Short communication

Vortex-assisted solid-phase extraction based on metal-organic framework/chitosan-functionalized hydrophilic sponge column for determination of triazine herbicides in environmental water by liquid chromatography-tandem mass spectrometry

Yanxiao Jiang[a], Zucheng Qin[b], Fanghui Liang[c], Jingkang Li[a], Ying Sun[a], Xinghua Wang[a], Pinyi Ma[a,*], Daqian Song[a,*]

[a] *College of Chemistry, Jilin University, Changchun 130012, China*
[b] *Hunan Warrant Pharmaceutical Company Ltd., Changsha 410000, China*
[c] *Department of Pharmacy, Changchun Medical College, Changchun 130031, China*

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ABSTRACT

In the presented work, MIL-101(Cr) and chitosan were directly embedded on the skeleton of melamine sponge material using a simple and environmentally friendly method. Chitosan acts not only as an adhesive during the preparation of functionalized sponges, but also as an adsorption adjuvant in herbicide detection. Unlike other polymers, chitosan has excellent hydrophilicity and contains numerous adsorption sites; thus, it enables the sponge material to be used for determination of contaminants in an aqueous phase. Scanning electron microscopic (SEM) analysis showed that the coating material was uniformly distributed on the skeleton of melamine sponge. The prepared material was used as a sorbent in a vortex-assisted solid-phase extraction and combined with high performance liquid phase tandem mass spectrometry for the extraction and trace determination of six triazines in water samples (Atraton, Desmetryn, Prometon, Ametryn, Prometryn and Dimethametryn). Several parameters that affect the extraction efficiencies were investigated. Under the optimal conditions (MIL-101(Cr) loading, 150 mg; sample pH, 7; salt concentration, 0%; adsorption time, 3 min; desorption solvent, 1.5 mL acetonitrile; desorption time, 4 min), the proposed method was successfully used in the determination of trace triazines in five real water samples (drinking water, tap water, lake waters and river water), satisfactory recoveries were obtained in the range of 78.9%–118.6%. The limits of detection of the proposed method in detecting triazine herbicides in spiked water samples ranged from 0.014 to 0.045 ng mL^{-1}.

1. Introduction

With continuous growth of the world population, food problem is one of the problems that human is facing. Field grass injury is one of the main factors leading to crop loss [1]. Herbicides have been widely used in agriculture to kill insects, fungi and other organisms that harm crop growth to increase crop yields [2–4]. The human dependency on herbicides not only causes the problem on changes of weed population and the increase of weed resistance [5,6], but also causes the problem on herbicide residues [7]. As a traditional herbicide, triazine inhibits the growth of weeds by disrupting their photosynthetic pathway. In agricultural farming and production processes, triazine herbicides not only can be transferred to food through crops, but also can enter the water system. The residues of herbicides and their metabolites in water can cause serious ecological problems [8,9], and even can directly endanger human health [10,11]. Therefore, it is highly important to develop a high sensitivity analytical method for detection of herbicide residue in water samples.

Recently, many methods for detecting herbicide residues have been reported, including capillary electrophoresis (CE) [12], surface-enhanced Raman spectroscopy (SERS) [13], gas chromatography (GC) [14] and liquid chromatography (LC) [15,16]. Combined with different sample pretreatment methods, liquid chromatography can be used to detect herbicide residues in different matrices. In addition, due to its low detection limit, the liquid chromatography has been widely applied to detect herbicide residues.

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* Corresponding authors.
  E-mail addresses: mapinyi@jlu.edu.cn (P. Ma), songdq@jlu.edu.cn (D. Song).

MIL-101(Cr) was first synthesized by Ferey using a hydrothermal method [17]. Due to its excellent properties, including high thermal stability, large surface area and modifiable outer-surface with large area, MIL-101(Cr) is a promising material for use in the adsorption/separation of organic pollutants [18–20]. Recent studies have shown that MIL-101(Cr) can be used as an adsorbent for the analyzing analytes in water samples [21,22]. However, the direct application of MIL-101(Cr) materials in sample pretreatment may require multiple centrifugation steps, causing the operation to be cumbersome.

Recently, MOF-based mixed matrix membranes (MMMs) have been prepared by dispersing MOF in a polyvinylidene difluoride matrix. The membranes have attracted increasing attention for its applicability in separation technology as they can be directly separated from the matrix without further centrifugation steps or the need of a magnet [23,24]. In addition, these MOF-polymeric composite membranes can retain the unique structural properties of the MOF materials and can enhance the performance of the polymeric membranes [25]. However, the preparation of polymeric membranes is time-consuming, requires additional equipment and cannot be done in batches; these are the disadvantages that limit the practical application and commercialization of the membrane materials. In addition, the hydrophobicity of the polyvinylidene difluoride (PVDF) also limits the application of the polymeric membranes in an aqueous phase. Among many available biopolymers, chitosan (CS) is a promising biopolymer for adsorption applications due to the presence of a large number of amino and hydroxyl groups [26,27]. These groups allow chitosan to be dissolved in acidic aqueous solution, making it a bioadhesive [28]. Numerous studies have shown that chitosan has good film-forming ability, adhesion characteristics and an ability to improve permeability [29–31]. The high porosity (> 99%) and the unique crosslinking network structure (skeleton diameter, 3–10 μm) of melamine sponge (MeS) provide the possibility for coating materials to modify the sponge [32]. In addition, the melamine sponge can be easily removed from the water phase to simplify the pretreatment steps.

In this study, a simple one-step infiltration method for the preparation of MIL-101(Cr)/CS-SC was proposed. The prepared material was used as an adsorbent in solid-phase extraction (SPE) in conjunction with HPLC-MS/MS to determine triazine herbicides. Several important experimental parameters were optimized to achieve high extraction performance. The proposed method was successfully applied to determine triazine herbicides in five real water samples (drinking water, tap water, lake waters and river water) under the optimized conditions.

