One-step fabrication of hydrophilic MIL-68(Al)/Chitosan-coated melamine sponge for vortex-assisted solid-phase extraction of parabens in water samples

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ABSTRACT

A novel vortex-assisted solid-phase extraction method based on MIL-68(Al)/Chitosan-melamine sponge column (or V-MIL-68(Al)/CS-SC-SPE) is presented in this paper. The MIL-68(Al)/Chitosan-sponge column was prepared by a simple infiltration method and a preparation process that does not consume organic solvents. Scanning electron microscopy was used to characterize the functionalized sponge columns, and the skeleton and pores of the melamine sponge were successfully modified with the coating material (MIL-68(Al) and chitosan). Chitosan was used successfully not only as an adsorption adjuvant material, but also as an adhesive in the preparation of MIL-68(Al)/CS coating sponge materials. The presented method was further combined with high performance liquid chromatography (HPLC) and used in the determination of trace parabens (including methyl-, ethyl-, propyl- and butyl-parabens) in environmental water samples. Several important factors that affect the extraction performance were investigated. Under the optimum conditions, the method was successfully used to detect the four kinds of parabens in different water samples (domestic water, lake water and river water). The limits of detection ranged between 0.21 and 0.50 ng/mL, and the relative standard deviations for all parabens were below 10.8%.

1. Introduction

Parabens, which are esters of p-hydroxybenzoic acid, have been widely used as protective additives since the 1920s because of their advantages such as high chemical stability, low production cost, non-volatility, and excellent antifungal and antimicrobial properties [1,2]. Numerous studies have shown that parabens can enter baby bodies through breast milk and cause negatively effects on their developmental processes [3]. Environmental waters are the final deposition site of all environmental contaminants, including residual parabens which might affect the endocrine system of humans, wildlife and aquatic life due to their weak estrogenic activities [4]. Moreover, continuous exposure to parabens, even at low concentrations, may potentially increase the risk of breast cancer [5,6] and male infertility [7]. As a result of widespread use of parabens, the detection of residual parabens has become an important safety issue.

Due to low concentration of the target analytes and complex matrix interferences, original matrix environments often cannot meet the requirement of direct analysis by an instrument. For this reason, an additional sample pretreatment is necessary for enriching and separating target analytes in complex environmental matrices. Different sample preparation methods, including liquid–liquid extraction (LLE) [8,9], solid phase extraction (SPE) [10,11] and cloud point extraction (CPE) [12], have been proposed and used in combination with HPLC to extract and detect trace parabens from environmental water samples. Among these methods, SPE has received wide attention owing to its advantages, including low solvent consumption and high enrichment factor [13,14]. Even so, traditional SPE normally requires several steps of centrifugation to achieve desirable separation and enrichment of target analytes; this has limited its application in chromatographic analysis.
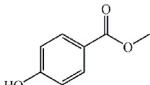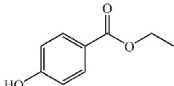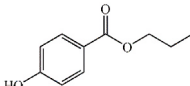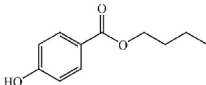
Melamine sponge (MeS), a three-dimensional (3D) porous material,

Table 1
Physical–chemical properties of target parabens.

Analyte	Abbreviation	CAS number	Molecular weight	Chemical formula	Retention time ± SD[a](min, $n = 5$)	pKa[b]	Structure
Methylparaben	MP	99-76-3	152.15	$C_8H_8O_3$	3.35 ± 0.01	8.31 ± 0.13	
Ethylparaben	EP	120-47-8	166.17	$C_9H_{10}O_3$	3.77 ± 0.02	8.31 ± 0.13	
Propylparaben	PP	94-13-3	180.20	$C_{10}H_{12}O_3$	4.42 ± 0.02	8.23 ± 0.15	
Buthylparaben	BP	94-26-8	194.23	$C_{11}H_{14}O_3$	5.44 ± 0.04	8.22 ± 0.15	

[a] Standard deviation (n = 5).
[b] K_a: acid dissociation constant. pKa values are obtained from SciFinder scholar database (25 °C).

has been widely applied in pollutant removal [15], gas separation [16] and oil/water separation [17,18] due to its excellent properties, including high porosity (>99%), open-hole structure, environmental friendliness, and commercial availability [18]. The unique structural properties of MeS enables it to be easily submersed in water systems so that it can rapidly and efficiently adsorb contaminants, while can be rapidly removed from the aqueous phase. However, due to the lack of functional groups on its surface, bare sponge cannot selectively detect trace analytes. Thus far, a number of functionalized methods for modifying sponge with adsorbent materials have been reported with an aim to improve the adsorptive property and selectivity of the sponge, rendering it with a wide variety of practical applications. The reported functionalization processes are time-consuming and cumbersome and require a large amount of organic solvents; and in some cases, they require additional equipment to complete the process [17,19]. In our previous work, a metal organic framework material (MIL-101(Cr)) was successfully loaded onto the skeleton of MeS using polyvinylidene difluoride (PVDF) as a coupling agent [20], and the functionalized sponge could excellently extract triazine herbicides. However, due to the hydrophobicity and weak extraction properties of PVDF, the direct use of the obtained materials in water sample analysis remains limited. Among many polymers, amino groups on the surface of chitosan enable it to better dissolve in acidic aqueous solution and form a bioadhesive [21]. In addition, high hydrophilicity and numerous adsorption sites (high contents of amino and hydroxyl functional groups) [22,23] allow CS to be used as a PVDF replacement material in functionalized sponge coating so that it can be directly used in water sample analysis.

In the present study, based on the combined advantages of MeS, we prepared a MIL-68(Al)/Chitosan-melamine sponge column (MIL-68(Al)/CS-SC) using chitosan as an adsorbent adjuvant and an adhesive. The preparation process of the functionalized sponge column requires only a one-step infiltration method and does not consume organic solvents. The MIL-68(Al)/CS-SC was subsequently used as an adsorbent to extract parabens in environmental waters, and the adsorbent could be quickly separated without centrifugation. Thus far, studies on using MIL-68(Al)/CS-SC as a vortex-assisted SPE adsorbent for extracting parabens from environmental water samples have not been reported.

