



Magnetic retrieval of graphene: Extraction of sulfonamide antibiotics from environmental water samples

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ABSTRACT

A new technique of retrieving graphene from aqueous dispersion was proposed in the present study. Two-dimensional planar graphene sheets were immobilized onto silica-coated magnetic microspheres by simple adsorption. The graphene sheets were used as adsorbent material to extract six sulfonamide antibiotics (SAs) from water samples. After extraction, they were conveniently separated from the aqueous dispersion by an external magnetic field. Under the optimal conditions, a rapid and effective determination of SAs in environmental water samples was achieved. The limits of detection for six SAs ranged from 0.09 to 0.16 ng/mL. Good reproducibility was obtained. The relative standard deviations of intra- and inter-day analysis were less than 10.7% and 9.8%, respectively.

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1. Introduction

Graphene, a two dimensional honeycomb lattice composed of carbon atoms, has attracted increasing interest because of its remarkable mechanical, thermal and electronic properties since its discovery in 2004 [1,2]. Its unique planar structure provides tremendous potential applications in many fields [3–14,16,17]. For example, graphene served as filler for the enhancement of mechanical and electrical properties in composite materials [3,4]; graphene-based materials were used as sensors for the sensitive and selective detection of biomolecules [5–8]; graphene/polymer composite was an effective candidate for supercapacitor because of its high specific capacitance and good cycling stability [9]. Besides, as graphene is an electron-rich, hydrophobic nanomaterial with large specific area and π - π electrostatic stacking property [10,11], it has been served as an extraordinarily wonderful adsorbent or extraction material [12,13]. For this purpose, the graphene was normally dispersed into the sample solution; centrifugation or filtration followed to separate or retrieve the tiny graphene from dispersion [12,14], which is a little troublesome and tedious.

To ease the retrieval procedure, magnetic adsorbent has been a solution. The retrieval of the adsorbent could be realized by external magnetic field [15]. Yang et al. reported a chemical precipitation method to load magnetic particles on GO to realize controlled delivery and release for targeted drug [16]. Chandra et al. prepared

magnetite–graphene hybrids composite and applied it to arsenic removal from water [17]. In such a way magnetic particles were loaded onto graphene, the resultant magnetic particle–graphene composite can respond to a magnet, which could realize the retrieval and separation of graphene from dispersion rapidly and effectively. However, the present available methods were mostly based on chemical modification of graphene. To avoid tedious procedure involved in the chemical modification, in this work, an easy-to-handle approach was presented.

The new method was established based on large surface area and two-dimensional planar structure of graphene. By adsorption with the aid of sonication, graphene was easily immobilized on silica-coated magnetite (designated $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{graphene}$). Thus, the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{graphene}$ had the magnetic nature, enabling the easy removal of the material after dispersion; meanwhile, graphene in the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{graphene}$ still had its own properties, indicating potential adsorption ability. Considering this, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{graphene}$ was used as an adsorbent to extract six sulfonamide antibiotics (SAs) from water samples. Parameters affecting the extraction efficiency were investigated in detail. Under the optimal conditions, a rapid, efficient method for the determination of SAs in environmental water samples was obtained.

2. Experimental

2.1. Chemicals and materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate (NaAc), ethylene glycol, polyethylene glycol (PEG, Mw = 10,000),

