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Preparation of a mixed stir bar for sorptive extraction based on monolithic material for the extraction of quinolones from wastewater

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ABSTRACT

In this study, a novel mixed mode monolithic material was prepared and acted as the SBSE coating. The monolithic material was prepared by in situ copolymerization of methacrylic acid-3-sulfopropyl ester potassium salt (MASE) and divinylbenzene (DB) in the presence of a porogen solvent containing cyclohexanol, 1-dodecanol, and water with azobisisobutyronitrile as initiator. The influences of the contents of the porogen solvent and monomer in the polymerization mixture on the extraction performance were investigated thoroughly. Several characteristic techniques, such as elemental analysis, scanning electron microscopy and infrared spectroscopy were used to characterize the monolithic material. To achieve optimum extraction performance for quinolones, several parameters, including pH value, desorption solvent, ionic strength in sample matrix, extraction and desorption time were investigated. The results show that under the optimized experimental conditions, the method has good sensitivity, linearity, simplicity and low cost. The extraction performance of present method to the target compounds was compared with commercial SBSE which using polydimethylsiloxane as coating and other SBSEs which based on monolithic materials. The comparative results indicate that present SBSE can extract the analytes more effectively than other SBSEs because both ion-exchange and hydrophobic interactions contribute to the extraction of quinolones.

1. Introduction

Stir bar sorptive extraction (SBSE) was developed at the Research Institute of Chromatography (Kortrijk, Belgium) in 1999 by Sandra and co-workers [1] and commercialised by Gerstel (Mülheim, Germany) under the name "Twister". Similar to solid-phase micro-extraction (SPME), SBSE is an equilibrium technique, but the amount of PDMS coated on the stir bar is 50–250 times higher than that on SPME fiber, which results in a significant increase in recovery and extraction capacity [2]. Combining with other separation instruments such as HPLC, GC and CE, SBSE has been widely used for enrichment and sensitive determination of priority organic trace-pollutants such as polycyclic aromatic hydrocarbons, phenols, pesticides, organophosphorus insecticides, hormones, odor compounds in water samples, as well as in other matrices [3–6]. However, to our best knowledge, there is no report that utilizing SBSE to extract antibiotics from water or other matrices. Therefore, using SBSE to enrich antibiotics is very important and necessary for extending the applicable field of SBSE and supplying a new pretreatment method for antibiotics.

Before using SBSE in the extraction of antibiotics, a key problem should be solved. Because of the apolar character of PDMS, which is the only commercial coating for SBSE, SBSE is mainly applied to extract non-polar and weakly polar compounds, and fails in the extraction of strongly polar compounds [7]. There are many polar groups in the molecular for most antibiotics. For example, there are carboxyl and amino groups in the quinolones, and belong to strong polar compounds [8]. Therefore, it is difficult to extract quinolones directly using commercial SBSE. A few of papers have described news coatings for SBSEs [9–13], these SBSEs showed better extractive performance for polar compounds than commercial SBSE, but these works did not relate to enrich antibiotics. In our previous research, a series of SBSEs based on monolithic materials (SBSEM) were prepared [14–21] and have been used to directly extracted apolar and polar compounds in water [14,15,17–20], urine [16] and milk samples [21]. However, the extraction performances for strongly polar antibiotics such as quinolones by SBSEM were not as good as expected. Wherefore, new coating for SBSE should be developed in order to extract antibiotics.

In present study, four quinolones were selected as target analytes. According to the structural characters of quinolones, there are hydrophobic groups-ring alkyl or benzene and strong polar carboxyl and amino groups. A novel SBSE coating based on poly (methacrylic acid-3-sulfopropyl ester potassium salt-divinylbenzene) monolithic material (SBSE-MADB) was designed

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and prepared. In the monolithic material, the sulfonic groups can produce cation-exchange with amino groups and vinylbenzene can produce hydrophobic interaction with ring alkyl groups and benzene in the quinolones. Then, a methodology combined the stir bar sorptive extraction and liquid desorption, followed by high performance liquid chromatography with diode array detection (SBSE–LD–HPLC/DAD) for the direct analysis of traces of quinolones in wastewater was developed. The results showed that the present method was very simple and sensitive in the determination of quinolones.