2. Experimental

2.1. Reagents and materials

Melamine sponges were purchased at a local market (Changchun, China). Aluminium chloride hexahydrate (AlCl₃·6H₂O, AR) was purchased from Beijing Chemical Works (Beijing, China). Terephthalic acid

(H_2BDC) was acquired from Energy Chemical (Shanghai, China). Chitosan (100–200 mPa s) was supplied by Aladdin Reagent Corporation (Shanghai, China). Chromatographic acetonitrile and ultrapure water were used as the mobile phase constituents in parabens separation, provided by J & K Scientific Co., Ltd. (Pittsburgh, USA) and a Milli-Q water purification system (Millipore, New York, USA), respectively. Dichloromethane, n-hexane, diethyl ether, ethyl acetate, and acetonitrile were obtained from Beijing Chemical Works (Beijing, China). All chemicals used were of analytical grade.

All paraben standards (methyl-, ethyl-, propyl- and n-butyl paraben, 99.9% purity) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The physico-chemical properties of the selected parabens are listed in Table 1. The individual standard stock solution of four parabens were prepared by dissolving the solid standard into the HPLC-grade acetonitrile. Mixed working solutions containing the four parabens studied were obtained by mixing the individual stock solutions with chromatographic acetonitrile. The resulting solution was placed in a refrigerator at 4 °C for future use.

2.2. Instrument

All Chromatographic analyses of parabens were performed on a high performance liquid chromatography apparatus (Agilent Technologies, 1260 Infinity HPLC, USA) equipped with an automatic injector, a column oven, a quaternary pump and a multiple wavelength detector (MWD). Parabens were separated on an eclipse XDB-C18 (Agilent Technologies, 3.5 μm particle size, 170 mm × 4.6 mm, USA) analytical column and the column temperature was set at 35 °C. The HPLC analysis was conducted in isocratic mode: ultra-pure water and HPLC-grade acetonitrile (35:65, v/v), 0.5 mL min⁻¹.

X-ray diffraction spectrometer (XRD, Rigaku Ultima IV, Japan) was employed to verify the synthesis of MIL-68(Al) material. Scanning electron microscope (SEM, Hitachi SU-8020, Japan) were used for characterize the morphology of MIL-68(Al) and functional sponge column. Nitrogen physisorption isotherms of MIL-68(Al) were measured by a surface area and pore analyzer instrument (Belsorp max, Microtrac BEL, Japan). A pH meter (Sartorius, PB-10, Germany) and a vortex mixer (Dragonlab, MX-S, China) were used to measure the pH value of solution and to accelerate the extraction rate of the targets, respectively.

2.3. Sample preparation

Three types of water samples, including domestic waters (drinking water, sample 1 and tap water, sample 2), lake waters (Yanhu lake, sample 3 and Qinghu lake, sample 4; Changchun, China) and river water
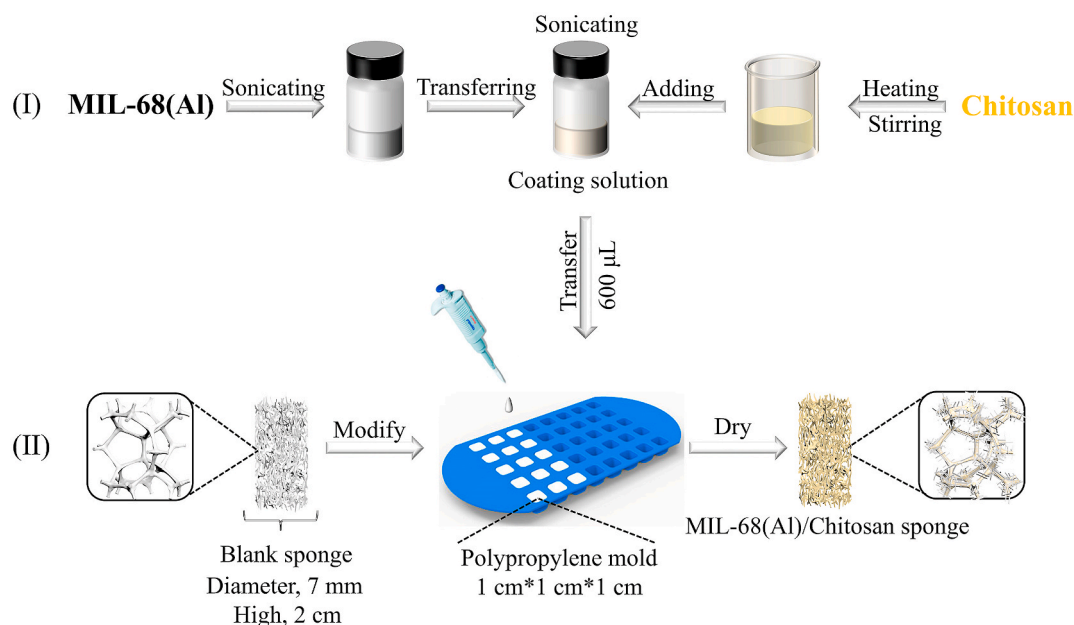
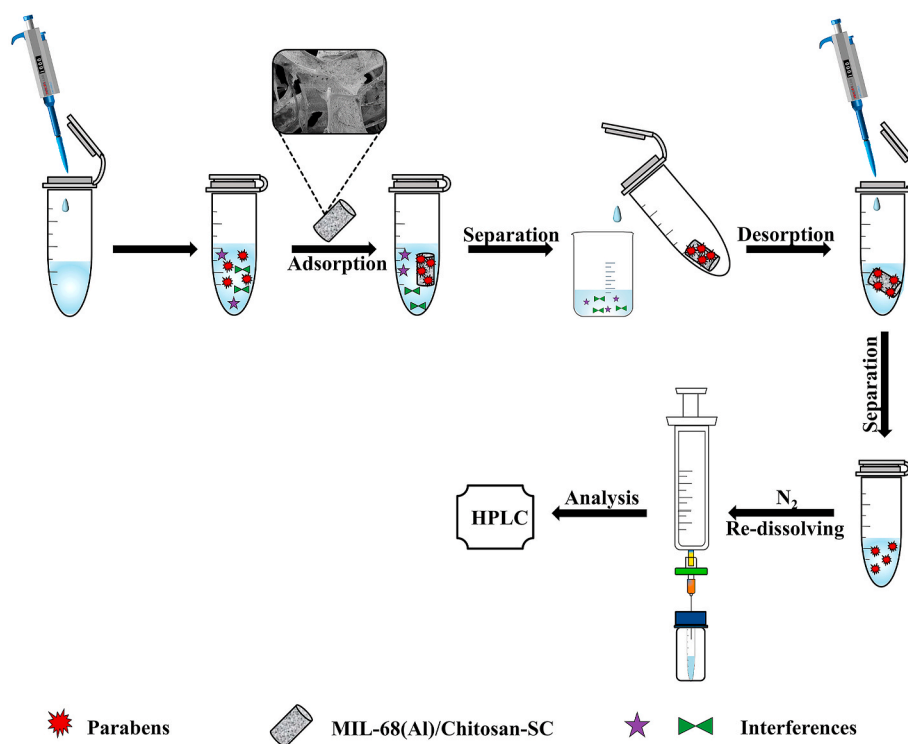**Fig. 1.** Preparation process of MIL-68(Al)/CS-sponge column.