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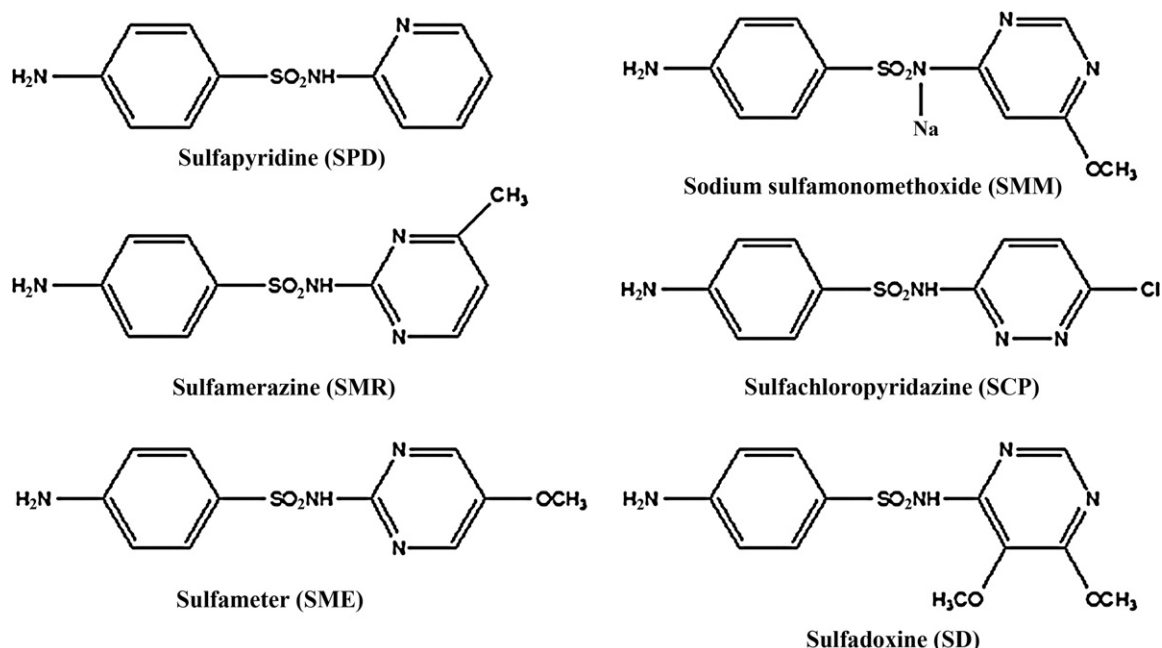


Fig. 1. Chemical structures of the studied SAs in this work.

alcohol, acetone and N, N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Analytical-grade methanol (MeOH) and acetonitrile (ACN) were bought from Concord Technology (Tianjin, China). Tetraethyl orthosilicate (TEOS) was obtained from the Chemical Plant of Wuhan University (Wuhan, China), which was used directly without further purification. Pure water used throughout the study was purified using an Aike apparatus (Chengdu, China).

Sulfapyridine (SPD), sulfamerazine (SMR), sulfameter (SME), sodium sulfamonomethoxide (SMM), sulfachloropyridazine (SCP) and sulfadoxine (SD) were purchased from Laboratories of Dr. Ehrenstorfer (Augsburg, Germany). Individual stock solutions of six SAs were prepared by dissolving 5.0 mg of the pure analytical standards in 10.0 mL of acetonitrile. For experiment, a working standard solution was prepared by combining aliquots of each of the six individual stock solutions and diluting with water to obtain a desired concentration. All of the above solutions were maintained at 4 °C in the dark. The chemical structures of the studied SAs in this work are shown in Fig. 1.

2.2. Synthesis of magnetic microspheres and graphene

Monodisperse magnetite (Fe₃O₄) was produced by solvothermal reduction method according to a previous report (see supporting information) [18]. Magnetic microspheres coated with silica layer (designated Fe₃O₄@SiO₂) were fabricated according to the Stöber method with some modification in basic alcohol/water mixture at room temperature (see supporting information) [19,20].

Graphene oxide (GO) was synthesized from graphite powder by a modified Hummers and Offeman method (see supporting information) [21]. Graphene was prepared by a low-temperature thermal reduction method (see supporting information) [22].

2.3. Extraction procedures

Fe₃O₄@SiO₂ (50 mg) and graphene (15 mg) were placed in a 15-mL vial and washed with phosphate buffer solution (PBS, 20 mM, pH 3.0), pure water and acetone in sequence. After adding 5.0 mL pure water and 3.0 mL DMF, the Fe₃O₄@SiO₂/graphene dispersive

solution was obtained by vortexing vigorously for 1 min (designated MGDS).

