Determination of sulfonamide compounds in sewage and river by mixed hemimicelles solid-phase extraction prior to liquid chromatography–spectrophotometry

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Abstract

Mixed hemimicelles-based solid-phase extraction was investigated for the preconcentration of five sulfonamides from environmental water samples prior to HPLC–spectrophotometry determination in this paper. A comparative study on the use of sodium dodecyl sulfate (SDS) coating γ -alumina or octadecyltrimethylammonium bromide (OTMABr) and OTMABr coating silica as sorbent materials were presented. The five analytes (sulfadiazine (SDA), sulfathiazole (STA), sulfapyridine (SPD), sulfamethazine (SMZ) and sulfamethoxazole (SMX)) were quantitatively adsorbed on OTMABr- γ -alumina and OTMABr-silica mixed hemimicelles, but OTMABr- γ -alumina was not adopted because it worked at a high pH (around 10), instead, OTMABr-silica was selected to overcoming the pH restriction. The analytes retained on the cartridge were quantitatively desorbed with suitable amounts of methanol. Factors influencing the extraction efficiency, such as the amount of surfactant, pH of sample and breakthrough volume were discussed. The proposed method had been applied to determining the five sulfonamides in several environmental water samples and concentration factors of 300 and 600 for SDA and other four analytes were achieved, respectively. Detection limits obtained ranged between 0.15 and 0.35 $\mu\text{g/L}$ for this five sulfonamides under the optimized conditions. The accuracy of the method was evaluated by recovery measurements on spiked samples, and good recovery results (89–113%) with precision of 3–6% were achieved.

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1. Introduction

Sulfonamides are widely used as a kind of antibacterial drugs in medical and veterinary applications, they are often prescribed for treatment of many human and animal infectious diseases [1,2]. Long-term use of the sulfonamides can result in serious side effects [3]. As a result, sulfonamides can be found in excreta of animal origin. These compounds can be leached from the above-mentioned substances and released into various environments through wastewater, and therefore, they are ubiquitous in various environmental matrices. Europe and Japan for instance

have acted the maximum residue levels of 100 and 20 ng/g in edible tissues and milk, respectively, referring to the sum of sulfonamides [4,5]. All these limits will be lowered based on improvement of analytical methods.

The concentration of sulfonamides is low (usually ppb level) in aqueous environmental samples and the environmental matrices composition is also complex, which make it difficult to determine these compounds directly and the use of preconcentration methods and clean steps prior to their analysis become necessary. Several papers have discussed the different methods of sample preparation, chromatographic separation and detection systems used in the analysis of sulfonamides [6–10]. Stoob et al. [7] applied online solid-phase extraction coupled directly to liquid chromatography–tandem mass spectrometry to determining 10 sulfonamides in surface waters, the detection limits were between 0.5 and 5 ng/L. Malintan et al. [10] applied SPE method to determining eight sulfonamides in wastewater with

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HPLC separation and UV absorbance detection, the limit of quantitation (LOQ) were between 5 and 7.5 ng/L. A number of other methods were described in literature including electrochemistry [11–13], spectrophotometric [14–16], ELISA [8,17] and MS [18,19] detection.

Solid-phase extraction (SPE) at present was the most popular sample preparation method and was commonly used for a wide range of compounds prior to LC analysis. It has many obvious advantages compared with liquid–liquid extraction, such as high preconcentration factors, low consumption of organic solvents and easy to operate. Hemimicelles and admicelles (mixed hemimicelles) have been recently emerged as excellent sorbent materials for the SPE of organic compounds [20–22]. These sorbent materials are produced by the adsorption of ionic surfactants on the surface of metal oxides, such as alumina, silica, and ferric oxyhydroxides. Generally, ionic surfactant adsorbed onto metal oxides can be divided into four steps [23–25]. In the first step adsorption of surfactant on metal oxides occurs through coulombic attraction between charged oxide surface and the oppositely charged surfactant head group (Henry's law zone), this one-to-one charge exchange of surfactant and adsorbed counter ions does not greatly change the charge of the solid particle. The second step involves strong lateral interaction between adsorbed monomers, resulting in the formation of primary aggregates, known as hemimicelles and this association greatly enhances the adsorption capability of the solid particle. The adsorption is thus driven both by hydrophobic interactions and electrostatic attraction, which results in the formation of both hemimicelles and admicelles (mixed hemimicelles). At the end of the step surfactant forms micelles in solution, the overall surface charge is neutralized and further adsorption is purely due to hydrophobic interactions with the surfactant tails. The process of solubilization of organic compounds in mixed hemimicelles is termed as "adsolubilization".