2. Experimental

2.1. Chemicals

Methacrylic acid-3-sulfopropyl ester potassium salt (MASE) (98%), divinylbenzene (DB) (80%) and 3-(trimethoxysilyl)propyl methacrylate (γ-MAPS) (95%) were supplied by Alfa Aesar (Tianjin, China); azobisisobutyronitrile (AIBN) (97%, recrystallized before use), trifluoroacetic acid (TFA), cyclohexanol (96%) and 1-dodecanol (97%) were purchased from Shanghai Chemical Co. (China); HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia (Fairfield, USA); Water used throughout the study was purified using a Milli-Q water purification system (Millipore, USA). *p*-Nitroaniline (*p*-NA) and aniline (A), were supplied from Alfa Aesar (Tianjin, China). Enrofloxacin (EN), sparfloxacin (SP), norfloxacin (NO) and ciprofloxacin (CI) were supplied by Chinese institute for the control of pharmaceutical and biological products (their pKa and log *P* values were shown in Table S1).

A standard solution of 100 μg/mL of each quinolone was prepared in methanol and renewed monthly. The standard mixtures of four quinolones were prepared by dissolving 2.00 mg of each compound in methanol in 100 mL volumetric flask. The stock solution was stored at 4 °C and diluted with Milli-Q water to give the required concentration.

2.2. Equipments and materials

HPLC analyses were carried out on a LC chromatographic system (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20A). Sample injection was carried out using a RE3725i manual sample injector with a 20 μL loop (Rheodyne, Cotati, CA, USA), all experiments were performed at room temperature.

The commercial stir bars (Twister; Gerstel, Mülheim a/d Ruhr; Germany) coated with 20 mm in length and 1.0 mm film thickness of PDMS. The SBSE based on poly (vinylpyridine-ethylene dimethacrylate) monolithic material (SBSE-VPED), based on poly (vinylpyrrolididone-divinylbenzene) monolithic material (SBSE-VPDB) and based on poly (vinylimidazole-divinylbenzene) monolithic material (SBSE-VIDB) were prepared in our lab [17–20]. The dimensions of SBSE-VPED, SBSE-VPDB and SBSE-VIDB were 30 mm in length and 1.0 mm monoliths thickness.

The morphologies of monolithic materials were examined by a Model XL30 scanning electron microscopy (SEM) instrument (Philips, Eindhoven, The Netherlands). Elemental analysis (EA) was carried out on PerkinElmer (Shelton, CT, USA) Model PE 2400. FT-IR was performed on an Avatar-360 FTIR instrument (Thermo Nicolet, Madison, WI, USA).

2.3. Preparation of SBSE-MADB

The procedure of preparation of glass bar contained an iron bar, pretreatment and chemical modifications of the glass bar were described previously [17–20]. AIBN was used as polymerization initiator (1% (w/w) of the total monomer amount) in the all polymerization reaction. Different monomers and porogen concentrations were used for different SBSE-MADB (Table 1). The monomer mixtures and porogen (80% (w/w) cyclohexanol, 10% (w/w) 1-dodecanol and 10% (w/w) water) were mixed ultrasonically into a homogenous solution, then the reactant solution was purged with nitrogen for 3 min. Subsequently, the reactant mixture was poured into a glass tube with definite diameter. The stir bar that has been pretreated was vertically immerged into the reactant mixture. The tube was sealed with septa and kept at 70 °C for 12 h. After the polymerization, the glass tube was cut off carefully with grindstone. Firm, integrated and polished monoliths could be obtained. The monolithic material on the bar was then Soxhlet-extracted with methanol for 24 h to remove the residue monomers, porogen, uncross-linked polymers and initiator. Finally, the stir bar was dried in air for 1 h to obtain the final SBSE-MADB (30 mm in length and 1.0 mm monoliths thickness).

2.4. Extraction and desorption mode

Stirring extraction and stirring liquid desorption modes were used. The samples were stirred with the prepared bars at 400 rpm at room temperature. A 50 mL mix solution of A and *p*-NA (5.0 μg/mL each) was used for the study of the effect of polymerization parameters on extraction efficiency. In the study of optimized conditions for the extraction of quinolones, 100 mL mix solution of 4 quinolones compounds (100 ng/mL each) was used. After the extraction, the SBSE-MADB was removed and immersed in 3.0 mL desorption solvent, stirred for a certain time to release the extracted analytes. The stripping solution was used directly for HPLC/DAD analysis. In order to regenerate the coating, the SBSE-MADB was immersed in a solvent for 2 h after each use. The solvent consisted of 0.2% TFA water (pH = 2.87) and methanol (V/V = 7/3).