Fig. 2. Schematic illustration of V-SPE procedure using MIL-68(Al)/CS-sponge column.

(Yitong river, Changchun, China), were collected for validating the present method. All original water samples were filtered through 0.22-μm nylon filter films prior to analysis. The freshly spiked samples at required concentration were prepared by adding mixed working solutions into blank water samples and stored at 4 °C in darkness.

2.4. Preparation of MIL-68(Al) and MIL-68(Al)/CS sponge column

MIL-68(Al) was prepared by the solvothermal method with minor modifications [24], and the specific synthesis steps are as follows. First,

H_2BDC (1.67 g, 10 mmol) and $AlCl_3 \cdot 6H_2O$ (1.63 g, 6.74 mmol) were dissolved in 50 mL of N, N-dimethylformamide (DMF) in a beaker using ultrasound-assisted method. The mixture was then transferred to a heavy-wall pressure bottle, in which it was stirred magnetically for 18 h at 130 °C. After cooling to room temperature, the obtained powder was washed several times with DMF while being sonicated to remove non-reacted reactants, and the same operation was repeated using methanol to further remove DMF both on the interior and exterior of the pores. Finally, the obtained MIL-68(Al) material was dried in an oven at 60 °C overnight.
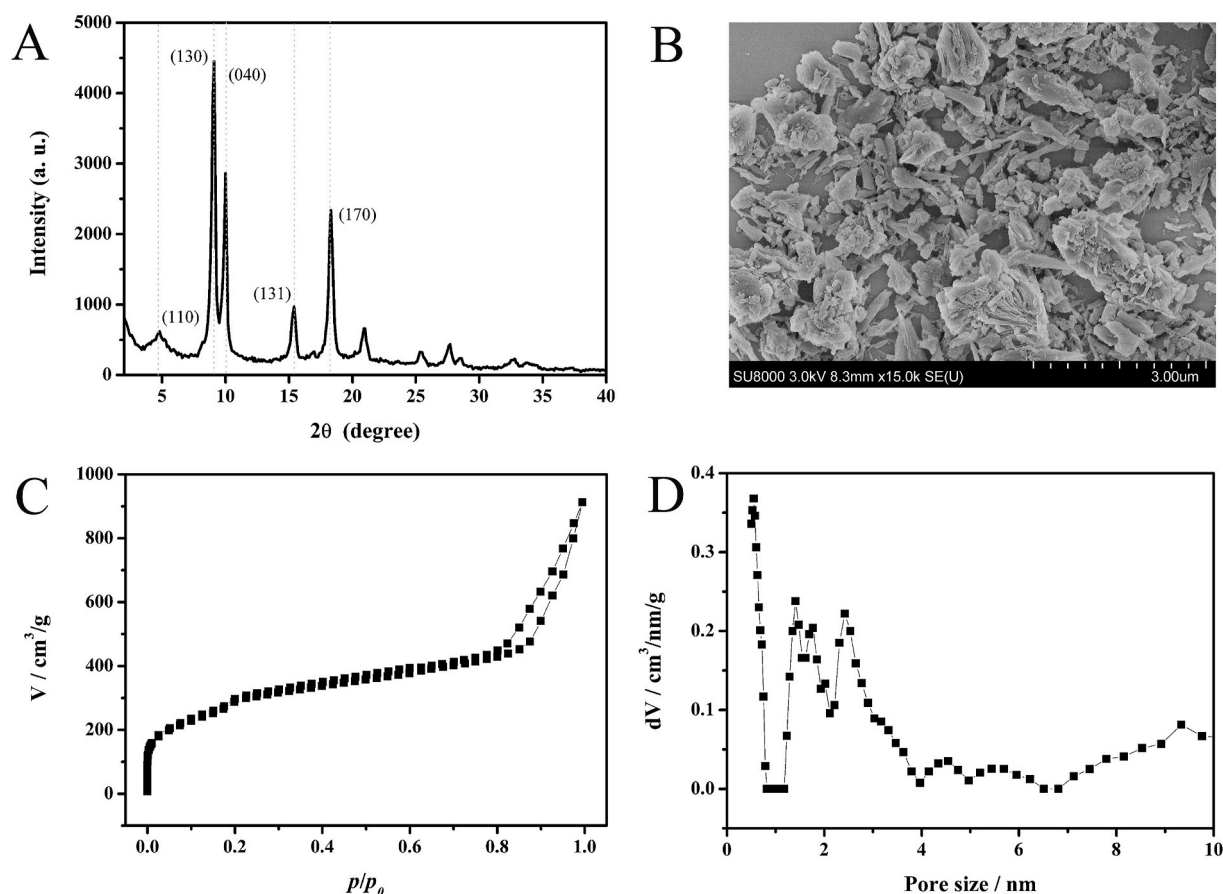
Fig. 3. Characterization of MIL-68(Al) material: (A) XRD pattern, (B) SEM image, (C) N_2 adsorption-desorption isotherms and (D) pore size distribution.

MIL-68(Al)/CS-functionalized sponge columns were prepared by a simple one-step infiltration method. The specific preparation process is as follows (Fig. 1). The commercial melamine sponge was first cut into the desired shape (diameter x height = 0.7 cm × 2.0 cm) using a punching machine. One hundred milligrams of MIL-68(Al) were added into 5 mL of ultrapure water while being bath sonicated for 20 min. One gram of chitosan solution (7.5 wt% in 0.8% acetic acid solution) was then added to the above solution and sonicated for 20 min to prepare a uniform coating solution. A blank melamine sponge column was pressed several times using a pair of tweezers into a polypropylene mold (1 cm × 1 cm x 1 cm) containing 600 µL of coating solution. Finally, the functionalized porous MIL-68(Al)/CS sponge was dried (at 85 °C for 12 h) and was then washed several times with methanol; thereafter, it was dried again at room temperature.