Mixed hemimicelles used in SPE have many advantages, such as high extraction yields, high breakthrough volumes, easy elution of analytes and high flow rate for sample loading. On the other hand, this kind of SPE technique requires no clean-up steps and easy and simple to regenerate, which can meet the need of rapid analysis. Furthermore, there are many kinds of surfactant available in commerce and it is easy to select a suitable surfactant as sorbent according to various environmental samples. These characteristics make mixed hemimicelles have a great potential for the SPE of organic compounds.

The objective of this work was to develop a simple and rapid approach for determining five sulfonamides at trace levels existed in sewage and river water and apply the SPE method based on mixed hemimicelles to concentrate these compounds. Mixed hemimicelles prepared by adsorption of SDS on γ -alumina and OTMABr on silica and γ -alumina were tried. Predominant experimental factors affecting the forming of mixed hemimicelles and the recoveries for these five sulfonamides were studied. The results of analyzing the target compounds in sewage and river samples using this technique were proven to be dependable and the analytical method of the SPE-LC–spectrophotometry based on OTMABr-silica was established. To our knowledge adsolubilization-based SPE for

the treatment of sulfonamides in sewage and river water samples was the first reported.

2. Experimental

2.1. Chemicals and materials

All reagents were of analytical grade and were used as supplied. Five sulfonamides were obtained from Sigma–Aldrich (USA) and their structure was listed in Table 1. A stock solution containing 200 mg/l each sulfonamide was prepared in methanol and stored under dark conditions at 4 °C. The surfactants SDS and OTMABr were supplied by Shanghai Reagent Corporation (Shanghai, China). Alumina (γ -form) and silica were supplied by Sigma–Aldrich (USA). The physical properties of these two metal oxides were as follows: alumina-surface area (155 m²/g); point of zero charge (pcz, 8.5); particle diameter range (50–200 μ m, mean value 100 μ m), mean pore size (58 Å); density (3.97 g/cm³). Silica-surface area (300 m²/g); point of zero charge (pcz, 2.9); particle diameter range (70–150 μ m), mean pore size (150 Å); density (1.15 cm³/g). HPLC-grade acetonitrile and methanol were supplied by Merck (Germany). Water used in all of the experiments was prepared using a compact ultrapure water system from Barnstead (Iowa, USA).

2.2. Sample collection

All water samples were collected from different district in Beijing. Influent and effluent wastewater samples were collected from Gaobeidian sewage treatment plants (Chaoyang district). Gaobeidian sewage treatment plant lies in the east of Beijing and it receives about the same level of domestic and industrial wastewater. The main applied treatment process was as follows:

Influent sewage → Filtrated through bar screen
→ Aerated grit channel → Primary precipitation
→ Aeration basin → Second precipitation
→ Secondary effluent water.

River water samples were taken from Small Qing River (Haidian district) and Jingmi Canal (Haidian district) in June 2006. Tap water samples were taken from our lab in Haidian district. All water samples were collected randomly. Samples were collected into pre-cleaned, light-preserved glass bottles and filtered through 0.22 μ m nylon membranes (Shanghai Institute of Pharmaceutical Industry, China) in order to remove suspended solids, then adjusted to pH 2 with 1 M HNO₃. The filtered samples were stored at 4 °C.

2.3. SPE based on mixed hemimicelles

A mixed hemimicelles-packed cartridge was prepared by modifying a Supelco ENVI-Carb (Supelco, USA) SPE Tubes (0.5 g, 6 mL, polypropylene). The active carbon packing of the cartridge was evacuated, and then 0.5 g silica was packed into the cartridge.

Table 1
Chemical structures, pKa and log $K_{o/w}$ value of the five sulfonamide compounds

Name	Abbreviation	Structure	pKa	Log $K_{o/w}$
Sulfadiazine	SDA		6.4	0.72
Sulfathiazole	STA		7.1	1.01
Sulfapyridine	SPD		8.4	0.83
Sulfamethazine	SMZ		7.4	0.87
Sulfamethoxazole	SMX		6.0	0.92

To prepare mixed hemimicelles column, 25 ml-containing 160 mg of OTMABr was passed through the cartridge column filled with 0.5 g silica. The water samples was adjusted to pH 6 and loaded into the column. Sample loading was performed by using a DOA-PIOU-BN vacuum pump (Mich., USA) at a flow rate of 5 ml/min. Target analytes were eluted with 4.0 ml methanol and the eluate was dried with a stream of nitrogen at 60 °C, and then dissolved in 0.5 ml methanol. The solution was stirred in an ultrasonic bath for 5 min and a 20- μ l of the eluate was injected into the HPLC system for analysis.