2.5. Chromatographic conditions

The separation was performed on a Kromasil C18 column (5 μm particle size, 250 mm × 4.6 mm I.D.). The mobile phase consisted of a mixture of 60% (V/V) ACN aqueous solution was used for the separation of A and *p*-NA. The detector was set at 205 nm; the flow rate was 1.0 mL/min and injection volume was 20 μL. Containing 0.2% TFA water solution (pH = 2.87) and ACN were used as the mobile phase A and B, respectively, for the separation of four quinolones. The composition gradient started with 20% B and 80% A, and then increased to 25% B in 8.0 min and increased continuously to 30% in 3.0 min, after holding to 13.0 min, the content of B decreased to 20% B in 3.0 min and held until the end of analysis. The detector wavelength was set at 269 nm for EN, 278 nm for NO and CI, 298 nm for SP; the flow rate was 1.0 mL/min; and the injection volume was 20 μL.

3. Results and discussion

3.1. Preparation and characterization of SBSE-MADB

In order to obtain the best extractive performance of SBSE-MADB, the effect of the contents of monomer and porogen on extractive efficiency was studied in detail. Aniline and *p*-nitroaniline was selected to investigate the effect of monomer and porogen concentrations on extraction efficiency. Considering the extraction performance and useful longevity, the optimized conditions for the preparation of SBSE-MADB were the proportion of MASE kept 10% in the monomer mixture, while the ratio of monomer mixture to porogen was 30–70% (w/w) (Bar 2). The SBSE-MADB showed good bar to bar reproducibility and excellent longevity under the optimized preparation conditions. The RSD ($n = 5$) of enrichment factors for aniline and *p*-nitroaniline

Table 1
Extraction efficiency of different SBSE-MADB for A and *p*-NA.

SBSE-MADB	Monomer mixture[a]		Polymerization mixture		Peak height	
	MASE (%, w/w)	DB (%, w/w)	Monomer mixture (%, w/w)	Porogen solvent (%, w/w)	A	*p*-NA
1	5	95	30	70	9,211	3561
2	10	90	30	70	10,093	3624
3	15	85	30	70	10,932	2998
4	20	80	30	70	11,398	2348
5	25	75	30	70	9,386	2611
6	30	70	30	70	7,721	1296
7	35	65	30	70	7,564	2214
8	40	60	20	80	7,480	1685
9	10	90	20	80	9,460	2722
10	10	90	25	75	8,776	2167
11	10	90	35	65	10,278	2900
12	10	90	40	60	9,735	2632
13	10	90	45	55	9,489	2542

[a] Weight fraction in monomer mixture.

were 3.51% and 4.54%, respectively. No decomposition was found during stirring and the bar could be used at least 60 times. The good reproducibility and stability indicate that poly (MADB) monolithic material is very suitable to be used as the layer of SBSE.

The poly (MADB) monolithic material under the optimal conditions (Bar 2) was characterized by EA, IR and SEM. Elemental analysis on the monolith demonstrated that its carbon content was 84.42% (w/w) and sulfur content was 2.15% (w/w), indicating that MASE and DB were successfully incorporated into the monolith during the polymerization process. Fourier-transform IR measurement (Fig. 1a) of the final monolithic structure further confirmed the polymerization of MASE and DB. The spectrum shows a strong peak around 2918.05 cm^{-1} which can be attributed to the CH_3 and CH_2 groups. Strong adsorption in the 1201.04 cm^{-1} and 1037.56 cm^{-1} can be due to S=O asymmetric and symmetric stretching bands, respectively, of sulfonic groups. The adsorption observed at 1633.73, 1598.70 and 1509.19 cm^{-1} indicates the existence of phenyl groups. Fig. 1b shows the SEM image of the poly (MADB) monolith at 6000× magnification. The even pore size and microglobules of the monolithic material can be clearly observed. The existence of even pore size distribution ensures poly (MADB) monoliths possess good permeability and favorable mass transfer in extraction applications.

3.2. Optimization of SBSE-MADB operating conditions

In order to investigate the extractive ability of SBSE-MADB for polar antibiotics, the SBSE-MADB was applied to direct extract trace concentration of four quinolones in water samples without derivatization. Several main parameters include pH value, desorption solvent, ionic strength, extraction and desorption time were studied in detail for optimizing the extraction conditions.