2. Experimental

2.1. Materials and chemicals

Commercial melamine sponges were bought from a local market (Changchun, China). The synthetic materials of MIL-101(Cr) can be found in Supplementary Information, Chitosan was provided by Aladdin Reagent Corporation (Shanghai, China). Chromatography methanol was used obtained by J&K Scientific Co., Ltd. (Beijing, China).

All standard substances of triazine herbicides (purity > 99%) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Their physico-chemical properties are listed in Table 1. The single standard solution was prepared by adding the required volume of the chromatographic-grade methanol to the solid triazine standard. The mixed working solution was prepared by mixing the single standard solution with HPLC-grade methanol and store at 4°C.

2.2. Real sample collection

Two domestic water samples (sample 1, drinking water and sample 2, tap water) were collected in our laboratory (Jilin University, Changchun, China). Three environmental water samples, include two lake waters (sample 3–4) and river water (sample 5), were collected in Changchun city (Yanhu, Qinghu and Yitong river, China). All water samples were filtered by a 0.22-μm nylon filter film before sample preparation.

2.3. Instrument

The chromatographic separation of triazine herbicides was performed on an Agilent 1260 Infinity HPLC apparatus equipped with a reverse phase Thermo syncronis C18 (50 mm × 2.1 mm, 1.7 μm particle size) analytical column. The LC analysis was conducted in isocratic mode: HPLC-grade methanol and ultra-pure water (90:10, v/v), 0.2 mL min^{-1}. The ultra-pure water was prepared by a Millipore purification device (New York, USA). The injection volume was set at 5 μL.

A Thermofisher TSQ Quantum Access MAX mass spectrometer was used for the identification and quantification of analytes with a multiple reaction monitoring (MRM) mode. The parameters of the ESI source (positive ionization mode) and MS/MS product ion were carefully optimized and the results are listed in Table 1. A Hitachi SU-8020 scanning electron microscope (SEM, Japan) and an Rigaku Ultima IV X-ray diffraction spectrometer (XRD, Japan) were used for the characterization of materials.

2.4. Preparation of MIL-101(Cr)/CS-modified sponge column

Melamine sponge was first cut into sponge columns (SC; height × diameter = 1.5 cm × 0.7 cm) using a hole puncher. The sponge columns were then washed with acetone and air dried. MIL-101(Cr) was added into a beaker containing 5 mL of deionized water and then treated with ultrasound for 20 min until the solution became homogeneous. After that, the chitosan solution (1.0 g, acetic acid/deionized water) was added to the above solution, and the resultant mixture was also treated with ultrasound. The sonicated solution (600 μL) was injected into a cube-shaped mold, and a melamine sponge was then pressed several times into the mold until a porous MIL-101(Cr)/chitosan-SC was formed. The obtained sponge column was dried overnight at 85°C. The preparation process of porous MIL-101(Cr)/CS-SCs is shown in Fig. 1.

2.5. Procedure for MIL-101(Cr)/CS-SC-SPE

Illustration of the MIL-101(Cr)/CS-SC-SPE procedure is depicted in Fig. 2. Firstly, 5 mL of spiked water sample (10 ng mL^{-1}, pH=7) was added into a centrifuge tube containing a MIL-101(Cr)/CS functionalized-sponge column followed by vortexing for 3 min. After adsorption, the water phase adsorbed in the functionalized sponge was then removed using a pair of tweezer, and the supernatant was also decanted. 1.5 mL acetonitrile was added to desorb the triazines from the MIL-101(Cr)/CS-SC by vortexing for 4 min. The MIL-101(Cr)/CS-SC was then taken out, and the remaining eluent (acetonitrile containing the desorbed triazines) that was adsorbed on the sponge was also squeezed out using a pair of tweezer. The eluent was evaporated to dryness at 40°C under a mild nitrogen stream, and was later redissolved in 1 mL of methanol. Finally, the resulting solution was filtered by a 0.22-μm nylon syringe filter before HPLC-MS/MS analysis.

Table 1

Physical-chemical properties, precursor ion, product ion, and collision energy of triazine herbicides.

Analyte	CAS number	Molecular weight	Chemical formula	Precursor ion (m/z)	Product ion (m/z)	Collision energy (V)	Tube lens (V)	Retention time (min)	pKa[a]	logP[b]	Structure
Atraton	1610-17-9	211.26	$C_9H_{17}N_5O$	212.13	170.2 100.2	17 29	70 70	1.66	4.31±0.41	2.52±0.23	
Desmetryn	1014-69-3	213.30	$C_8H_{15}N_5S$	214.07	82.3 172.13	31 16	62 62	1.64	3.66±0.41	2.46±0.23	
Prometon	1610-18-0	225.29	$C_{10}H_{19}N_5O$	226.12	187.4 142.1	16 22	65 65	1.73	4.36±0.41	2.88±0.23	
Ametryn	834-12-8	227.33	$C_9H_{17}N_5S$	228.08	186.1 68.3	19 37	64 64	1.73	3.71±0.41	2.97±0.22	
Prometryn	7287-19-6	241.36	$C_{10}H_{19}N_5S$	242.09	158.1 200.1	22 18	70 70	1.84	3.76±0.41	3.32±0.23	
Dimethametryn	22936-75-0	255.38	$C_{11}H_{21}N_5S$	256.04	68.3 186.1	39 19	70 70	1.95	3.69±0.10	3.83±0.23	

[a] Ka: acid dissociation constant.

