

Magnetic solid-phase extraction for the analysis of bisphenol A, naproxen and triclosan in wastewater samples

Guo Li, Ruoyu Deng, Guilong Peng, Chun Yang, Qiang He, Ying Lu and Huilan Shi

ABSTRACT

Magnetic Fe₃O₄ graphene oxide nanocomposite was synthesized by chemical coprecipitation method and characterized by scanning electron microscopy, Fourier transform infrared spectra and X-ray diffraction. A simple, rapid, convenient and environmentally friendly method was developed for separation and pre-concentration of trace amounts of bisphenol A, naproxen and triclosan in wastewater samples by high performance liquid chromatography with magnetic Fe₃O₄ graphene oxide nanocomposite as the adsorbent for magnetic solid-phase extraction. Various parameters possibly influencing the extraction performance such as amount of the adsorbent, extraction time, sample pH and elution conditions were optimized. Under the optimal working conditions, the developed method showed good linearity ($R > 0.9997$) in the range of 1–200 µg/L, and the limits of detection are between 0.5 and 0.8 µg/L. The enrichment factors are in the range of 81–89. The repeatability of the method, expressed as relative standard deviation, is 3.36–4.26%.

Key words | bisphenol A, naproxen, solid-phase extraction, triclosan

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INTRODUCTION

Pharmaceutical and personal care products (PPCPs) are used and disposed of every day. They have become a class of emerging contaminants and have attracted increasing attention due to their adverse effects on human health and their potential bioaccumulation (Gibbons *et al.* 2011; Jiménez-Díaz *et al.* 2014). PPCPs are primarily introduced into the aquatic environment through excreta, disposal of expired or unused medicine, aquaculture, and animal feeding. Many studies have indicated that the effluent from wastewater treatment plants (WWTPs) is one of the major pathways of PPCPs into the natural aquatic environment (Rosi-Marshall & Royer 2012; Sun *et al.* 2014). Consequently, advanced analytical methods are extremely important to monitor the presence of pharmaceuticals in the wastewater. The occurrence of PPCPs in trace concentration levels, with extremely diverse groups in a complex waste matrix, makes

their detection and analysis quite demanding (Archana *et al.* 2016). Therefore, the development of a fast and sensitive analytical method for the systematic investigation of trace-level amounts of PPCPs in the aquatic environment is of great importance. Several methods such as matrix solid-phase dispersion (MSPD) (Aguilar-Arteaga *et al.* 2010), solid-phase extraction (SPE) (Lee *et al.* 2005), ultrasound assisted emulsification–microextraction (USAEME) (Cabaleiro *et al.* 2011) and dispersive liquid–liquid microextraction (DLLME) (Guo *et al.* 2009) have been used for the separation and pre-concentration of PPCPs in aquatic environments.

Recently, a new type of SPE technique termed as magnetic solid-phase extraction (MSPE), combining extraction and separation, as well as clean-up and concentration of analytes into a single step, has gained increasing attention

in the sample preparation method (He *et al.* 2014; Chen & Zhu 2016; Peña Crecente *et al.* 2016; Amiri *et al.* 2017; Li *et al.* 2017). In MSPE procedures, the magnetic adsorbents can be easily collected by applying an external magnetic field; this replaces the centrifugation or filtration in traditional SPE steps, thus greatly simplifying the procedure and enhancing the extraction efficiency (Jiang *et al.* 2013; Sun *et al.* 2013). In addition, the magnetic adsorbents can be reused, which is both economical and efficient.

Graphene oxide (GO), the oxidized derivative of graphene, is accessible through the oxidation of natural graphite powder (Zhu *et al.* 2010). GO contains abundant reactive oxygen functional groups on its nanosheet surface in the form of epoxy, hydroxyl, and carboxyl groups, which make it extremely hydrophilic and highly dispersive (Yin *et al.* 2014; Xiao *et al.* 2017). This makes GO hard to separate directly from aqueous solution. To overcome this problem, the preparation of magnetic GO composite is a superior choice, which can ensure the convenient magnetic separation after adsorption.

In the past few years, the use of magnetic GO in sample preparation to adsorb trace analytes has also received increasing attention (Han *et al.* 2012; Kazemi *et al.* 2015; Sun *et al.* 2015; Nazari *et al.* 2016). In the present study, we synthesized magnetic Fe₃O₄ graphene oxide (Fe₃O₄/GO) as adsorbent for the extraction, pre-concentration, and determination of three commonly used chemicals (bisphenol A, naproxen, and triclosan) frequently detected in wastewater. It was characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectra and X-ray diffraction (XRD). This method is fast, simple and has good application prospects for detection of trace levels of PPCPs in environmental water samples.