3.2.1. The effect of pH value

The effect of sample pH on the extraction efficiency was investigated in the range from 2.0 to 10.0. As shown in Fig. 2, when the other conditions were constant, the pH value affected the extraction efficiency of SBSE-MADB for quinolones strongly. The results showed that the extraction efficiencies improved significantly with the increase of pH value from 2.0 to 5.0 and decreased with pH value increased continuously for the four quinolones. This interesting trend may be explained as following: Although there were protonation of nitrogen atoms in quinolones, sulfonic groups in the monolithic materials did not produce ionization at low pH value. Therefore, there were only hydrophobic interactions contributed to extraction when pH value was 2.0. Sulfonic groups could possess negative charge through ionization when pH value increased, so cation-exchange and hydrophobic interac-

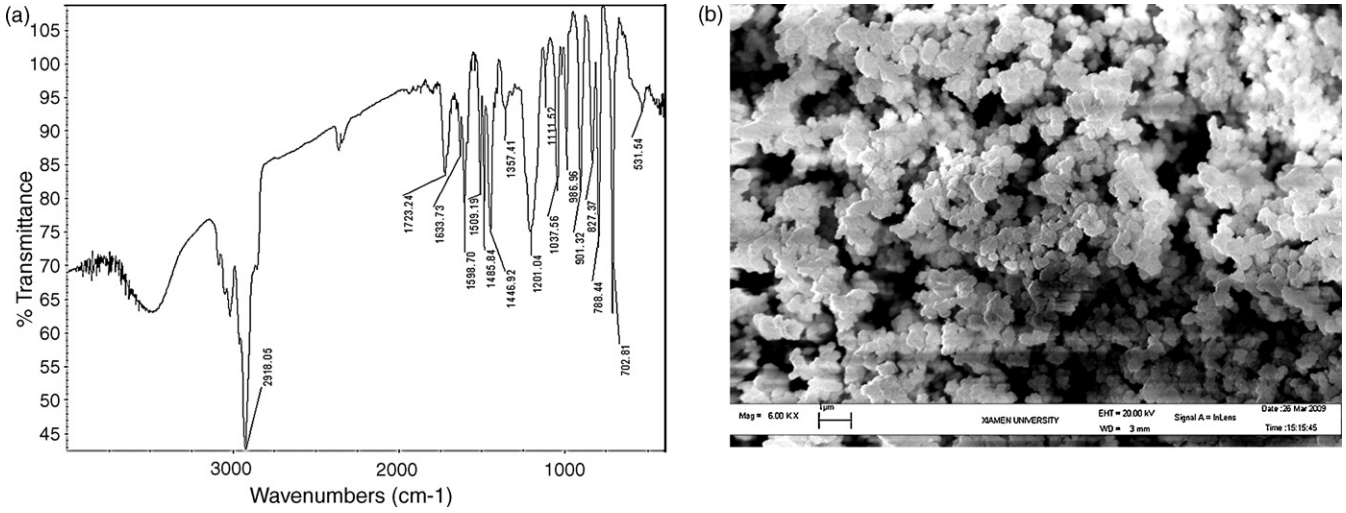

Fig. 1. IR spectrum of poly (MADB) (a) and SEM image of poly (MADB) monolith at 6000× magnification (b).

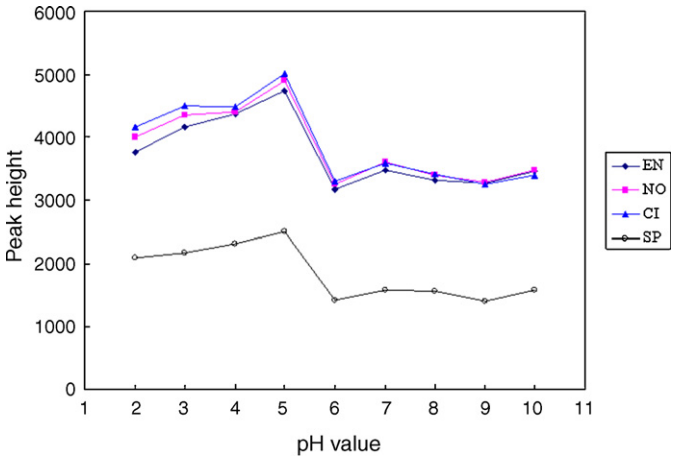

Fig. 2. The effect of pH of the sample matrix on extraction efficiency.
Conditions: extraction and desorption time were 0.5 h and 1.0 h, respectively; methanol/water (pH value 1.3) (V/V = 2/1) binary solvent was selected as desorption solvent; no salt was added.
The sample pH values were adjusted by 0.1 mol/L HCl and 1.0 mol/L NaOH.

tions between coating and analytes contributed to extraction when pH value increased and the extractive performance reached maximum when pH value was 5.0, in which all the four quinolones possessed positive charges (could be understood from the pKa values in Table S1). When the pH value increased continuously, the ion-exchange interaction was weaken and even disappeared because of lack of protonation of nitrogen atoms, although there were negative charges on the sulfonic groups. At the same time, the carboxyl groups in the quinolones would produce negative charges at high pH value. Hereby, there were ionic repulsion produced by the carboxyl in analytes and sulfonic groups in the coating with the increase of pH value. The ionic repulsion would decrease the extraction performance of SBSE-MADB. The above discussion suggests that the extraction mechanism of SBSE-MADB for quinolones includes cation-exchange interaction produced by sulfonic groups in the monolithic materials and amino groups in quinolones except for hydrophobic interaction. From the experimental results, setting the pH value of matrix at 5.0 was recommended for the extraction of quinolones in water matrix with the SBSE-MADB.