2.5. V-MIL-68(Al)/CS-SC-SPE procedure

The vortex-assisted MIL-68(Al)/CS-SC-SPE procedure for extracting parabens from water samples is depicted in Fig. 2. MIL-68(Al)/CS-SC was first placed in a 10 mL centrifuge tube containing 5 mL of spiked sample (pH 5.0), and the tube was vortexed for 4 min. After adsorption, the supernatant was discarded, and the aqueous phase remained in the porous MIL-68(Al)/CS-SC was discarded with an aid of a pair of tweezers. Three milliliters of ethyl acetate were then added to a centrifuge tube, which was then vortexed for 6 min to desorb the targets. Finally, the MIL-68(Al)/CS-SC was removed, and the resulting desorption solution was evaporated under gentle nitrogen stream at 45 °C and was then redissolved in 100 µL of acetonitrile. Five microliters of the analytical solution were filtered through a 0.22 µm syringe filter and was then injected into an HPLC system for analysis.

3. Results and discussion

3.1. Characterization of MIL-68(Al) and MIL-68(Al)/CS-SC materials

The prepared MIL-68(Al) material was characterized successively by XRD, SEM and N_2 adsorption isotherms, and the results can be found in Fig. 3. The XRD pattern (Fig. 3A) indicated that the characteristic peaks (4.8°, 8.8°, 9.7°, 14.5° and 17.5°) of the MIL-68(Al) material were similar to those previously reported [25]. According to the SEM image (Fig. 3B), the prepared MIL-68(Al) material consisted of needle-like crystals with different lengths and were disorderly arranged. Fig. 3C and **D** shows the adsorption isotherm and pore diameter distribution of the MIL-68(Al), respectively. The result indicated that the isotherms belonged to the type-I isotherms, and the pore diameter was less than 3 nm. The BET surface area and pore parameter (V_{pore}) of the prepared MIL-68(Al) were 1171.6 m^2/g and 0.8 cm^3/g, respectively.

Scanning electron microscopy was used to verify the successfulness of the MIL-68(Al)/CS sponge column preparation method. Chitosan-functionalized sponge column without MIL-68(Al) was also prepared for comparison. As illustrated in Fig. 4B-a, the blank melamine sponge had a 3D crosslinking network structure with a smooth surface. The melamine sponge had wide skeleton diameters (3–10 µm) and contained numerous pores (diameters = 100–200 µm), which provide the sponge with excellent capacity as a support skeleton for the loading of the coating material. The optical photographs (Fig. 4A, a-c) showed the slightly yellowish color of the sponge due to the presence of chitosan that was used in the modification, and the color of the sponge did not change significantly when the sponge was further modified with MIL-68 (Al). Further, compared to that of the blank sponge, the skeleton of the chitosan-functionalized sponge was slightly rough, and the chitosan was embodied the skeleton and the pores of melamine sponge. This proves
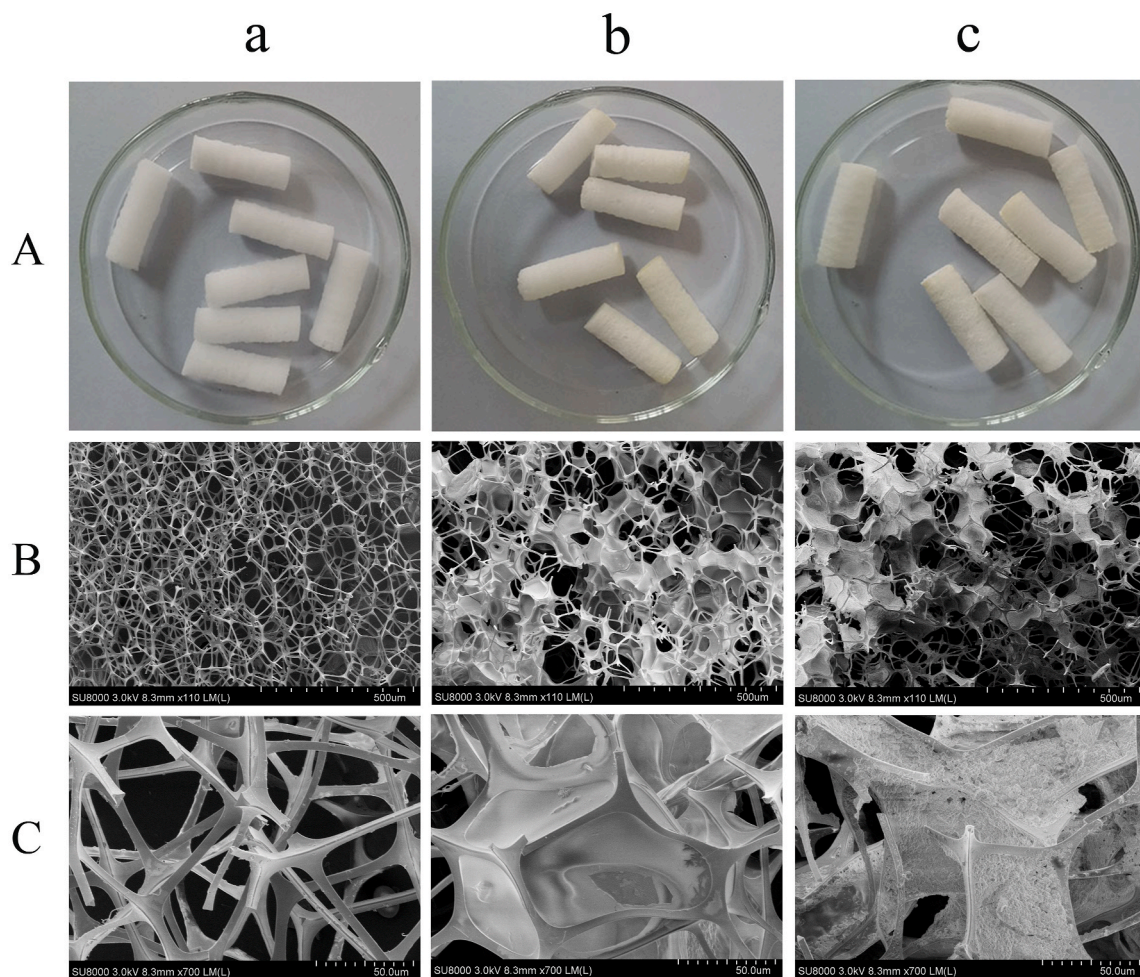
Fig. 4. Photographs (A) of functionalized sponge columns: a, blank; b, chitosan; and c, MIL-68(Al)/Chitosan. The corresponding SEM images at different magnifications: B, at × 110 magnification; and C, at × 700 magnification.