2.4. HPLC analysis

The sulfonamides were separated and quantified by using a liquid chromatography–spectrophotometry system (P680 HPLC Pump with an AD25 Absorbance Detector, Dianox, USA). The analytical column was a 250 mm Diamonsil-C₁₈ column (4 μ m particle diameter and 4.6 mm i.d.) supplied by Dikma Technologies (Beijing, China). The mobile phase consisted of water (the pH was adjusted to 3 with H₃PO₄, solvent A) and acetonitrile–water (acetonitrile:water, 75:25, v/v, solvent B). The

gradient elution program was as follows: isocratic conditions with 85% A:15% B for 5 min and then linear gradient from 15 to 40% B in 10 min, keep for 10 min then linear gradient from 40 to 15% B in 3 min. The flow rate was set at 1 ml/min. Spectrophotometry detection of analytes was performed at 260 nm.

3. Results and discussion

3.1. The protonation and ionization of sulfonamides

The general structure of sulfonamide is as follows:

the five sulfonamides in this paper can be distinguished by the different $-R$ group, which were shown in Table 1. In acidic pH range sulfonamide compounds become protonated via $-NH_2$ group and have positive charge, while sulfonamide begins to ion-

ize at the pH nearer to their pK_a value and have negative charge. However, sulfonamides still have great hydrophobic function due to the phenyl group.

3.2. Effect of the amount of surfactant

The effect of the amount of surfactant on the adsolubilization of sulfonamides was studied in batch mode and the experiments were carried out as follows: a aqueous solution containing 0–240 mg SDS/g alumina (pH = 2), 0–240 mg OTMABr/g alumina (pH = 10) or 0–880 mg OTMABr/g silica (pH = 6) was added to an aqueous suspension of 0.5 g γ -alumina or silica, respectively. The solution pH was adjusted with 1.0 M NaOH and HNO₃. To the mixed hemimicelles system, 0.5 ml containing 200 mg/l each sulfonamide solution were added. Total volume of the solution system was 25 ml in a 250 ml glass vial with a cap. All the equilibrium was carried out at 25 ± 1 °C temperature in a water bath with 5 min vigorous stirring. Then the solids were separated by filtering through 0.22 μ m nylon membranes and the supernatant was analyzed using HPLC–spectrophotometry.

The experimental results were shown in Fig. 1. As can be seen from Fig. 1(A) that with the increasing amount of SDS the adsorption extent of sulfonamides had no obvious changing trend and sulfonamides hardly sorbed onto the SDS- γ -alumina mixed hemimicelles. According to the literature [20,21], the SDS- γ -alumina at pH 2 should form mixed hemimicelles easily and have a great potential to sorb hydrophobic compounds. However, the experimental results were opposite, which may be explained that at the condition pH 2 the sulfonamides were protonated and had positive charge, then a repelling force would produce between the sulfonamides and alumina surface with positive charge. Furthermore, this repelling func-

tion plays a more important role compared with hydrophobic function. The Fig. 1(B, C) described that with the increasing amount of OTMABr, the sorption amount increased remarkably then decreased when the added amount of OTMAB exceeded 60 mg for alumina and 200 mg for silica, respectively. The increase in sorption can be explained by the gradual formation of hydrophobic mixed hemimicelles on the surface of γ -alumina and silica, maximum sorption were obtained in the range of 30–60 mg SDS and 100–200 mg OTMABr, respectively. The main difference was the adsorption percentage of SDA, which was about 40 and 80% for γ -alumina and silica, respectively. The decrease in sorption was due to the reason that with more surfactant added the SDS and OTMAB molecules began to form micelles in the bulk aqueous solution, furthermore, the micelles made the sulfonamides distribute into the solution again. For the OTMABr-alumina system, the sulfonamides had deprotonated and the surface of alumina was negative charged under pH 10 conditions; similarly, for the OTMABr-silica system the sulfonamides had protonated and the surface of silica was positive charged under pH 6 conditions, so a repelling force should exist in two systems. However, Fig. 1(B, C) showed that the two system both had strong adsorption ability for the sulfonamide compounds, which can be explained that the hydrophobic interactions between the sulfonamides and formed mixed hemimicelles governed the retention of analytes under the experimental conditions. Log $K_{o/w}$ was used extensively to demonstrate compound hydrophobic properties and Table 1 listed the log $K_{o/w}$ of the five sulfonamides. Fig. 1(B, C) also showed that the different sorption amount of the five sulfonamides appeared to be closely correlated with log $K_{o/w}$, which also proved that the extractability of sulfonamides mainly depended on the hydrophobic properties of the analytes.