3.2.2. The effect of desorption solvent

Because cation-exchange and hydrophobic interaction contribute to the extraction of quinolones on SBSE-MADB, appropriated desorption solvent should be selected. In this study, methanol/water (pH value 1.3) binary solvent was selected as desorption solvent. The content of methanol in the desorption solvent varied from 50% to 90% (V:V). Fig. 3 shows that the extraction efficiencies reach maximum for all studied quinolones when methanol content is 80%. Therefore, methanol/water (pH value 1.3) (V/V = 80/20) was chosen as the desorption solvent.

3.2.3. The effect of ionic strength

According to our previous research [16–21], the extraction performance of SBSE for polar compounds strongly depends on the ionic strength in the sample matrix and appropriate ionic strength would increase the extraction performance. However, the present research results showed that the extractive efficiencies decreased with the increased concentration of NaCl (Fig. 4). The main reason might be that Na^+ would contact with sulfonic groups, and leaded less sulfonic groups could interact with amino groups in the targets. Therefore, the extraction performance decreased when more NaCl was used to increase the ionic strength in the matrices. No addition of any salt was adopted in the following studies.

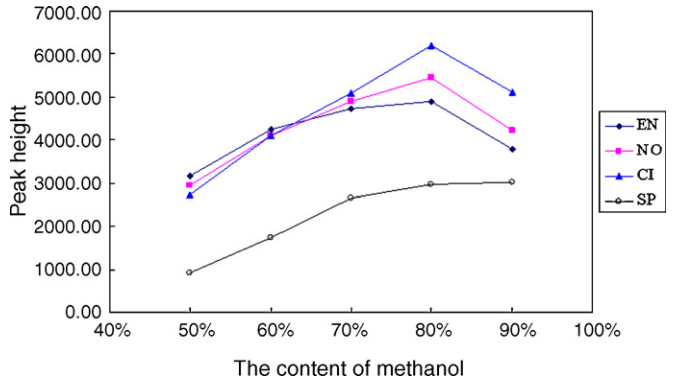

Fig. 3. The effect of desorption solvent on extraction efficiency.
Conditions: extraction and desorption time were 0.5 h and 1.0 h, respectively; pH value was 5.0; no salt was added.

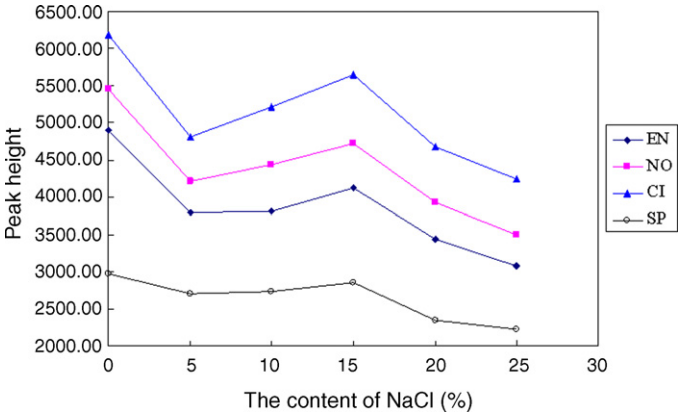

Fig. 4. The effect of NaCl addition on extraction efficiency.
Conditions: extraction and desorption time were 0.5 h and 1.0 h, respectively; pH value was 5.0; methanol/water (pH value 1.3) (V/V = 80/20) binary solvent was selected as desorption solvent.

3.2.4. The effect of extraction and desorption time

Fig. 5 shows the effect of extraction time on the extraction efficiencies for quinolones. The extraction time was varied from 5 min to 90 min. Results indicated that the extraction efficiencies increased when the extraction time increased from 5.0 min to 60 min and decreased afterwards except for SP. The sharp slopes of the profiles between 5.0 and 60 min indicated that the monolithic materials showed remarkable extraction capacity towards these analytes. Balancing the sensitivity and the time consumed, extrac-