[b] P: octanol-water partition coefficient. pKa and logP values are obtained from SciFinder scholar database (25°C). Spray voltage, 3.5 KV; Vaporizer temperature, 300°C; Sheath gas pressure, 35 dpi; Aux gas pressure, 15 dpi; Capillary temperature, 350°C.
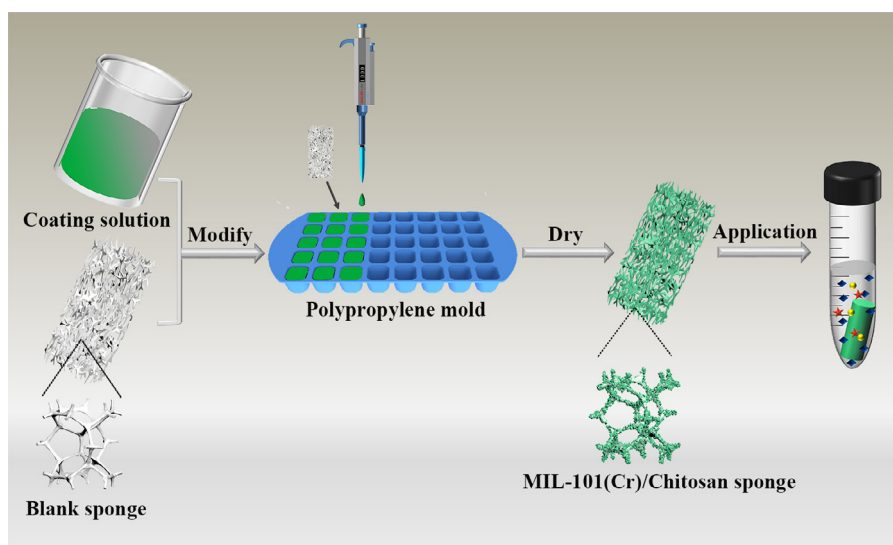
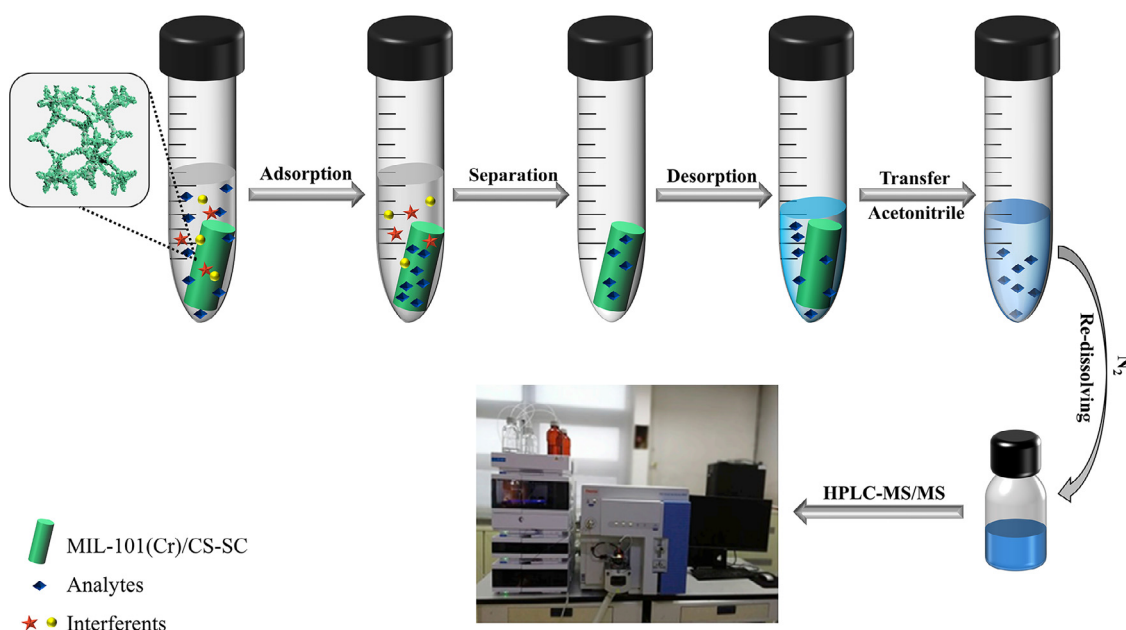**Fig. 1.** Preparation of MIL-101(Cr)/CS-sponge columns.

Fig. 2. Schematic diagram of MIL-101(Cr)/CS-SC-based vortex-assisted SPE procedure.

3. Results and discussion

3.1. Characterization

MIL-101(Cr) was prepared by the hydrothermal method described in Hatton et al., [33] and the procedure can be found in Supplementary Information. The X-ray diffraction (XRD) patterns (Fig. 3L) of the MIL-101(Cr) is in good agreement with the previously reported characteristic peaks of MIL-101(Cr) [17]. The SEM image (Fig. 3L) shows that MIL-101(Cr) crystals have octahedral shape with an average size of 194 nm.