Fig. 5. Effect of loading amount of MIL-68(Al) (A), salt concentration (B), sample pH (C) and adsorption time (D) on recoveries of parabens. Spiked concentration was 300 ng/mL. Mass distribution of blank SC (E) and MIL-68(Al)/CS-SC (F) (n = 100).

Fig. 6. Effect of type (A) and volume (B) of desorption solution and desorption time (C) on recoveries of parabens. Spiked concentration was 300 ng/mL.
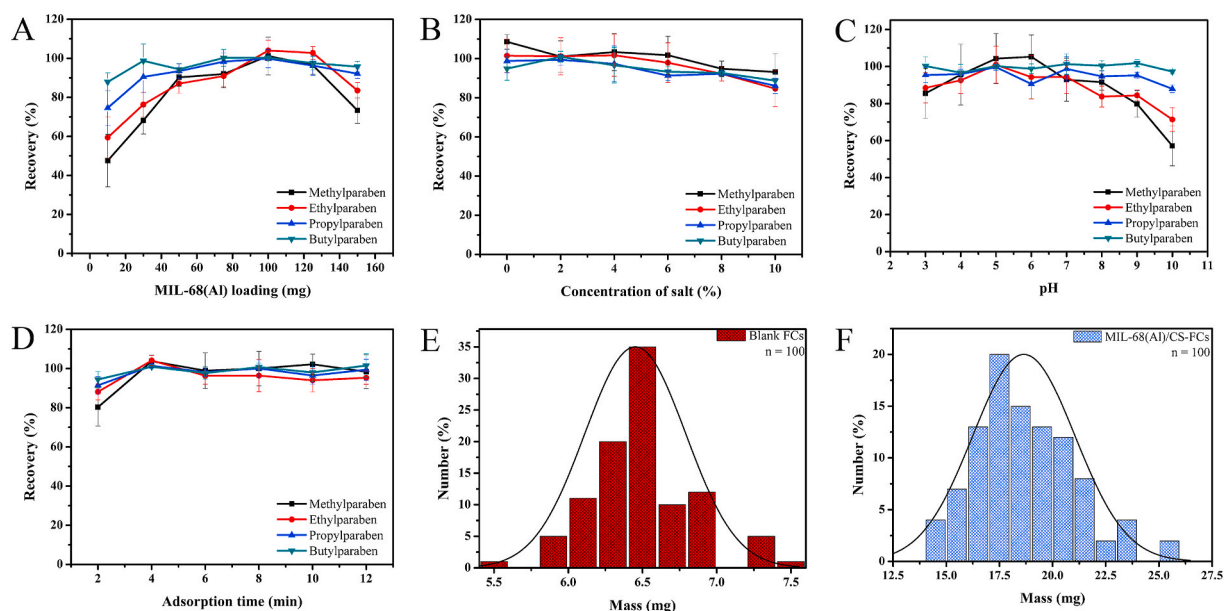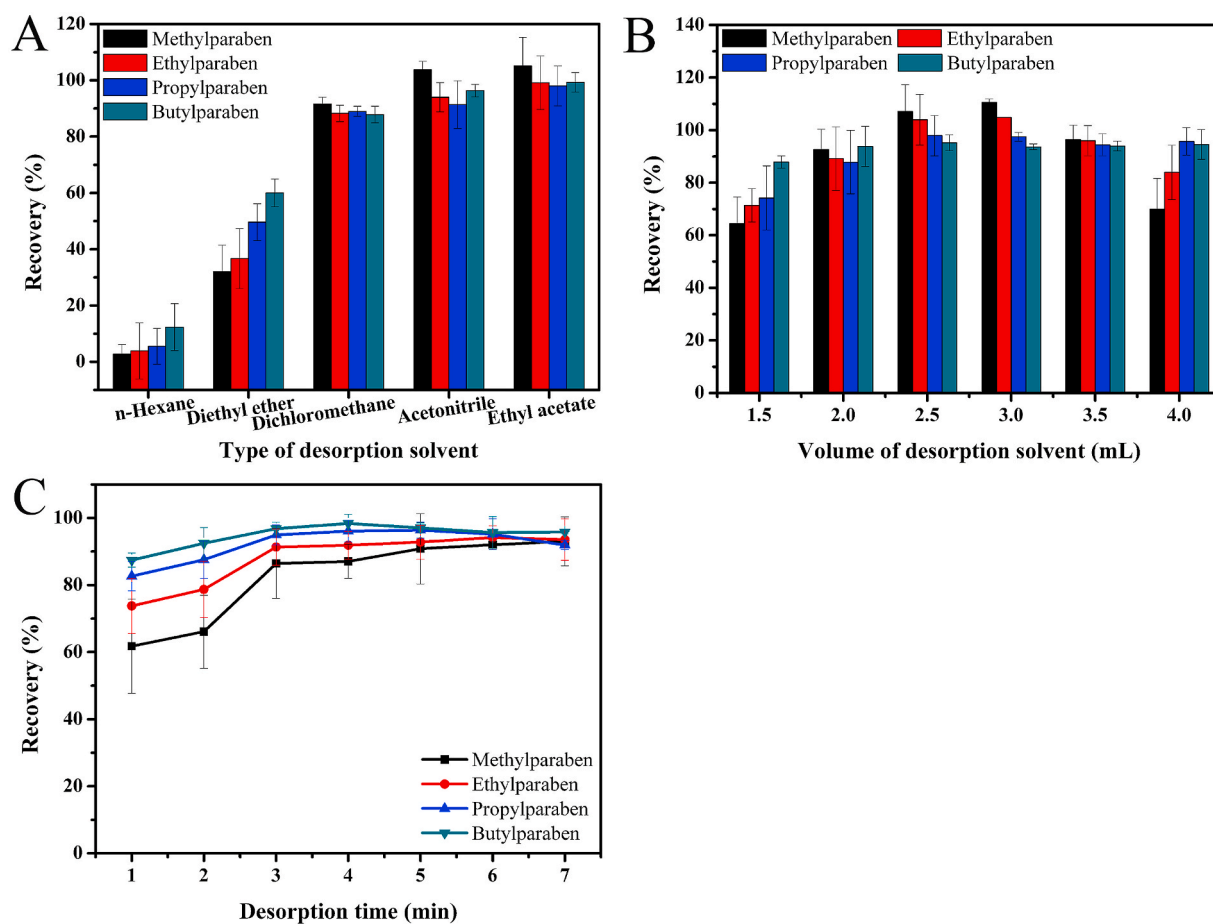
that chitosan was successfully grafted onto the sponge. Fig. 4B and C displays the MIL-68(Al)/CS-functionalized sponge at different multiples. The results showed that MIL-68(Al) was successfully coated onto the skeleton and the pores of sponge due to the action of chitosan as an adhesive agent.