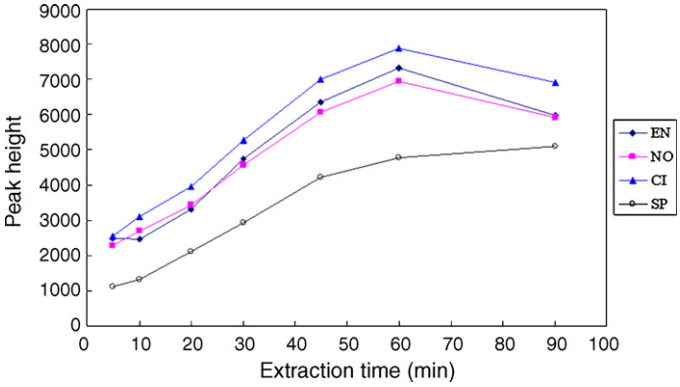

Fig. 5. The effect of extraction time on extraction efficiency.
Conditions: desorption time was 1.0 h; pH value was 5.0; methanol/water (pH value 1.3) (V/V = 80/20) binary solvent was selected as desorption solvent; no salt was added.

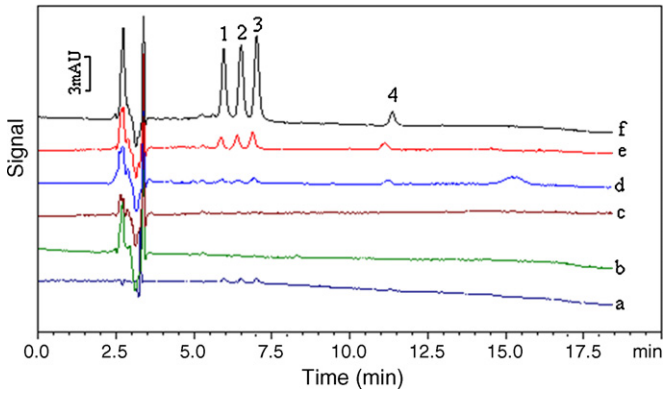

Fig. 6. HPLC chromatograms of four quinolones.
(a) Direct injection of spiked water sample with each quinolone at 100 ng/mL.
(b) Spiked water sample with each quinolone at 100 ng/mL and treated with SBSE-PDMS;
(c) Spiked water sample with each quinolone at 100 ng/mL and treated with SBSE-VPED;
(d) Spiked water sample with each quinolone at 100 ng/mL and treated with SBSE-VIDB;
(e) Spiked water sample with each quinolone at 100 ng/mL and treated with SBSE-VPDB;
(f) Spiked water sample with each quinolone at 100 ng/mL and treated with SBSE-MADB;
Peaks: 1 = EN; 2 = NO; 3 = CI; 4 = SP. The detector wavelength was 278 nm.

tion time of 60 min was selected for further studies. The effect of liquid desorption time on result was also studied. It was found that the 40 min was enough for desorption of target compounds from SBSE-MADB when the extraction time was 60 min. Consequently, 60 min and 40 min were adopted for extraction and desorption procedure, respectively, in the following research.

From the above experimental result, the optimized parameters for the extraction of quinolones from water matrix with the SBSE-MADB were the following: the pH value of matrix was 5.0; using methanol/water (pH value 1.3) binary solvent (V/V = 80/20); no salt was added in the matrix; extraction and desorption time were 60 min and 40 min, respectively.

3.2.5. Comparison of extraction performance with other SBSE

Four quinolones compounds spiked at 100 ng/mL level were analyzed by SBSE–LD–HPLC/DAD method under the above optimized conditions. The typical chromatogram is shown in Fig. 6f. Fig. 6b, c, d and e showed the results that quinolones were extracted by SBSE-PDMS, SBSE-VPED, SBSE-VIDB and SBSE-VPDB, respectively, under the same conditions. From Fig. 6, it can be seen that SBSE-MADB possesses the highest extraction performance for quinolones among the five SBSEs. The excellent extraction performance for SBSE-MADB can be contributed to the existence of sulfonic groups and phenyl groups in monolithic material. The sulfonic groups can interact with amino groups in quinolones through cation-exchange interaction under weakly acid condition. Phenyl groups can produce hydrophobic interaction with phenyl groups or ring alkyl groups in quinolones. The double interactions that lead to quinolones can be extracted effectively by SBSE-MADB. While for other SBSEs, only hydrophobic interactions contribute to the extraction of quinolones. Especially, for SBSE-VPED, SBSE-VIDB and SBSE-VPDB, the ionic repulsion produced by the protonation of nitrogen atoms in monolithic materials and quinolones would minify the hydrophobic interactions. Therefore, SBSE-VPED, SBSE-VIDB and SBSE-VPDB showed very good extractive performance for polar compounds such as phenols and aromatic amines, but showed very poor extractive efficiencies for quinolones. The comparative results tell us that for different targets, different coatings for SBSE should be developed. Due to the high extraction capacity of SBSE-MADB, great enhancement of the peak height can be obtained, which indicates that a lower detection limit will be achieved.