The prepared MIL-101(Cr)/CS-SC was characterized by SEM, and the results are presented in Fig. 3. Sponges containing different MIL-101(Cr) loadings were prepared (all by the same procedure), and a blank sponge (a sponge without MIL-101(Cr)) was used as a control. The results illustrated in Fig. 3(A–K) show that the color of the MIL-101(Cr)/CS-SCs was gradually deepen as the MIL-101(Cr) loading increased. As shown in Fig. 3A, the unmodified SC is white and has a 3D network structure with aperture sizes ranging from 100 to 200 μm. This is the unique structure that allows the sponge to act as a support for the loading of MIL-101(Cr) and CS on its surface and in its pores. It can be seen from Fig. 3(A and B) that the chitosan was successfully modified on the blank sponge and the sponge color did not change significantly. By contrast, the unmodified SC and MIL-101(Cr)/CS-SCs were distinctly different: the thickness and density of the coating appeared to increase with increasing MIL-101(Cr) loading. These findings indicate that the MIL-101(Cr)/CS-SCs were successfully prepared by the present method. The increasing number of the adsorption sites allows the adsorbent to efficiently adsorb the target analytes. The optimal loading will be discussed in more detail in Section 3.2.
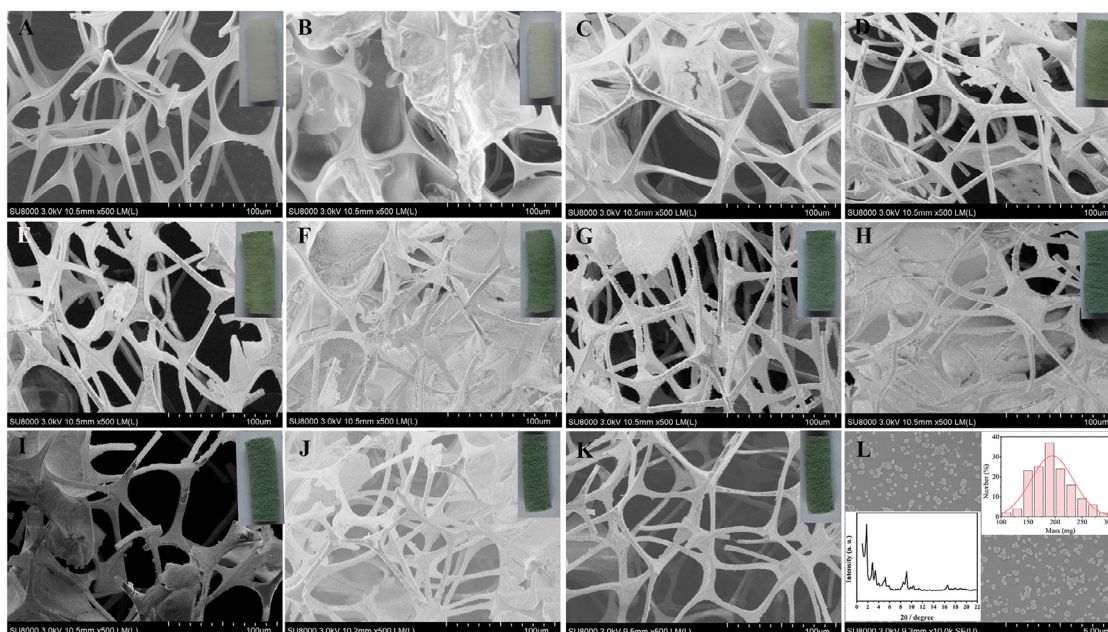
Fig. 3. SEM and digital images of blank sponge column (A), sponge column modified with CS (B), and sponge columns modified with MIL-101(Cr) at different loadings: 10, 30, 50, 75, 100, 125, 150, 175, and 200 mg (C–K). SEM image (L) of the prepared MIL-101(Cr), inset: X-ray pattern and particle size distribution.
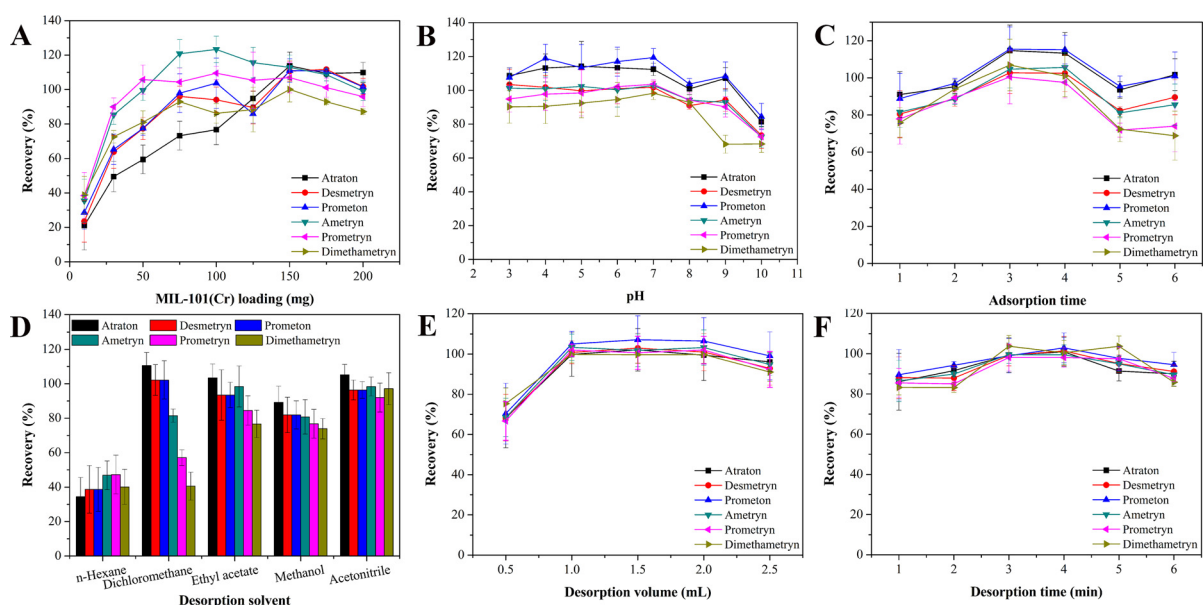

Fig. 4. Effects of MIL-101(Cr) loading (A), sample pH (B), adsorption time (C), type of desorption solvent (D), volume of desorption solvent (E), and desorption time (F) on recovery; spiked concentration of 10 ng mL^{-1}.

3.2. Optimization of conditions

3.2.1. Effect of MIL-101(Cr) loading

To obtain optimum loading, MIL-101(Cr)/CS-sponge columns were prepared using different amounts of MIL-101(Cr) (10, 30, 50, 75, 100, 125, 150, 175, and 200 mg), and their performances were compared. As shown in Fig. 4A, the functionalized sponge had the best extraction recoveries for all triazines when the amount of MIL-101(Cr) added was 150 mg, and the extraction recoveries were slightly decreased when the loadings were higher than 150 mg. This is due to the insufficient reagent for desorption of target analytes from excessive loading of MIL-101(Cr). Hence, the loading of 150 mg was selected for subsequent experiments. Nine MIL-101(Cr)/CS-SCs were prepared per batch using the cur-

rent method. The mass distribution diagram ($n = 50$) of the blank sponge, chitosan-modified sponge and the MIL-101(Cr)/Chitosan-sponge column modified with MIL-101(Cr) at the optimal loading is presented in Fig. 5. After coating treatment-functionalization, the mass of sponge column changed from 6.02 mg to 9.67 mg and 22.75 mg, revealing the successful coating of chitosan and MIL-101(Cr)/Chitosan onto sponge column, respectively.