When extracting SAs from water samples, the procedure was similar to our previous work with minor modification [23–25]. In brief, an aliquot of MGDS was added into a spiked water sample, and the mixture was vortexed vigorously for a prescribed period for extraction. Then an external magnet was attached to the outside bottom of the vial and the Fe₃O₄@SiO₂/graphene was gathered to the bottom of the vial. The supernatant was discarded. 1.0 mL of desorption solvent was added to the vial, and was vigorously vortexed for a period. Afterwards the magnet was attached to the outside bottom. The solvent was collected and evaporated to dryness under a gentle stream of nitrogen gas at 35 °C, and was reconstituted with 0.1 mL mobile phase for the subsequent HPLC-UV analysis.

2.4. Instrumental and analytical conditions

Atomic force microscopic (AFM) images were taken using a Digital Nanoscope IV MultiMode SPM (Veeco, USA) in tapping mode. Transmission electron microscopy images were obtained from JEM-2100F transmission electron microscope (TEM, JEOL, Japan). The powder X-ray diffraction (XRD) measurements were recorded on a D/MAX-RB X-ray powder diffractometer (RIGAKU, Japan) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with scattering angles (2θ) of 5–80°. Raman spectra of samples were recorded at a wavelength of 514.5 nm (He–Ne laser) by Renishaw Invia Laser Confocal Raman Microspectroscopy. Magnetic properties of the materials were characterized by a PPMS-9 vibrating sample magnetometer (QUANTOM, USA).

The HPLC system was LC-20A (Shimadzu, Japan) which consists of binary LC-20AD pumps, a DGU-20A₃ degasser, a SPD-20A ultra-violet detector, a SIL-20A autosampler and a CTO-20AC column oven. A LC-solution workstation (Shimadzu, Japan) was utilized to control the system and also for data processing. The analytical column was Inertsil[®] ODS-4 column (GL Sciences INC., 150 mm \times 4.6 mm i.d., 5 μ m). The column oven temperature was maintained at 35 °C. The optimized mobile phase was acetonitrile-phosphate buffer solution (PBS, 20 mM, pH 4.9) (25/75, v/v) and

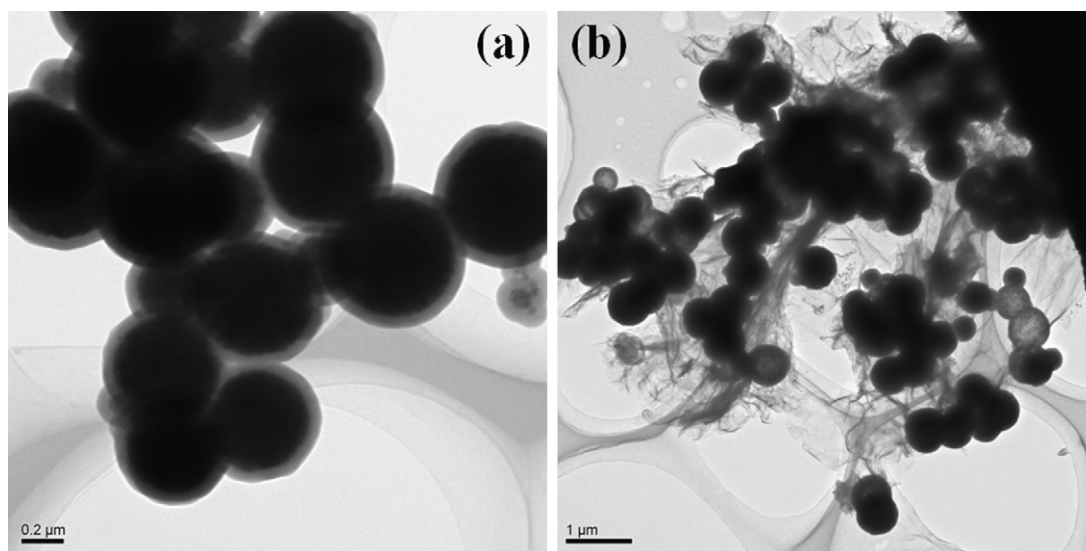


Fig. 2. TEM images of Fe₃O₄@SiO₂ (a) and Fe₃O₄@SiO₂/graphene (b).

the flow rate was 1.0 mL/min. The UV detection was 269 nm and the sample injection volume was 20 μL.

2.5. Sample preparation

Water samples were prepared by spiking PBS (20 mM) with analytes at a known concentration (50 ng/mL) to study the extraction performance under different conditions.