Fig. 1. Effect of the amount of (A) SDS, (B) OTMABr mixed hemimicelles formed on alumina and (C) OTMABr mixed hemimicelles formed on silica for the adsolubilization of sulfonamides: ($\diamond$) SDA, ($\square$) STA, ($\triangle$) SPD, ($\blacksquare$) SMZ and ($\blacklozenge$) SMX. pH: (A) 2, (B) 10 and (C) 6.

Fig. 2. Influence of pH on the adsorption of sulfonamides: ($\diamond$) SDA, ($\square$) STA, ($\triangle$) SPD, ($\blacksquare$) SMZ and ($\blacklozenge$) SMX. Amount of metal oxide: 0.5 g of (A) OTMABr- γ -alumina and (B) OTMABr-silica.

3.3. Effect of the pH

The pH of the solution was one of the prime factors that drastically influenced the adsorption behavior of the mixed hemimicelles system. In the present study, the effect of pH had been observed by varying the pH in the range 1.7–11. The experiments were carried out in batch mode above-mentioned in Section 3.2. The selected amount of OTMABr for alumina and silica was 40 and 160 mg, respectively. As can be seen from Fig. 2 that the pH did not affect the adsorption amount of sulfonamides obviously by OTMABr- γ -alumina in the range of 2–8 and by OTMABr-silica in the range of 1.7–3.3, while when the pH up to 8 for alumina and 3.3 for silica, the sorption amounts both increased dramatically. The significant increase can be ascribed to the formation of mixed hemimicelles on the surface of metal oxide when pH was above the pcz value of alumina and silica, respectively. The Fig. 2(A) also demonstrated that SDA still had poorer sorption percentage of about 40% than that of 80% in Fig. 2(B).

According to above experimental results, SPE of sulfonamides based on OTMABr- γ -alumina mixed hemimicelles system needs high pH value (pH 10), which may lead to some depositions in wastewater, furthermore, the sorption efficiency of SDA was poor. So, we selected the OTMABr-silica mixed hemimicelles as sorbent to carry out next experiments.

3.4. Breakthrough volume and desorption

The breakthrough volume for each sulfonamide on OTMABr-silica sorbent was determined through passing increasing volume (50–500 ml) of influent wastewater sample spiked with 1 μ g of each sulfonamide at pH 6. The cartridge was filled with 500 mg silica and loaded with solution containing 160 mg OTMABr, then determining the recovery of each sulfonamide. Breakthrough was considered to occur when the recovery was below 95%. It was found to be 150 ml for SDA and 300 ml for the other four sulfonamides. By drying the eluate with a nitrogen flow and redissolving the analytes in 0.5 ml methanol, the preconcentration factors of 300 for SDA and 600 for STA, SPD, SMZ and SMX were achieved, respectively. The sample flow rate experiments (1–10 ml/min) were carried out using deionized water spiked with 1 μ g of each sulfonamide

under the selected breakthrough volume. Flow rate was considered too fast when recovery of the eluate was below 95%. The experimental results indicated that the recoveries were all above 95% when sample rate was in the range of 1–5 ml/min; when sample rate increased to 8 and 10 ml/min, the recoveries of SDA was reduced to 80 and 60% and that of the four other sulfonamides were reduced to 85 and 70%, respectively.

Desorption of sulfonamides from the OTMABr-silica mixed hemimicelles column was studied with different organic solvents (acetonitrile, methanol) and 0.01 M HNO_3 . Quantitative recoveries of sulfonamides were obtained using 4 ml methanol. When using 4 ml acetonitrile, the recoveries were 70, 85, 89, 86 and 81% for SDA, STA, SPD, SMZ and SMX, respectively. Higher volume acetonitrile (8 ml) was required for eluting sulfonamides completely. When using 4 ml 0.01 M HNO_3 , the recoveries were 57, 68, 69, 84 and 82% for SDA, STA, SPD, SMZ and SMX, respectively. Thus, 4 ml methanol was recommended for elution.

3.5. Analytical performance

Calibration curves were run using 150 and 300 ml deionized water for SDA and four other sulfonamides both spiked with 0.3–30 ng/ml sulfonamides, respectively. According to the overall SPE procedure and HPLC analysis method above-mentioned, the calibration curves were established. The slope of the calibration curves was 129.6 ± 2.9 , 237.8 ± 1.6 , 242.3 ± 4.9 , 245.7 ± 5.7 and $287.6 \pm 3.5 \text{ ng}^{-1}$ with the correlation coefficients (r) 0.996, 0.995, 0.997, 0.998, 0.991 for SDA, STA, SPD, SMZ and SMX, respectively. The correlation coefficients obtained indicated good fits for all sulfonamides in this method.