MATERIALS AND METHODS

Chemicals and reagents

Graphite powder, NH₃·H₂O, HCl, NaOH, FeCl₃·6H₂O, FeSO₄·7H₂O, KMnO₄, H₂SO₄, bisphenol A, naproxen, and triclosan were purchased from Aladdin (Shanghai, China). High performance liquid chromatography (HPLC)-grade methanol, ethanol, propanol, acetone and acetonitrile were obtained from Chongqing Boyi Chemical Factory (Chongqing, China). Deionized water was prepared with an SZ-2 system (Shanghai Lu West Analytical Instruments, Shanghai, China).

Synthesis of graphene oxide and magnetic graphene oxide

Graphene oxide was prepared from natural graphite by a modified Hummers' method (Mahpishanian & Sereshti 2014). The Fe₃O₄/GO was prepared through the chemical coprecipitation of Fe(III) and Fe(II) ions in the presence of GO. The prepared GO was dispersed in high purity water (2 mg/mL) and ultrasonicated for 2 h to obtain a clear dispersion of GO. The mixed water solution of FeCl₃·6H₂O (1.92 g) and FeSO₄·7H₂O (0.69 g) was added slowly to 100 mL of 2 mg/mL GO suspension. The solution was heated to 85 °C under nitrogen atmosphere, and a 30% ammonia solution was added to adjust the pH to 10. After being rapidly stirred for 1.0 h, the solution was cooled to room temperature. The black precipitate was then collected using a magnet while the solution was decanted, washed with double distilled water, and then vacuum dried at 70 °C.

Material characterization

SEM micrographs were taken using an SU-8010 microscope (Hitachi, Japan). A Tensor 27 spectrometer (Bruker Co., Germany) was used to obtain FTIR spectra. XRD measurements were performed using a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu K α radiation ($\lambda = 5406 \text{ \AA}$).

MSPE procedure

All extraction experiments were conducted in 100 mL glass vials. Briefly, the pH of the sample solution was first adjusted to ~6 with HCl, and 20.0 mg of Fe₃O₄/GO was added to 50 mL of sample solution containing analytes. After vigorous stirring for 15 min, the adsorbent was isolated from the aqueous solution by applying an external magnetic field. The target compounds were ultrasonically extracted from the Fe₃O₄/GO with methanol for 3 min, and the extract was separated from the adsorbent by a magnet. After that, the eluent was evaporated until dry under a mild nitrogen stream at room temperature, and then diluted to 0.5 mL with mobile phase. Finally, the solution was filtered through a 0.45 μm PTFE (polytetrafluoroethylene) filter membrane and analysed by HPLC.

Sample preparation

Wastewater samples were obtained from two large WWTPs (Chongqing, China). The water samples were first filtered through a 0.45 μm membrane, the pH was adjusted to ~6,

and the samples were stored at 4 °C under dark conditions until analysis.

Instrumentation and experimental conditions

The analyses were performed with a Shimadzu LC-20AT series HPLC system equipped with a solvent delivery pump, an SPD-20A UV-Vis detector, and an LC solution work-station (Shimadzu, Japan). The pH values were measured using a Model PHB-5 pH-meter (Analytical Instruments Co., Ltd. Shanghai, Shanghai, China). An ultrasonic water bath (Model KQ-400KDE, Kunshan Ultrasound Instruments Company, Jiangsu, China) was used to prepare the GO solution. A UV-Vis spectrophotometer (DR5000, Hach, USA) was used to determine the maximum ultraviolet absorption wavelength of the target compounds.

The HPLC separation was performed on a Phenomenex C18 column (150 × 4.6 mm i.d., 5 μm particle diameter). Methanol (B) and water with 0.2% acetic acid (A) were used as the mobile phase with the gradient program as follows: 0–5 min, 75–90% B; 5–10 min, 90% B; 10–15 min, 90–75% B; 15–20 min, 75% B. The flow rate was maintained at 0.8 mL/min. The column temperature was maintained at 40 °C, and the injection volume was 20 μL. The maximum ultraviolet absorption wavelength is 282 nm for bisphenol A, 272 nm for naproxen, 281 nm for triclosan, respectively; therefore 275 nm was selected for UV-Vis detection to obtain good sensitivity.