Environmental water samples were collected from the East Lake (Wuhan, China), sewage outfall of a hospital and a fermentation factory. Before experiment, all the water samples were filtered through 0.45 μm microporous membranes and stored in brown glasses at 4 °C in the refrigerator.

3. Results and discussion

3.1. Magnetic retrieval of graphene

Since graphene sheets are hydrophobic, they are apt to aggregate or adhere onto suspending particles in aqueous solution. In such a case, if introducing magnetic particles into graphene dispersion solution, the graphene will adsorb onto the particles or the particles will be trapped within the graphene sheets. No matter how they interact with each other, it endows the graphene with magnetic operational convenience. As a result, the graphene can be readily used for extraction applications.

3.2. Characterization of materials

In our study, AFM, Raman, XRD and TGA studies confirmed the thermal reduction of GO and the formation of graphene (see supporting information). Fig. 2 shows the typical HRTEM images of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂/graphene. As shown in Fig. 2a, a silica layer coated on the outside surface of the spherical Fe₃O₄ can be clearly observed, which could effectively avoid corrosion of Fe₃O₄ in acidic medium. The Fe₃O₄@SiO₂ was spherical, narrowly distributed with average size of ca. 400 nm. From Fig. 2b, it could be seen that Fe₃O₄@SiO₂ was not only mixed up or blended with graphene but also was entrapped within the graphene sheets. The presence of Fe₃O₄@SiO₂ with the graphene endows the latter the magnetic merit, leading to the convenient separation or retrieval from dispersion. Fig. 3 shows the magnetization curves

measured at 300 K for the resultant materials. All curves had no magnetic hysteresis loops. The saturation magnetization values were 72 emu/g for Fe₃O₄, 43 emu/g for Fe₃O₄@SiO₂ and 21 emu/g for Fe₃O₄@SiO₂/graphene, respectively. The relatively high saturation magnetization value of Fe₃O₄@SiO₂/graphene ensures the complete magnetic separation of graphene within ~60 s using a common magnet.

3.3. Extraction optimization

In our experiments, several parameters, including desorption solution, sample pH, desorption time, extraction time and the amount of graphene were investigated to achieve the best extraction efficiency of graphene for SAs.

3.3.1. Desorption solution

Three solvents including methanol, acetonitrile and acetone were studied as desorption solution. The desorption capabilities of these solvents are depicted in Table 1, it can be seen that, under the same extraction and elution conditions, acetone provided the best results. By adding ammonium hydroxide as a modifier in a proportion of 0.5% (v/v), the recoveries for most of the analytes increased in comparison with the pure organic solvents. There-

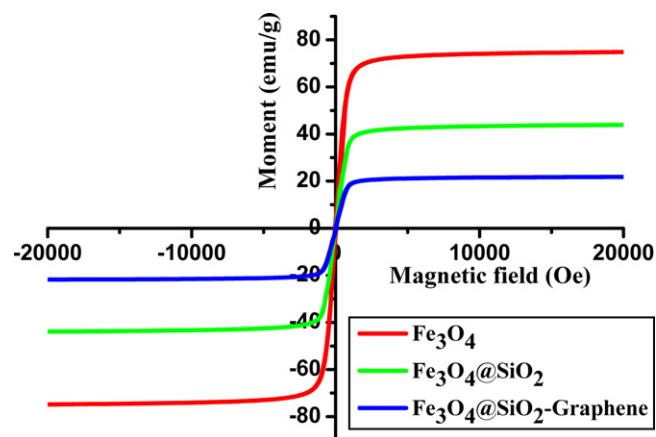


Fig. 3. Room-temperature magnetization curves of Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂/graphene.

Table 1
Analytes recoveries (%) obtained by elution with different eluents after extraction.

Analytes	SPD	SMR	SME	SMM	SCP	SD
Methanol	33.7	27.1	37.6	52.3	52.2	42.3
Methanol containing ammonium	37.8	29.9	42.1	60.3	62.6	47.2
Acetonitrile	38.0	30.1	42.0	60.4	60.8	46.8
Acetonitrile containing ammonium	40.0	31.5	44.3	64.9	67.5	50.2
Acetone	40.9	32.3	45.9	65.7	66.4	51.0
Acetone containing ammonium	45.6	33.3	45.3	70.6	71.6	52.6

fore, acetone containing 0.5% ammonium hydroxide was used as the optimal desorption solution.