3.2.2. Effect of sample pH

The sample pH can affect the binding site on the surface of the adsorbent and the existing form of the analytes, thus can affect their extraction efficiency. In this study, the effect of the sample pH from pH 3 to pH 10 on the extraction recovery was investigated. The pKa values (acidity coefficient) of the six triazines were
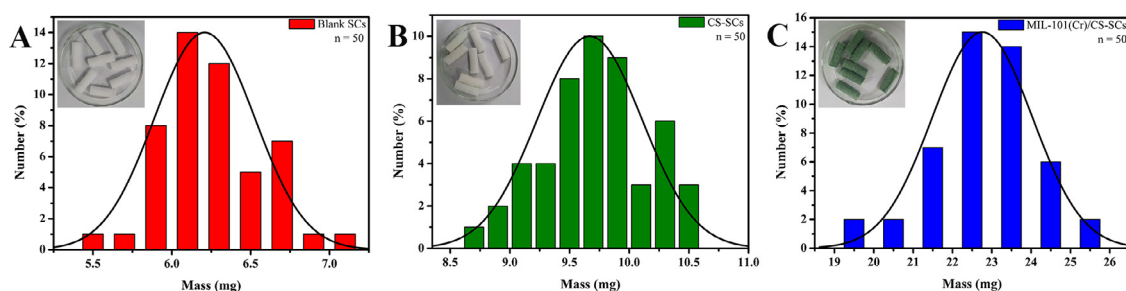
Fig. 5. Mass distribution of blank SC (A), CS-SC (B) and MIL-101(Cr)/CS-SC (C) ($n = 50$).

obtained from SciFinder scholar database, namely atraton, 4.31; desmetryn, 3.66; prometon, 4.36; ametryn, 3.71; prometryn, 3.76; dimethametryn, 3.69. There parameters indicate that all triazines studied are weakly basic and may hydrolyzed under relatively low pH conditions. The result shown in Fig. 4B indicates that the extraction recovery rate gradually decreased when the pH value was greater than 7; the maximal recovery was obtained at pH 7. It is likely that that the interaction between terephthalic acid molecules of skeleton and OH^{-1} under alkaline condition cause the skeleton to collapse. Thus, pH 7 was selected for subsequent experiments.

3.2.3. Effect of salt concentration

To investigate the effect of salt concentration on the extraction efficiency of the adsorbent, a series of experiments at different NaCl masses ranging from 0% to 10% were conducted. The results showed that the extraction recoveries of all triazine herbicides were significantly reduced in the presence of NaCl compared to those of the samples in the absence of NaCl (Fig. S1). It is likely that a small increase of ionic strength may enhance the solubility of compounds. However, as the concentration of NaCl increases, the recovery rate gradually increases. This result may be due to the salting-out effect. Generally, the solubility of analytes in aqueous phase decreases with the increasing ionic strength if the ionic strength in the solution increases beyond a certain value. Nevertheless, the recoveries of the triazine herbicides in the NaCl concentration range investigated were smaller than the recoveries when no NaCl was added. Thus, no NaCl addition was used in subsequent experiments.

3.2.4. Effect of adsorption time

The effect of the adsorption time from 1 to 6 min on the extraction efficiency was examined. As shown in Fig. 4C, the extraction equilibrium was achieved at the adsorption time of 3 min. To ensure the extraction of all triazines is complete and to reduce the pretreatment time, the adsorption time of 3 min was used in subsequent experiments.

3.2.5. Effects of desorption condition

The desorption condition can significantly affect the extraction performance during the sample pretreatment. In the study, five solvents commonly used in chromatographic analysis and their volumes were compared. As can be seen in Fig. 4D, the extraction recoveries of all triazines obtained when acetonitrile was used as the desorption solvent were significantly higher than those obtained when most other solvents were used. This is probably associated with the ACN's broad eluting strength being capable of extracting pesticides of a wide polarity range. The effect of volume of the desorption solvent acetonitrile was also studied. Results shown in Fig. 4E indicate that the maximum recoveries of all triazines were achieved when the volume was 1.5 mL. Thus, 1.5 mL of acetonitrile was chosen in subsequent experiments.

The influence of vortex time from 1 to 6 min used during desorption was also examined. According to Fig. 4F, the extraction

recovery was not significantly fluctuated when the vortex time was larger than 4 min. Considering that high extraction efficiency should be achieved at the shortest possible pre-processing time, 4 min was chosen as a reasonable desorption time.

3.3. Method validation and application

3.3.1. Analytical performance and application in real samples

To investigate the analytical performance of the MIL-101(Cr)/CS-SC-SPE method, several analytical parameters including precisions, linearity, and limits of detection (LODs) were determined under the optimal conditions. The intra-day and inter-day precisions were evaluated by analyzing five replicated spiked samples (5 ng mL^{-1} and 10 ng mL^{-1}) for a day and once a day for five consecutive days, and expressed as relative standard deviation (RSD%). The formula for recovery is described as follows [34]:

$$Recovery = \frac{Amount_{found}}{Amount_{spiked}} \times 100\%$$

where Amount$_{found}$ and Amount$_{spiked}$ represent the amounts of the analytes in the original and spiked sample respectively. The recoveries and RSDs were 83.0–118.7% and 2.3–12.1%, respectively. The commercial availability of sponges makes them widely used for the removal of pollutants in the environment, such as pigments [35], dyes [36] and organic contaminants [37]. However, due to lack of functional groups, blank sponge cannot be used for selective detection of trace analytes. The interaction between the π-π interaction between terephthalic acid molecules loaded on MOFs' surface and analytes, as well as unsaturated metal sites of the sponge material and heteroatoms of analytes, benefit the extraction of analytes by the prepared MIL-101(Cr)/CS-sponge material. The HPLC–MS/MS chromatograms shown in Fig. 6 indicated the functionalized sponge possess good selectivity for the extraction of trace triazine. The working curves of triazines were constructed by plotting the peak areas of the targets in various spiked samples versus the corresponding concentrations. As shown in Table 2, the method had good linearity at the range of 0.50–50.0 ng mL^{-1}, and the correlation coefficients of the regression equations (r) of all triazine herbicides were greater than 0.9930. The limits of detection (LODs) of the proposed method were calculated based on 3 times of the standard deviations of blank samples ($n = 11$) and slopes of the corresponding calibration lines (3sigma/k). The results shown in Table 2 indicate that the LODs with respect to all triazine herbicides were as low as 0.045 ng mL^{-1}. The values were lower than the maximum residue limit (MRL) (0.1 ng mL^{-1}) established in the legislation for an individual triazine in drinking water. These results indicate that the proposed method can be used as a reliable method to detect trace triazine herbicides in water samples.

To verify the applicability of the proposed method, five real water samples spiked at three concentrations (5 ng mL^{-1}, 10 ng mL^{-1} and 50 ng mL^{-1}) were analyzed. The original water samples were examined with the guidance of a national standard of China (GB/T

Table 2
Analytical performance of the present method.

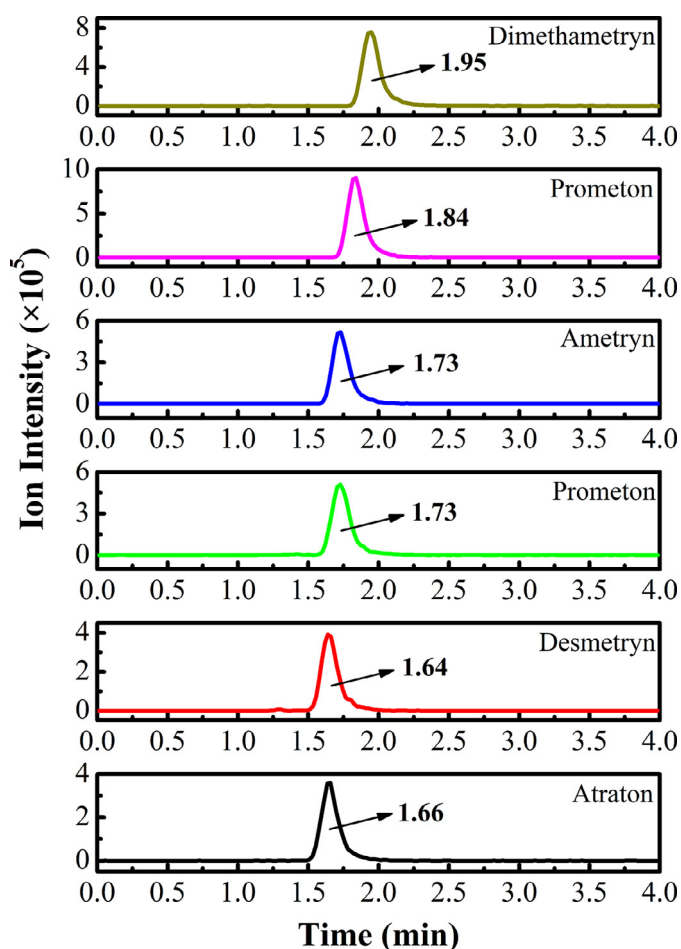| Analyte	Linear range (ng mL^{-1})	Regression equation	Correlation coefficient (r)	Spiked (ng mL^{-1})	Intra-day ($n = 5$) Recovery (%)	RSD (%)	Inter-day ($n = 5$) Recovery (%)	RSD (%)	LOD (ng mL^{-1})
Atraton	0.5–50.0	y = 191200.3x + 264454.1	0.9977	5	107.8	2.3	102.2	10.4	0.016
				10	118.7	11.3	100.7	9.9	
Desmetryn	0.5–50.0	y = 217628.8x + 299160.6	0.9979	5	117.6	2.8	105.4	8.0	0.037
				10	109.3	11.0	107.6	10.1	
Prometon	0.5–50.0	y = 210436.2x + 295640.1	0.9962	5	102.2	5.8	101.9	6.2	0.018
				10	110.5	11.6	105.3	7.7	
Ametryn	0.5–50.0	y = 308460.7x + 516879.4	0.9962	5	111.6	4.3	100.0	9.3	0.014
				10	114.1	12.1	106.4	8.6	
Prometryn	0.5–50.0	y = 336580.2x + 660792.2	0.9930	5	97.9	10.4	83.0	8.9	0.020
				10	113.4	10.8	103.1	7.7	
Dimethametryn	0.5–50.0	y = 562733.1x + 318646.3	0.9989	5	98.8	9.6	95.6	7.7	0.045
				10	106.4	4.3	101.3	4.3	

Fig. 6. HPLC–MS/MS chromatograms of spiked sample 1 obtained under the optimized extraction conditions. Peaks: (1), atraton; (2), desmetryn; (3), prometon; (4), ametryn; (5), prometryn; and (6), dimethametryn. Spiked concentration, 10 ng mL^{-1}.

Fig. 7. The extraction recoveries of MIL-101(Cr)/CS-sponge columns after the multiple repeated use. Spiked concentration, 10 ng mL^{-1}.

triazines has decreased slightly after reused for three times, but it can still reach 82.8%.