3.3. Validation of the SBSE-MADB–LD–HPLC/DAD method

The blank water samples were spiked with four target analytes and taken for analysis to evaluate the developed method. The data of linear dynamic range, correlation coefficients, extractive efficiencies, LODs, LOQs, and reproducibility for the quinolones under the optimized experimental conditions are listed in Table 2. It can be seen from the data that the SBSE-MADB–LD–HPLC/DAD methodology presents a good performance. The linear dynamic range of a 100 mL sample was 5.0–100 μg/L with good linearity ($R^2 > 0.98$). The extractive efficiencies of four quinolones ranged from 62.23% to 72.87%. The LOD and LOQ were determined at a concentration at which signal-to-noise ratios were equal to 3 and 10, and those were in the range of 0.37–0.56 and 1.22–1.86 μg/L, respectively. The LOD and LOQ were low enough to analyze trace quinolones in water matrix. The precision of the proposed method was evaluated using inter-assay repeatability calculated as RSD on five replicates, and were found the RSDs between 2.88 and 10.63%, respectively.

Comparative study of our developed method with other reported sample preparation procedures was performed and the results are presented in Table 3. Comparing with other methods, lower LOD can be obtained in the present method than other methods with same kind of detector. Generally, determination of quinolones by MS detector [26,27,31,32] was more sensitive than using HPLC method with UV detection [22,23,25,29]. However, the proposed method exhibited a greater sensitivity than other analytical methods with MS detector, except for solid-phase dispersion-LC–MS–MS and SPME-LC–MS–MS because tandem MS detectors were used.

The experimental and comparative results well indicate that the SBSE-MADB–LD–HPLC/DAD method can be used to effectively analyze ionic quinolones in water matrix.

Table 2
Linear dynamic range, correlation coefficients, LODs and LOQs, inter-assay precisions achieved for the quinolones.

Phenols	Linear range[a] (μg/L)	R^2	LOD[b] (μg/L)	LOQ[c] (μg/L)	Extractive efficiency (%)[d]	Inter-assay[e] variability (RSD%, $n = 5$)
EN	5.0–100.0	0.9948	0.41	1.38	65.80	5.02
NO	5.0–100.0	0.9959	0.42	1.41	64.23	2.88
CI	5.0–100.0	0.9947	0.37	1.22	64.28	3.63
SP	5.0–100.0	0.9818	0.56	1.86	72.87	10.63

[a] Spiked level includes 5.0 ng/mL, 10 ng/mL, 20 ng/mL, 50 ng/mL, and 100 ng/mL, respectively.
[b] S/N = 3.
[c] S/N = 10.
[d] The extraction efficiency is calculated from the equation: $E = (30S_A/CS_B) \times 100\%$, where E is the extraction efficiency, S_A, S_B and C are the peak height of after extraction, peak height of 1 mg/mL quinolone and the spiked concentration, respectively.
[e] Assays at 100 ng/mL level.

Table 3
Comparison of the limits of detection (ng/mL or ng/g) of our method with other methods.

Methods	EN	NO	CI	SP	Reference
LE-HPLC–DAD	3	/	3	/	[22]
MISPE-HPLC–UV	60	70	50	/	[23]
LE-HPLC–FLD	/	/	2	/	[24]
ASE-HPLC–DAD	600	1000	1000	/	[25]
SPE-LC–ESI-MS	/	0.8	0.6	1.7	[26]
SPE-LC–MS–MS	<11	<11	<11	/	[27]
SPE-HPLC–MS	/	/	15	/	[28]
SPE-ITP-CZE-UV	10	/	50	/	[29]
SPE-LC–ESI-MS–MS	<20	<10	<15	/	[30]
SPME-LC–MS–MS	0.6	0.3	0.6	/	[31]
Solid-phase dispersion-LC–MS–MS	/	/	0.1	/	[32]
SBSE-HPLC–UV	0.41	0.42	0.37	0.56	Our method

