%, respectively. These results indicated the method had high sensitivity and good reproducibility. Therefore, the DME-HPLC method could accurately quantify trace SUs.

3.4. Application of the DME-HPLC to real water samples

In order to verify the practical feasibility of MIL-53–PVDF MMM, three real water samples were analyzed. The HPLC chromatograms of blank (a) and spiked (b) tap water (A), seawater (B) and surface water (C) samples were shown in Fig. 9. As seen, endogenous SUs were not detected in the real water samples. The spiked water samples with low, medium and high concentrations of 0.10, 1.00 and 8.00 μgL⁻¹, respectively, were prepared for recovery experiments. Each concentration point was measured in triplicate. The average value, RSDs, and spiked recoveries of three measurements were calculated. As listed in Table S6, satisfactory recoveries were attained of 79.88–111.00% with RSDs of 1.69–14.67% for the spiked tap water samples, 77.60–111.00% with RSDs of 1.28–13.09% for the spiked seawater samples, and 80.67–107.13% with RSDs of 1.50–14.41% for the spiked surface water samples, respectively. The results suggested that the MIL-53–PVDF MMM was practically feasible for highly efficient DME of SUs in complicated environmental water samples, and consequently the SUs monitoring and removal from aqueous environments could be successfully performed by DME-HPLC.

3.5. Regeneration of MIL-53–PVDF MMM

To investigate the possibility of reusing MIL-53–PVDF MMM, adsorption-desorption cycles were performed on DME and the results were shown in Fig. 10. After 25 cycles, the recoveries of...
SUs decreased by about 20%, indicating that MIL-53–PVDF MMM had high stability and good reusability.

3.6. Method performance comparison

In order to compare the analysis performance toward SUs determination by HPLC-UV in water sample of the developed DME method with those reported analytical methods, several pretreatment techniques were chosen, including LLE [1], SPE [64,65], SPME [7,8], SPMEM [6], SBS [9], and continuous flow liquid membrane extraction (CFLME) [10,11], as summarized in Table 1. For traditional sample preparation methods, the LLE is laborious, time-consuming and labor-intensive; the SPE requires an extraction device and its extraction column is easy to block; the CFLME requires additional power equipment and consumes more energy. But the sample pretreatment method we use, MOF based DME, is simple to operate and requires no additional equipment. It is worth mentioning that the LOD of our established method is the lowest (Table 1). In addition, the LOD is lower than that of some methods using HPLC-MS detection [2,3,66]. In general, our prepared MIL-53–PVDF MMM is easily separated from water and exhibits good recyclability and reusability, and thereby the developed method possesses the advantages of high sensitivity, easy operation and better application prospect.

4. Conclusions

In summary, novel MIL-53–PVDF MMM was prepared for DME of seven SUs in environmental water samples coupled with HPLC, and a simple, fast, efficient and sensitive method was established for SUs determination. The MIL-53–PVDF MMM presented high stability and enrichment ability, and could be effectively reused for at least 25 cycles, as well as good application perspectives in the enrichment of pollutants in aqueous environments. Given the advantages, further research should focus on the development of MOFs and relevant polymers to improve the performances of MMM, and thereby MMM related highly efficient, convenient and reliable pretreatment techniques.

Declaration of Competing Interest

The authors declare no conflict of interest.

Acknowledgements

The authors acknowledge support from the National Natural Science Foundation of China (21547002, 21804010, 21876199), the National Science Foundation of Shandong Province (ZR2019MB046), and the Department of Science and Technology of Shandong Province of China (GG20170929005).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2019.06.082.

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