3.3.2. Comparison of methods

The performance of the developed MIL-101(Cr)/CS-SC-based vortex-assisted SPE method in the determination of triazine herbicides was compared with that of other reported methods, including GC [39], HPLC [40,41], GC-MS [42] and HPLC-MS/MS [43,44]. The details of the comparison are summarized in Table 4. Several other main aspects of the extraction method, including sample matrix, amount of organic solvent consumption, operating time, detection method, recovery, RSDs and LODs, were also compared. Compared with the traditional SPE, the present extraction method is considerably simpler as it does not need additional centrifugation steps or external magnets, and the MIL-101(Cr)/CS-sponge column used in the present method can be quickly separated from the sample solution. In addition, the volumes of the organic solvents and the operating times (adsorption and desorption times) required for the MIL-101(Cr)/CS-SC-based vortex-assisted solid-phase extraction method were significantly lower than those required for other reported methods. Moreover, its LODs were far lower than the maximum residue limits established in the EU legislation. These data suggest that the established MIL-101(Cr)/CS-SC-based vortex-assisted solid-phase extraction method can determine trace triazines in water samples.

In addition, chitosan-functionalized sponge and blank sponge (without MIL-101(Cr) and chitosan) were also prepared and used as controls to explore the extraction performance. As depicted in Fig. 8A, the extraction performance of the blank sponge col-

21925-2008) [38]. Results showed that there was no triazine herbicides found in the unspiked real water sample. The typical HPLC–MS/MS chromatograms is illustrated in Fig. 6. The extraction recoveries of all triazines in the spiked samples extracted under the same conditions were in a range of 78.9%–118.6% with RSDs below 14.5%. The detailed results can be found in Table 3.

To assess the reusability of the MIL-101(Cr)/CS-sponge material, acetonitrile was used as a cleaning solvent for the reuse of the material. The results shown in Fig. 7 indicated that the recoveries of
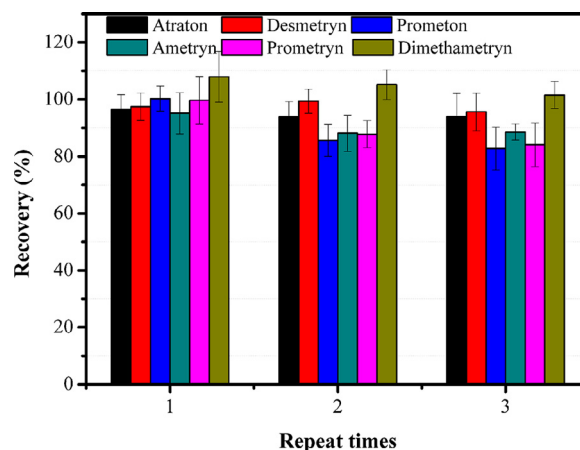
Table 3
Analytical results of real and spiked samples ($n = 3$).

Sample	Spiked (ng mL^{-1})	Atraton Recovery (%)	RSD (%)	Desmetryn Recovery (%)	RSD (%)	Prometon Recovery (%)	RSD (%)	Ametryn Recovery (%)	RSD (%)	Prometryn Recovery (%)	RSD (%)	Dimethametryn Recovery (%)	RSD (%)
Sample1	0	ND											
	5	106.4	0.8	118.6	3.4	99.8	3.8	110.2	5.4	93.0	8.6	94.1	7.5
	10	100.9	7.2	101.4	7.2	103.0	7.4	99.5	4.8	98.2	4.8	100.5	6.2
	50	89.0	5.8	89.4	9.7	88.2	7.1	88.7	10.7	86.1	7.4	88.3	7.4
Sample2	0	ND											
	5	97.6	6.2	102.2	7.6	97.2	3.4	104.5	5.1	103.7	4.1	99.7	6.1
	10	85.0	3.0	98.7	5.6	97.6	5.9	106.5	6.4	100.9	6.7	98.9	4.6
	50	89.5	1.6	96.1	2.6	92.8	9.8	88.8	5.9	94.3	4.3	97.0	5.2
Sample3	0	ND											
	5	85.1	7.3	86.2	6.8	91.9	14.0	80.6	6.8	80.3	9.2	93.8	6.0
	10	82.3	5.3	92.8	4.0	97.8	4.8	103.0	3.7	107.2	3.5	93.3	3.0
	50	80.3	4.6	89.4	6.8	83.6	8.0	85.7	4.6	94.2	8.2	100.4	2.3
Sample4	0	ND											
	5	102.1	6.7	103.7	7.1	108.2	8.1	94.8	1.8	90.1	6.8	91.0	6.5
	10	101.7	4.8	103.7	4.1	105.7	2.5	106.5	3.3	101.6	1.8	95.6	3.0
	50	94.1	1.8	96.5	6.6	98.4	5.0	96.6	2.6	102.8	4.5	100.5	10.4
Sample5	0	ND											
	5	85.1	14.5	84.4	4.1	90.0	1.0	87.8	2.5	78.9	1.5	100.0	0.4
	10	81.9	7.6	94.4	5.8	95.7	1.3	98.0	5.6	100.6	7.1	103.8	6.4
	50	82.4	5.4	93.3	4.4	86.6	9.6	87.7	6.8	94.2	7.1	100.0	9.2

ND, not detected.

Table 4

Comparison of the MIL-101(Cr)/CS-sponge column based on V-SPE method with other reported methods.