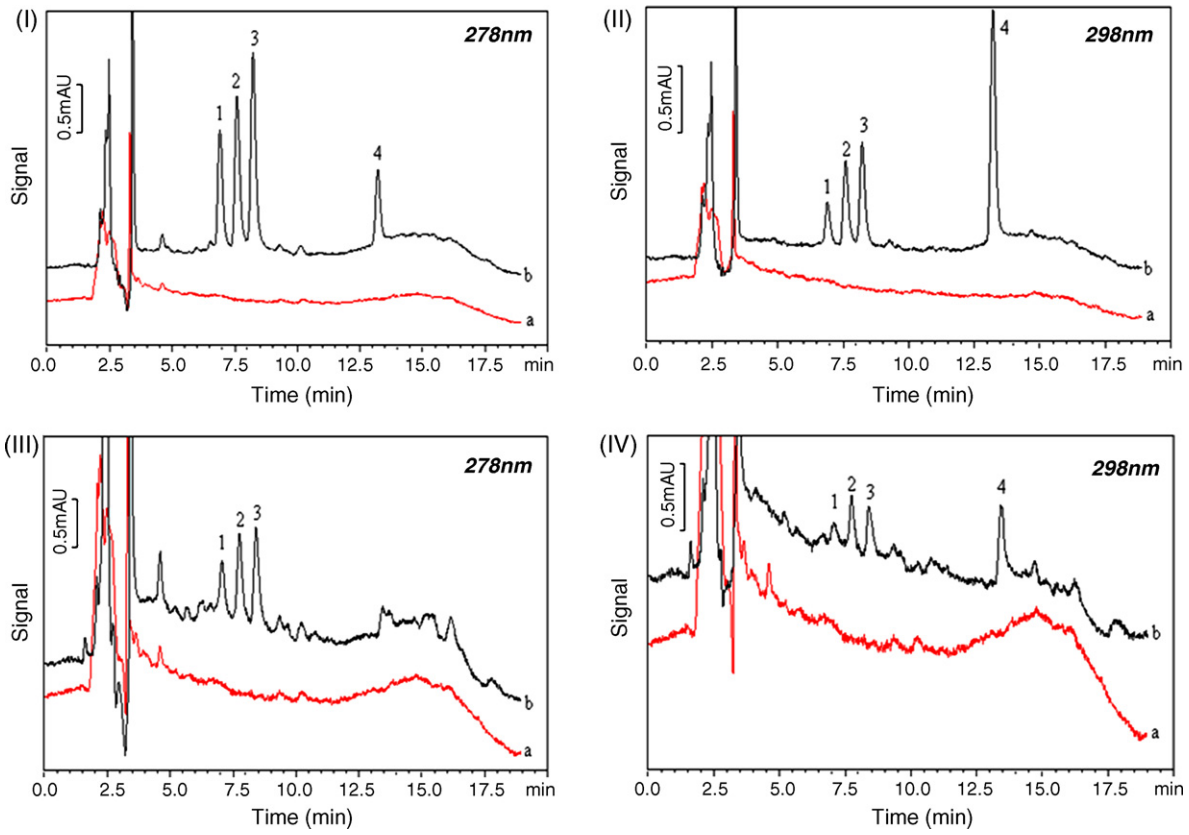

Fig. 7. HPLC chromatograms of real water samples from Xiamen wastewater treatment plant.
(I) Inlet wastewater detected at 278 nm; (II) Inlet wastewater detected at 298 nm;
(III) Outlet wastewater detected at 278 nm; (IV) Outlet wastewater detected at 298 nm;
In figure I–IV, a and b represent direct inject without treatment with SBSE-MADB and treatment with SBSE-MADB, respectively.
Peaks: 1 = EN; 2 = NO; 3 = CI; 4 = SP.

3.4. Analysis of environmental wastewater samples

Two water samples obtained from Xiamen wastewater treatment plant were analyzed by the present methodology. From Fig. 7, it can be seen that four quinolones were detected before and after treatment. Although the concentrations of targets decreased obviously, quinolones could not be cleared completely after treatment. For example, 8.61 ng/mL and 1.84 ng/mL were detected for EN before and after treatment, respectively.

In our future research, the SBSE-MADB will be used to extract other antibiotics such as sulfonamides and β-lactam antibiotics in different matrices, to extend the applicable field of SBSE-MADB.

4. Conclusions

In this work, a novel SBSE with poly (methacrylic acid-3-sulfopropyl ester potassium salt-divinylbenzene) monolithic material extractive phase was prepared. The new SBSE could extract quinolones effectively through cation-exchange and hydrophobic interaction and showed higher affinity to quinolones than commercial SBSE-PDMS and other SBSEs which based on monolithic materials. The combination of SBSE-MADB–LD–HPLC/DAD was successfully applied to the determination of quinolones in wastewater matrix, at the trace level. In comparison with the existing extraction methods for quinolones determination, the proposed method was simple, sensitive, inexpensive, stable and environmen-

tal friendly. Therefore, it will be useful and practical in the screening and determination of quinolones in environmental and biological samples, such as water and urine.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2009.09.072.

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