3.2. Optimization of V-MIL-68(Al)/CS-SC-SPE conditions

In order to obtain the best extraction performance of V-MIL-68(Al)/CS-SC-SPE in extracting parabens from water samples, a single factor optimization was adopted to optimize several conditions that may affect such performance, including MIL-68(Al) loading, salt concentration, sample pH, adsorption time, desorption time, and type and volume of desorption solution. The spiked concentration was 300 ng/mL.

3.2.1. Effect of MIL-68(Al) loading

Effect of MIL-68(Al) loading on the performance of V-MIL-68(Al)/CS-SC-SPE in extracting parabens was investigated. Functionalized sponge samples containing different MIL-68(Al) loadings (10, 30, 50, 75, 100, 125 and 150 mg) were prepared by the same procedure, and the best loading was selected. The results are shown in Fig. 5A. The extraction efficiency gradually increased when the MIL-68(Al) loading was increased from 10 to 100 mg and then decreased slightly when the loading exceeded 100 mg. This observation could be attributed to excessive use of adsorbent which could reduce the extraction efficiency by depressing the desorption process. Thus, MIL-68(Al) at a loading of 100 mg was selected for subsequent experiment. The dried sponge column with MIL-68(Al) at the optimal loading amount had an average mass of 18.7 mg (Fig. 5F, n = 100).

3.2.2. Effect of salt concentration

To examine the influence of ionic strength on the extraction recoveries, a series of experiments were performed in the presence of different amounts of NaCl (0%–10%, w/v), which was added during the extraction. According to the results illustrated in Fig. 5B, the presence of NaCl caused the extraction recoveries of all parabens to decrease slightly. The addition of NaCl increased the viscosity and density of the solution, thus inhibiting the mass transfer from occurring, resulting in decreased recoveries. Considering the simplicity and the high performance of the extraction process, NaCl addition was not conducted in the subsequent experiment.

3.2.3. Effect of sample pH

Sample pH plays an important role in the extraction of targets in most sample pretreatment, as it can affect both the charge and density of the species on the adsorbent surface, as well as the forms of the target analytes. Therefore, the effect of pH values of the sample solution, ranging from pH 3 to pH 10, on the extraction recoveries was studied. The results shown in Fig. 5C indicated that the optimal extraction recoveries were obtained at pH 5. Additionally, when the sample pH was higher than 5, the obtained extraction efficiencies decreased markedly, which probably due to the collapse of the skeleton of MIL-68(A1) under moderately or highly alkaline condition. Thus, in further experiments, the pH value was adjusted to 5.

3.2.4. Effect of adsorption time

Effect of adsorption time on the extraction recoveries of all parabens was investigated at increasing vortex times from 2 to 14 min. As can be seen in Fig. 5D, the adsorption equilibrium was achieved within 4 min, and further increasing the vortex time had no significant effect on the

Table 2
Analytical performance of the present method.

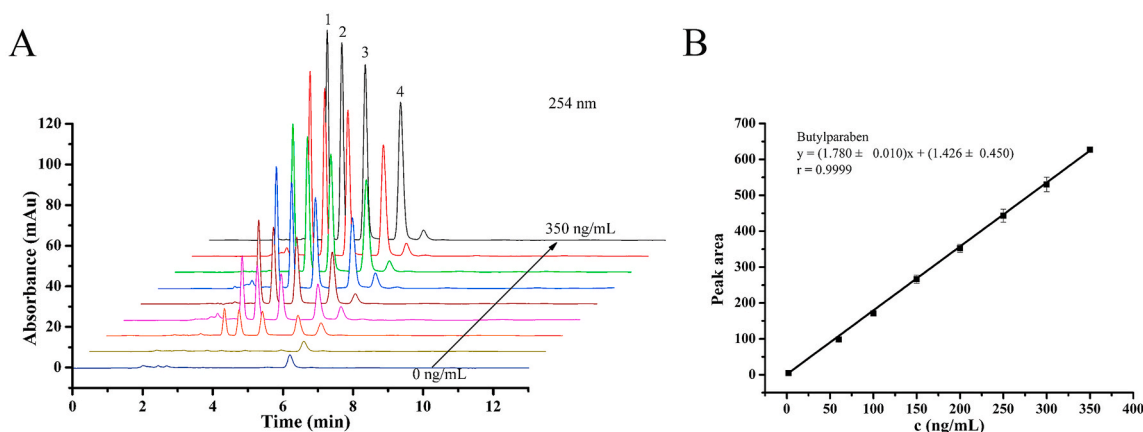| Analyte	Linear range (ng/mL)	Regression equation	Correlation coefficient(r)	Spiked (ng/mL)	Intra-day (n = 5)		Inter-day (n = 5)		LOD(ng/mL)
					Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
Methylparaben	2.0–350.0	$y = (1.543 \pm 0.059)x + (-0.820 \pm 0.499)$	0.9949	60	86.1	6.9	97.4	7.5	0.21
				300	105.2	9.1	103.1	8.2	
Ethylparaben	2.0–350.0	$y = (1.677 \pm 0.040)x + (0.303 \pm 0.080)$	0.9980	60	84.3	8.9	95.3	7.1	0.32
				300	102.2	9.2	98.8	8.3	
Propylparaben	2.0–350.0	$y = (1.834 \pm 0.004)x + (-0.423 \pm 0.011)$	0.9999	60	91.6	5.4	94.8	2.7	0.31
				300	99.0	3.4	97.0	3.8	
Butylparaben	2.0–350.0	$y = (1.780 \pm 0.010)x + (1.426 \pm 0.450)$	0.9999	60	91.3	5.0	97.0	4.1	0.50
				300	99.1	3.9	98.5	3.2	

Fig. 7. HPLC chromatograms (A) of unspiked drinking water (sample 1) and drinking water spiked with different concentrations of parabens (2, 60, 100, 150, 200, 250, 300 and 350 ng/mL). Peaks: 1, methylparaben; 2, ethylparaben; 3, propylylparaben; and 4, buthylparaben. A plot of chromatographic response (B) versus concentration of butylparaben in sample 1 extracted using the MIL-68(Al)/CS sponge column-based V-SPE method.

Table 3
Analytical results of real and spiked samples.