The practical detection limits were estimated using influent wastewater as a typical sample for it having the high BOD of 129 mg/L and the most complex matrix in the five collected water samples. As we determined the concentration of five sulfonamides in influent wastewater beforehand and found that the SDA and STA had no readout signals in spectrophotometer while the concentration of other three sulfonamides were between 0.35 and 0.64 $\mu\text{g/L}$, so we spiked 0.50 $\mu\text{g/L}$ SDA and STA into the influent wastewater, respectively, and used this water sample to evaluate the practical detection limits. The practical detection limits were evaluated from six independent overall determina-

Table 2
Determination and recoveries of sulfonamides in real water samples

Samples	Added ($\mu\text{g/L}$)					Founded ^a ($\mu\text{g/L}$)					Recovery ^b (%)				
	SDA	STA	SPD	SMZ	SMX	SDA	STA	SPD	SMZ	SMX	SDA	STA	SPD	SMZ	SMX
Tap water	0	0	0	0	0	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c					
	0.3	0.3	0.3	0.3	0.3	0.28	0.29	0.32	0.34	0.31	92 $\pm$ 3	98 $\pm$ 4	101 $\pm$ 3	113 $\pm$ 5	102 $\pm$ 6
Jingmi canal river	0	0	0	0	0	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c					
	0.3	0.3	0.3	0.3	0.3	0.27	0.29	0.31	0.29	0.30	90 $\pm$ 5	96 $\pm$ 3	102 $\pm$ 5	98 $\pm$ 6	101 $\pm$ 3
Small Qing river	0	0	0	0	0	n.d. ^c	0.52	n.d. ^c	0.34	0.33					
	0.3	0.3	0.3	0.3	0.3	0.29	0.80	0.29	0.65	0.61	95 $\pm$ 6	98 $\pm$ 4	96 $\pm$ 5	103 $\pm$ 6	96 $\pm$ 3
Gaobeidian influent	0	0	0	0	0	n.d. ^c	0.35	n.d. ^c	0.58	0.64					
	0.3	0.3	0.3	0.3	0.3	0.27	0.67	0.28	0.84	0.96	91 $\pm$ 5	103 $\pm$ 6	96 $\pm$ 5	95 $\pm$ 3	103 $\pm$ 3
Gaobeidian effluent	0	0	0	0	0	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	0.56					
	0.3	0.3	0.3	0.3	0.3	0.27	0.29	0.32	0.31	0.84	89 $\pm$ 5	95 $\pm$ 6	105 $\pm$ 5	104 $\pm$ 3	99 $\pm$ 3

^a Mean of three determinations.

^b Standard deviation for three determinations.

^c Not detected.

tion of sulfonamides concentration and calculated by using the standard deviation (S_0) of 3 [26]. The detection limits were 0.35, 0.26, 0.16, 0.15 and 0.15 $\mu\text{g/L}$ for SDA, STA, SPD, SMZ and SMX, respectively. The precision was evaluated by six independent and continuous extractions of the influent wastewater samples spiked with 1 μg of each sulfonamide. The relative standard deviation ranged from 3 to 6%, which indicated the good precision of this method.

3.6. Analysis of real water samples

The proposed method was applied to the analysis of some real environmental water samples, and the experimental results are shown in Table 2. No sulfonamides were found in the tap and Jingmi canal river water. For the case of other three water samples, only STA, SMZ and SMX were found. The accuracy of this method was evaluated by the recovery test, which was carried

Fig. 3. Solid-phase extraction/LC–spectrophotometry chromatograms. (A) Standard solution containing 1 mg/l of each compound (B) Jinmi river water sample, and (C) influent wastewater sample. 1, SDA; 2, STA; 3, SPD; 4, SMZ; 5, SMX.

out with standard sulfonamides mixture-spiked water samples. Recoveries ranged between 89 and 113% for five sulfonamides and the results are fairly satisfactory. The chromatograms of a river water sample and influent wastewater sample were shown in Fig. 3.

4. Conclusions

A simple, rapid and reliable method was developed for the solid-phase extraction of five sulfonamides in several environmental water samples by using a OTMABr-silica-packed cartridge. The use of mixed hemimicelles SPE technique was effective for concentrating traces of sulfonamides in water prior to HPLC analysis. The strong hydrophobic interactions between the surface of the mixed hemimicelles and sulfonamides resulted in their high retention, however, the analytes retained on OTMABr-silica can be easily desorbed with methanol and no carryover is observed in the next analysis. Good recoveries and precision of this method were obtained, which showed that OTMABr-silica SPE method have high analytical potential for preconcentration of other traces of organic pollutants from water samples.

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