3.3.2. Sample pH

Sulfonamides are amphoteric compounds whose molecular status is influenced by the sample pH. Therefore, the pH is expected to be a key factor affecting extraction of sulfonamides to graphene. The pH optimization was performed in 20 mM phosphate buffer solution over the pH range from 1.5 to 9.0. The effect of pH on the extraction was presented in Fig. 4. The highest extraction efficiency for the six SAs was obtained at the pH of 3.0. It is consistent with a previous report, in which the pH-dependent adsorption between carbon nanotubes and SAs were observed [26]. Probably π - π electron coupling between the SAs and graphene plays an important role in the sorption.

At the pH of 3.0, most SAs existed in neutral forms and a few in protonated forms. In such cases, the SAs can be adsorbed onto graphene sheets by π - π electron coupling and hydrophobic interaction. When the sample pH is higher than the pK_{a2} of the compounds, the molecules would possess negative charges, which made the SAs less hydrophobic and also suppressed the π - π electron coupling with the graphene [27–29]. As a result, the SAs could not be efficiently adsorbed onto the sorbent and consequently decreased the extraction performance. To obtain high extraction efficiency, the sample solution was adjusted to pH 3.0 for further studies.

3.3.3. Extraction and desorption time

The desorption time was investigated by increasing the vortex time from 1 to 15 min. The results are shown in Fig. 5. It can be observed that 3 min was enough to elute the SAs from the sorbent.

The extraction time was also investigated. The results are shown in Fig. 4S, which demonstrates that as the extraction time increased from 0.5 to 4 min, the peak areas for most of the analytes increased as expected. Prolonged extraction time did not increase the peak areas of target analytes significantly. Therefore extraction time was fixed at 4 min.

3.3.4. The amount of graphene

To achieve good extraction and recoveries towards the target SAs, the graphene amount was investigated from 0 to 1.0 mg. As shown in Fig. 5S, the peak areas of these SAs increased rapidly when the graphene amount increased from 0 to 0.1 mg, indicating the remarkable enrichment ability of graphene. From the result it can be concluded that the $Fe_3O_4@SiO_2$ particles almost have no enrichment ability towards the SAs. The peak areas of the six SAs increased slightly when the graphene amount increased from 0.1 to 1.0 mg. Considering the detection sensitivity and consumption of graphene, 0.3 mg of graphene was employed in the studies.

On the basis of the above discussion, the optimal extraction conditions were as follows: the sample solution at the pH of 3.0, 0.3 mg of graphene, the extraction time of 4.0 min, acetone containing 0.5% ammonium hydroxide as the desorption solution and 3.0 min for the desorption.

Six SAs were analyzed under these optimal experimental conditions and Fig. 6 shows the chromatograms of them obtained by HPLC-UV analysis with or without extraction. After extraction, an obvious enhancement of the peak height was observed, indicating the remarkable preconcentration ability of the graphene.

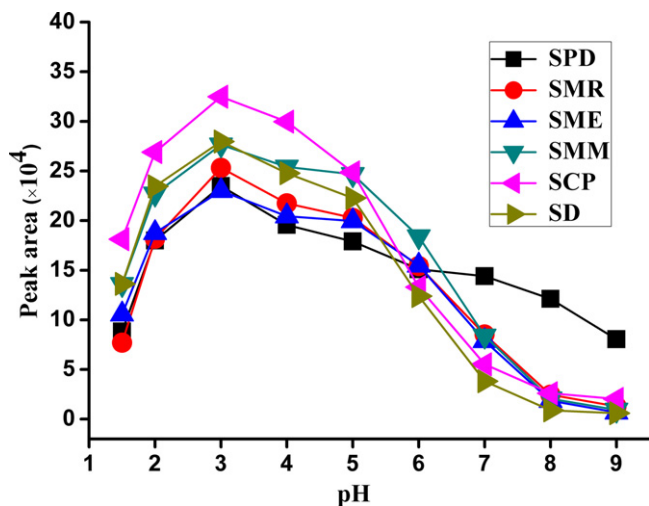


Fig. 4. Optimization of the pH of the sample solutions. Sample solutions with each SA spiked at 50 ng/mL were prepared with PBS (20 mM). The pH was adjusted by phosphoric acid. Other conditions were as follows. Extraction time was 8 min. The SAs were eluted from the graphene by 1 mL of acetone containing 0.5% (v/v) ammonium hydroxide with vortex for 5 min. The amount of graphene was 0.5 mg.