Matrix	Analytes	Extraction method	Organic solvent (mL)	Operating time	Analytical technique	Recovery (%)	RSD (%)	LODs (ng mL^{-1})	Ref.
Wine	Organophosphorus triazine	USVA-DLLME[a]	1 mL NaH$_2$PO$_4$ 250 μL C$_2$H$_4$Cl$_2$	30 s vortex + 10 min ultrasound	GC-NPD	92.0–103.4	≤9.0	0.007–0.07	[39]
Tea beverage	Triazines	EA-DLLME[b]	0.3 g sodium bicarbonate 1 mL ionic liquid 0.37 g NH$_4$PF$_6$ 4 mL diethyl ether	2 min extraction 5 min centrifugation + 3 min shake + 4 mL diethyl ether evaporation	HPLC-UV	76.3–135.9	9.3	0.08	[40]
Environmental water	Triazines	MSPE[c]	5 mL methanol 0.5 mL ACN	20 min shake + 1 min vortex	HPLC-DAD	89.0–96.2	3.4–5.2	0.025–0.040	[41]
Natural water	Nine herbicides	SPME[d]		30 min extraction + 10 min desorption	GC-MS/MS	–	≤15.0	0.01	[42]
Tap water Environmental water	Triazines	MIP-SPE[e]	3 mL acetic acid/ACN	10 min shake + 3 min ultrasound + 3 mL acetic acid/CAN evaporation	HPLC-MS/MS	88.0–100.0	2.0–9.0	0.007–0.068	[43]
Lake water Juice	Triazines	MIP-SPE	3 mL methanol 3 mL 5% ammonia-ACN	1 min ultrasound + 10 min shake + 3 mL 5% ammonia-ACN evaporation	HPLC-MS/MS	85.0–101.0	≤7.0	0.02–0.07	[44]
Drinking water Tap water Environmental water	Triazines	V-MIL-101(Cr)/CS-SPE[f]	1.5 mL ACN	3 min adsorption + 4 min desorption + 1.5 mL ACN evaporation	HPLC-MS/MS	78.9–118.6	0.4–14.5	0.014-0.045	This work

[a] Ultrasound vortex assisted dispersive liquid-liquid microextraction.
[b] Effervescence-assisted dispersive liquid-liquid microextraction.
[c] Magnetic solid-phase extraction.
[d] Solid-phase microextraction.
[e] Molecularly imprinted polymer-solid-phase microextraction.
[f] Vortex-assisted solid phase extraction based on MIL-101(Cr)/Chitosan-sponge column.
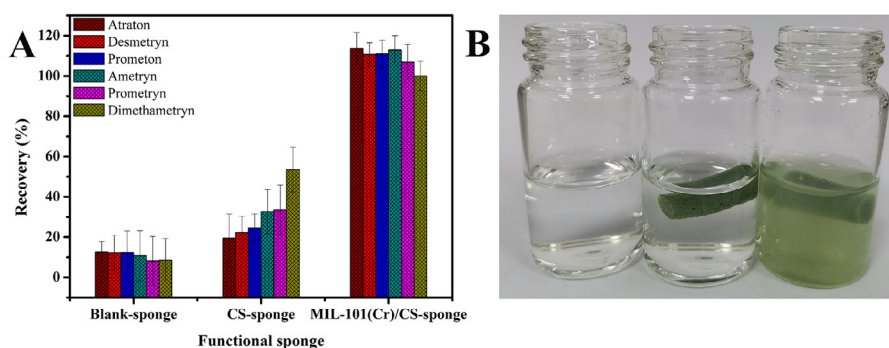
Fig. 8. The comparison (A) of different load materials on the recoveries of triazines. Photographs (B) of water sample (left), MIL-101(Cr)/CS-sponge (middle, water sample) and MIL-101(Cr)-sponge (right, water sample).

umn was not as satisfactory as that of the MIL-101(Cr)/CS-SC. Additionally, the recoveries decreased in the following order: MIL-101(Cr)/CS-sponge > CS-sponge > blank-sponge. The excellent extraction performance of the MIL-101(Cr) may be attributed to its unique structure. The large windows allow the analytes to easily enter the cages. In addition, the unsaturated metal sites on the skeleton of the MIL-101(Cr) may also covalently interact with the heteroatoms in analytes. The log P values of triazines studied from 2.46 to 3.83 were obtained from SciFinder scholar database and listed in Table 1. Results showed that the analytes were relatively polar and more easily adsorbed by MOFs with unsaturated metal sites [4,45]. Although the extraction performance of chitosan-modified sponge to triazine herbicides is significantly lower than that of MIL-101(Cr)/CS-modified sponge, it is still higher than the extraction performance of blank sponge. Sponges only modified by MIL-101(Cr) (without CS) were also prepared by the same experimental procedure. As can be seen Fig. 8B, the MIL-101(Cr)-modified sponge column without the assistance of chitosan exhibited poor mechanical ability. These indicate that chitosan can act as not only an adsorption adjuvant during the determination of triazines, but also an adhesive during the preparation of functionalized sponges.

4. Conclusion

A novel analytical method, MIL-101(Cr)/CS-SC-based vortex-assisted solid-phase extraction, was proposed and successfully applied to extract triazine herbicides from water samples. MIL-101(Cr)/CS-sponge columns (SCs) were successfully prepared by a simple method; they had good mechanical stability and cost-effectiveness, thus may potentially be applied in commercial applications. The addition of chitosan not only could avoid the problem of poor polymer adsorption capacity, but also could solve the problem of hydrophobicity. The present method has many advantages over other existing methods, such as simplicity, high sensitivity, low amount of organic solvents required for analysis, and unnecessity of centrifugation step during dispersive solid-phase extraction. The experimental data also showed that the MIL-101(Cr)/CS-SC had excellent adsorption capacities for all herbicides tested and could be successfully applied to analyze five real water samples. The present work provides a foundation for the exploitation of other MOFs or nano-adsorbed materials as a coating material, as well as for the use of chitosan to functionalize sponge column that can be used for analysis of organic pollutions in environmental water samples.

Declaration of Competing Interest

There are no conflicts to declare.

CRediT authorship contribution statement

Yanxiao Jiang: Methodology, Data curation, Investigation, Writing - original draft, Writing - review & editing. **Zucheng Qin:** Methodology, Investigation, Writing - review & editing. **Fanghui Liang:** Conceptualization, Writing - review & editing. **Jingkang Li:** Conceptualization, Writing - review & editing. **Ying Sun:** Conceptualization, Writing - review & editing. **Xinghua Wang:** Formal analysis, Writing - review & editing. **Pinyi Ma:** Conceptualization, Resources, Project administration, Funding acquisition, Writing - review & editing. **Daqian Song:** Conceptualization, Supervision, Resources, Project administration, Funding acquisition, Writing - review & editing.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2021.461887.

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