Sample	Spiked (ng/mL)	Methylparaben		Ethylparaben		Propylylparaben		Buthylparaben	
		Recovery(%)	RSD(%)	Recovery(%)	RSD(%)	Recovery(%)	RSD(%)	Recovery(%)	RSD(%)
Sample 1	0	ND							
	60	97.0	9.0	94.1	8.7	94.6	3.8	96.2	5.2
	300	106.1	9.2	102.1	9.4	98.8	3.8	99.0	3.9
Sample 2	0	ND							
	60	95.3	2.1	90.4	5.9	83.9	5.9	90.0	3.8
	300	89.2	3.0	89.9	3.0	93.6	2.5	95.4	2.0
Sample 3	0	ND							
	60	90.1	1.8	88.6	5.0	87.7	3.5	92.2	2.9
	300	93.1	4.0	97.6	9.7	90.7	0.3	95.3	2.4
Sample 4	0	ND							
	60	99.2	10.7	90.0	10.7	98.5	4.8	95.5	1.1
	300	97.2	10.8	92.0	8.8	94.0	5.1	96.0	2.5
Sample 5	0	ND							
	60	89.2	8.8	88.4	8.0	94.8	7.0	93.0	5.6
	300	93.1	9.3	95.4	4.1	93.2	2.3	97.4	2.8

ND, not detected.

extraction efficiency. Therefore, 4 min was considered the optimal adsorption time and was selected in subsequent experiment.

3.2.5. Effects of desorption condition

Desorption is another crucial step of the whole extraction process. In order to improve the extraction efficiency and reduce the consumption of organic solvents, several important factors affecting the desorption process, including the type and volume of the desorption solvent and the desorption time, were optimized. Five organic solvents (n-hexane, dichloromethane, diethyl ether, ethyl acetate, and acetonitrile) that have different polarities and are commonly used in chromatographic

analysis were selected as desorption solvents, and their effects on the extraction performance of parabens were explored. As clearly demonstrated in Fig. 6A, ethyl acetate had higher desorption efficiency with regards to all parabens than other solvents. The effect of volumes of ethyl acetate (the desorption solvent) from 1.5 to 4.0 mL was evaluated. The results shown in Fig. 6B indicated that 3.0 mL of ethyl acetate was the suitable volume for sample analysis, thus was selected in subsequent experiment.

The effect of desorption time from 1 to 7 min on the recoveries of parabens was investigated. As can be seen in Fig. 6C, the desorption time of 6 min was sufficient to desorb the analytes, and the best extraction

Table 4
Comparison of the presented method with other reported methods.

Analytes	Matrix	Extraction method	Determination technology	Operating time(min)	V_{org}[a](mL)	Recovery (%)	RSD(%)	LODs(ng/mL)	Ref.
Parabens	Environmental water Cosmetic creamUrine	VA-D-m-SPE[b]	HPLC-DAD	33	2 mL methanol	61.3–101	≤15	1.5–2.6	[26]
Phthalates Parabens	Cosmetic product	SEM[c]	HPLC-DADGC-MS	30	1000 mL 40% methanol aqueous solution + 15 mL Methanol	85–108	4.2–8.8	–	[27]
Parabens	Water sample	UA-SPE[d]	UPLC-MS/MS	35	1 mL ethyl acetate	78.75–102.1	≤7.4	0.09–0.45	[28]
Parabens	Water sample Cosmetic sample	FSALLME[e]	GC-FID	–	60 μL carbon tetrachloride	97–109	≤9.4	0.5–1.0	[29]
Parabens	PlasmaUrine	DLLME-SFODs[f]	HPLC-UV	14.5	0.65 mL methanol + 58 μL 1-decanol	80.3–110.7	0.9–7.22.2–8.9	0.2–0.40.1–0.4	[30]
Parabens	Domestic water Lake water River water	V-MIL-68 (Al)/CS-SC-SPE[g]	HPLC-MWD	10	3 mL ethyl acetate	83.9–106.1	0.3–10.8	0.21–0.50	This work

[a] Total volume of organic solvents consumed per sample.
[b] Vortex-assisted dispersive micro-solid-phase extraction.
[c] Solvent extraction method.
[d] Ultrasound-assisted solid-phase extraction.
[e] Fast syringe assisted liquid-liquid microextraction.
[f] Dispersive liquid-liquid microextraction-solidification of floating organic drops.
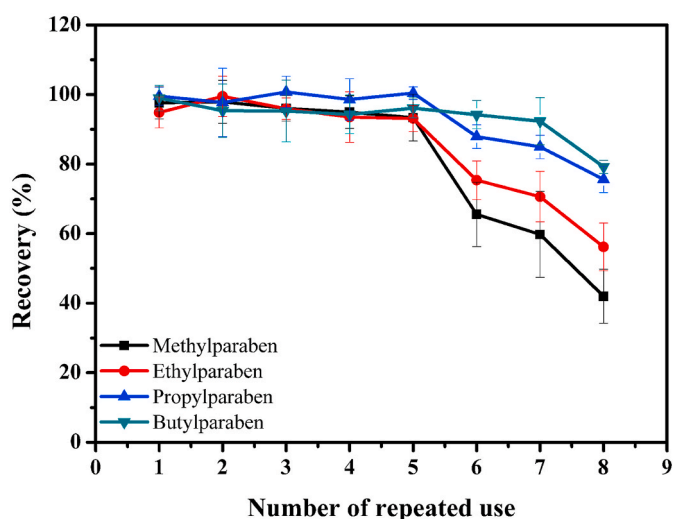[g] Vortex-assisted solid phase extraction based on MIL-68(Al)/Chitosan-sponge column.

Fig. 8. Reusability of the MIL-68(Al)/CS sponge columns. Spiked concentration, 100 ng/mL.

performance with regards to all parabens was also achieved at this desorption time. In addition, the extraction recoveries were not changed significantly when the desorption time was further increased. Therefore, the optimal desorption time (the vortex time) of 6 min was selected in subsequent experiment.

3.3. Method validation

3.3.1. Analytical performance

Five real spiked water samples at two different concentrations (60 ng/mL and 300 ng/mL) were analyzed to evaluate the applicability of the V-MIL-68(Al)/CS-SC-SPE method.

The precision of the method was evaluated by measuring intra- and inter-day relative standard deviations (RSDs, %) at two different concentrations. The intra- and inter-day RSDs were determined using the analytical results obtained in the recovery experiments conducted for five times in the same day and for five consecutive days, respectively. The results shown in Table 2 indicated that the recoveries of intra- and

inter-day were in a range of 84.3%–105.2% with RSDs of less than 9.2%. Therefore, the method had satisfactory repeatability.