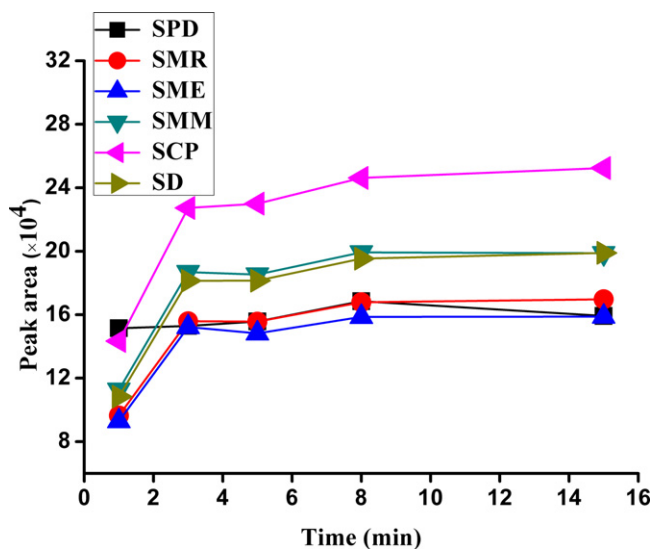


Fig. 5. Optimization of the desorption time. Sample solutions with each SA spiked at 50 ng/mL were prepared with PBS (20 mM, pH 3.0). Extraction time was 8 min. The SAs were eluted from the graphene by 1 mL of acetone containing 0.5% (v/v) ammonium hydroxide with vortex for 1, 3, 5, 8 and 15 min. The amount of graphene was 0.5 mg.

Table 2

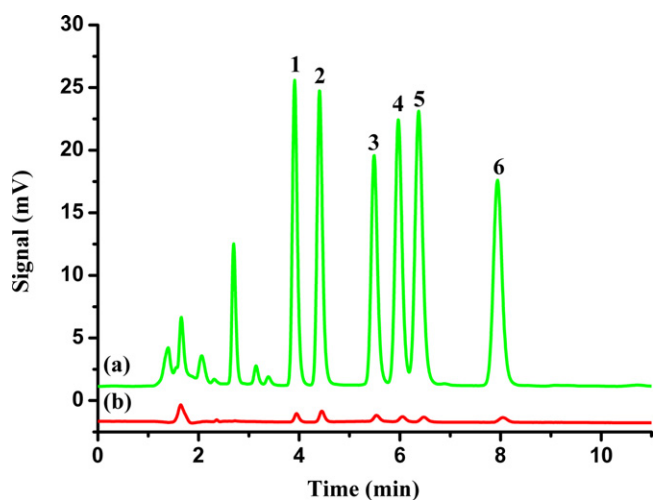
The linear range, regression data, limits of detection (LODs), limits of quantification (LOQs) for the SAs from water samples.

Analytes	Linear range (ng/mL)	Calibration curves			LOD (ng/mL)	LOQ (ng/mL)
		Slope	Intercept	R ² value		
SPD	0.5–100	3194.8	6067.3	0.9971	0.09	0.32
SMR	0.5–100	2233.0	10380.2	0.9885	0.10	0.32
SME	0.5–100	3047.2	7879.5	0.9957	0.13	0.43
SMM	0.5–100	3759.6	6533.0	0.9982	0.12	0.43
SCP	0.5–100	4428.0	5983.7	0.9995	0.13	0.44
SD	1–100	3745.3	5433.2	0.9983	0.16	0.53

Table 3

Method precisions at three different concentrations for the extraction of the SAs from water samples.

Analytes	Intra-day precision (RSD%, n = 4)			Inter-day precision (RSD%, n = 4)		
	1 ng/mL	10 ng/mL	100 ng/mL	1 ng/mL	10 ng/mL	100 ng/mL
SPD	5.1	3.3	4.9	7.8	8.6	6.1
SMR	7.7	5.3	5.2	4.2	6.7	6.7
SME	10.7	5.7	4.8	5.3	9.8	6.3
SMM	8.4	3.7	5.9	8.0	8.6	5.6
SCP	7.2	4.3	5.9	5.1	4.8	4.6
SD	8.1	5.2	5.2	5.4	8.1	5.2

**Fig. 6.** Chromatograms of the six SAs obtained by HPLC-UV analysis with (a) or without (b) extraction. The sample solution was spiked at 50 ng/mL for each of the SAs. Peaks: 1, SPD; 2, SMR; 3, SME; 4, SMM; 5, SCP; 6, SD.

3.4. Validation of the method

Under the optimized conditions, a serial of experiments with regard to the linearity, limit of detection (LOD), limit of quantification (LOQ) and reproducibility were performed to validate the proposed method. The linear regression analysis was performed using peak areas against the concentrations of the respective analytes. The linear regression, the LOD and LOQ data are listed in Table 2. The LODs and LOQs were calculated as the concentration corresponding to the signals of 3 and 10 times the standard deviation of the baseline noise, respectively. The LOD and LOQ for six SAs were found to be 0.09–0.16 ng/mL and 0.32–0.53 ng/mL, respectively.

The reproducibility of the method was determined by the intra- and inter-day precisions. The intra- and inter-day relative standard deviations (RSDs) were calculated with the SAs spiked at three different concentration levels in water. Four parallel extractions of a sample solution over a day gave the intra-day RSDs, and the inter-day RSDs were determined by extracting sample solutions that had been independently prepared for four contiguous days. The results are summarized in Table 3. The intra- and inter-day RSDs were less than 10.7% and 9.8%, illustrating the acceptable reproducibility achieved by the method.

Table 4Recoveries and precisions of the SAs in the analysis of three environmental water samples.^a

Sample	Analytes	Founded (ng/mL)	Recovery (%)	RSD (% , n = 4)
The East Lake water	SPD	7.95	79.5	4.5
	SMR	10.41	104.1	3.4
	SME	8.92	89.2	4.0
	SMM	7.93	79.3	5.5
	SCP	8.48	84.8	4.3
	SD	7.64	76.4	4.3
Sewage outfall of a hospital	SPD	7.42	74.2	7.1
	SMR	8.81	88.1	7.3
	SME	8.01	80.1	12.8
	SMM	7.64	76.4	10.6
	SCP	7.74	77.4	6.9
	SD	7.52	75.2	5.7
Waste water of a fermentation factory	SPD	8.60	86.0	0.3
	SMR	8.82	88.2	8.0
	SME	8.93	89.3	4.1
	SMM	8.56	85.6	3.8
	SCP	7.95	79.5	3.3
	SD	8.19	81.9	1.6

^a Real water samples were spiked at 10 ng/mL.

3.5. Analysis of environmental water samples

Under the optimized conditions, the proposed method was applied to the determination of the SAs in three kinds of environmental water samples including lake water, sewage outfall of a hospital and wastewater of a fermentation factory. The recoveries were determined by comparing the calculated amounts of SAs from the spiked environmental samples with the total spiking amounts. As listed in Table 4, the recoveries of the six SAs from three environmental water samples were in the range from 74.2 to 104.1% with the RSDs less than 12.8%. The results demonstrate that the precision and accuracy of the present method were acceptable.

4. Conclusion

A magnetic composite of graphene and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was prepared by simple adsorption. The two components within the composite endow manipulative convenience as well as adsorption capability for the material. It was used as an extraction media for the enrichment of trace amount of six sulfonamide antibiotics in environmental water samples. The study demonstrates that the proposed material is effective and efficient for sample preparation. Most importantly, it solves a problematic issue of graphene's retrieval or separation from dispersion, which would considerably expand the application of graphene in analytical chemistry.

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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.2011.01.022.

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