The calibration curve was plotted using the chromatographic peak response (area) and the corresponding concentration of paraben extracted using the MIL-68(Al)/CS sponge column-based V-SPE method in each spiked sample. For all parabens, a good linear correlation (r = 0.9949–0.9999) was obtained over the concentration range of 2–350 ng/mL, and the corresponding linear regression equations are listed in Table 2 (Fig. 7B; also see Fig. S1, Supporting Information). The limits of detection (LODs; signal-to-noise ratio S/N = 3) with respect to all parabens were in a range of 0.21–0.50 ng/mL, which are similar or lower than other reported methods; the results obtained are given in Table 2 and the detailed method comparison can be found in section 3.3.3 (Table 4).

3.3.2. Detection of parabens in real samples

The proposed method was then applied to analyze parabens in real water samples to evaluate its applicability. The HPLC chromatograms of the spiked samples at different concentrations are shown in Fig. 7A. The results showed that the target parabens in the un-spiked samples were undetectable. The recoveries of all parabens are listed in Table 3. The good extraction recoveries (83.9–106.1%) and acceptable precision (10.8%) prove that the present method can be used as a suitable extraction method of trace paraben in environmental water samples.

3.3.3. Reusability of the MIL-68(Al)/CS-SCs

To investigate the reusability of MIL-68(Al)/CS sponge columns, the MIL-68(Al)/CS-SCs were treated for two cycles of vortexing in ethyl acetate and drying at 50 °C for 3 h before reuse. Fig. 8 shows the experimental results: A significant change in the recoveries of parabens after using the SC 5 times was not observed.

3.3.4. Comparison with other reported methods

To further evaluate the performance of the present method, five previously reported methods [26–30] for determining parabens in different matrices were compared with the present method, and the detailed results are summarized in Table 4. The introduction of melamine sponge column could simplify the solid phase extraction method and diminish the centrifugation step and additional magnetism required to separate the adsorbents, which are the advantages of the present method over other reported methods. In addition, short operating time,
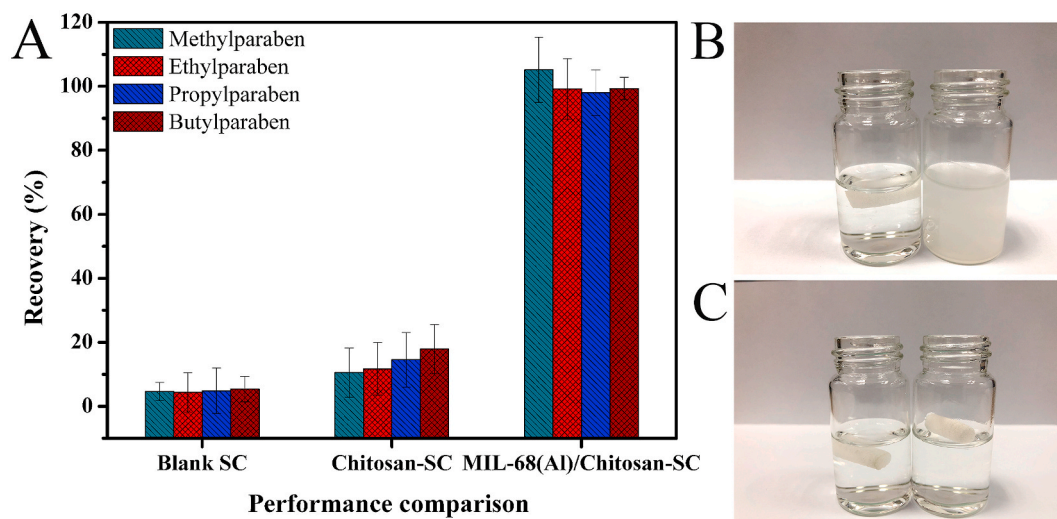
Fig. 9. Comparison (A) of extraction recoveries of parabens by blank-, chitosan- and MIL-68(Al)/CS-sponge columns. Photographs (B) of functionalized sponge columns after extraction: left, MIL-68(Al)/Chitosan-SC; and right, MIL-68(Al)-SC. Hydrophilicity (C) of functionalized sponge columns: left, MIL-68(Al)/Chitosan-SC; and right, MIL-68(Al)/PVDF-SC.

low solvent consumption and low LODs make this method highly applicable for paraben trace detection.

Furthermore, comparison of the performance of the blank-, CS- and MIL-68(Al)/CS-sponge columns in extracting the target parabens using V-SPE are shown in Fig. 9A. The extraction recoveries of all parabens could be ranked in an increasing order as follows: blank-SC < CS-SC < MIL-68(Al)/CS-SC, which indicates that although the chitosan-SC had lower recoveries than that of MIL-68(Al)-SC, it could still act as an adsorption adjuvant in the extraction of the four target parabens.

The MIL-68(Al) sponge without chitosan was prepared under the same condition. This MIL-68(Al) fell off from the sponge after being hand-shaken for just a few times (Fig. 9B, Movie 1); thus, it cannot meet the requirement of fast solid phase extraction without centrifugation. Besides, the hydrophilicity of chitosan (Fig. 9C) also makes the functionalized sponge to become available for water sample analysis, as compared to other polymer (PVDF) adhesives reported in the literature. These data prove that chitosan can be used as an adhesive in the preparation of functionalized sponge column by a one-step infiltration method and as an adsorption adjuvant in the extraction of target analytes in water samples.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.talanta.2020.121799

4. Conclusion

In the present work, a new sample pretreatment method, V-MIL-68(Al)/CS-SC-SPE, was proposed and successfully applied to determine parabens in environmental water samples. For the first time, chitosan was used not only as an adsorption assistant, but also as an adhesive in the preparation of functionalized sponge materials. Melamine sponge was selected as an adsorbed base material in the vortex-assisted SPE to simplify the separation procedures under non-magnetic conditions. With simple one-step infiltration, excellent mechanical stability and low cost, the MIL-68(Al)/CS sponge has a promising commercial value. This study provides a new avenue for the exploration of other functionalized coating adsorbent materials using chitosan as a binder and for the preparation of new functionalized sponges for the detection of other contaminants in other complex matrix samples.

Credit author statement

Yanxiao Jiang: participation and design in the whole work; drafting of the article; data analysis. Bo Zhang: participation in part of the work. Jingkang Li: participation in part of the work. Ying Sun: guidance in the revision of experimental manuscripts. Xinghua Wang: guidance in the revision of experimental manuscripts. Pinyi Ma: guidance in the revision of experimental manuscripts. Daqian Song: guidance and final approval of the version to be published.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2020.121799.

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