RESULTS AND DISCUSSION

Characterization of sorbents

The morphological structure of GO and Fe₃O₄/GO was investigated by SEM. Figure 1(a) clearly shows the sheet-

like structure of the GO and Figure 1(b) shows Fe₃O₄ nanoparticles in the size range of 100–200 nm, dispersed on the surface of GO indicating that the Fe₃O₄ nanoparticles are successfully decorated on the surface of the GO to form nanocomposites. Figure 2 shows the FTIR spectra of the GO and Fe₃O₄/GO powders. As indicated, the main characteristic absorption bands in the FTIR spectra of GO and magnetic GO are similar. The presence of a broad and intense peak at 3,411 cm⁻¹ can be ascribed to the O-H stretching vibrations of the C–OH groups. The C=O stretching is located at 1,739 cm⁻¹. The absorption band at 1,628 cm⁻¹ can be ascribed to aromatic C=C bonds. The absorption bands at 1,219 and 1,049 cm⁻¹ are attributed to C–O stretching of the epoxy and alkoxy groups, respectively. Moreover, the peaks at 568 cm⁻¹ could be ascribed to lattice absorption of Fe₃O₄. This evidence confirms the successful synthesis of Fe₃O₄/GO. The XRD pattern of the GO and Fe₃O₄/GO are presented in Figure 3. The diffraction peaks at 2θ = 10.6° (001), could be ascribed to the reflection of the GO. This indicated that GO was successfully fabricated without a graphite peak. For Fe₃O₄/GO, in comparison with GO, the peak at 10.6° completely disappeared, indicating GO has been reduced to reduced graphene oxide. The diffraction peak at 2θ = 30.4°, 35.6°, 43.2°, 53.3°, 57.3° and 62.9° can be assigned to (220), (311), (400), (422), (511), and (440), respectively. Therefore, Fe₃O₄ nanoparticles were successfully deposited onto the surface of GO.

Optimized MSPE procedures

In order to achieve good extraction and recoveries towards the target analytes, various extraction conditions were optimized by analysing 50 mL of aqueous solution containing each analyte at 100 μg/L level. The experimental

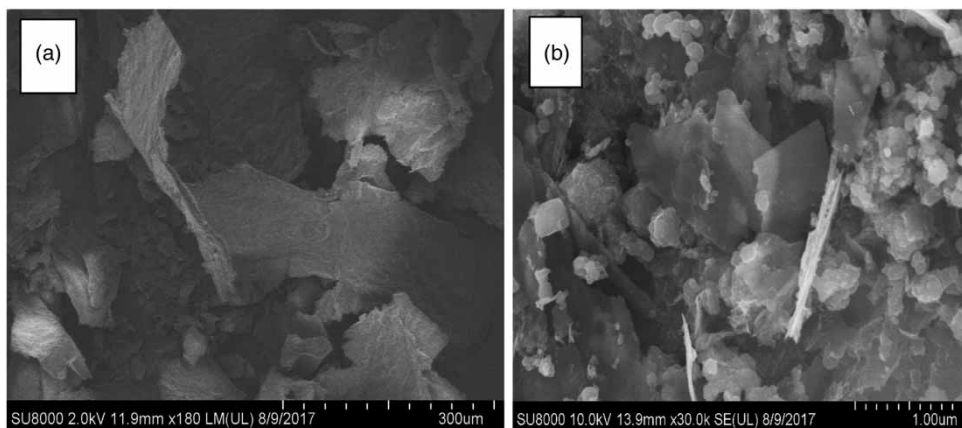


Figure 1 | SEM images of GO (a) and Fe₃O₄/GO composite (b).

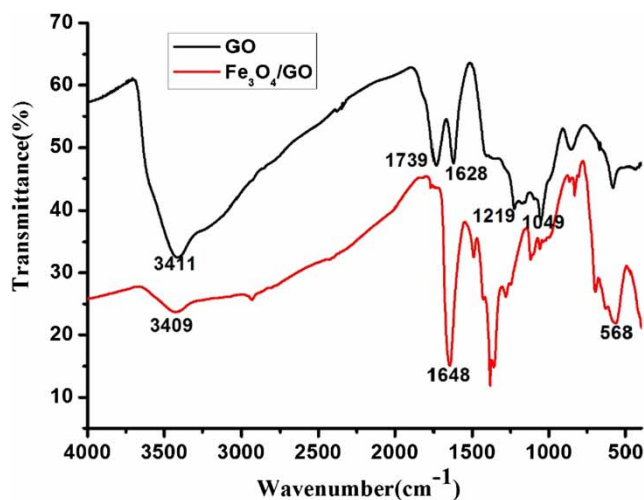


Figure 2 | FTIR spectra of GO and Fe₃O₄/GO.

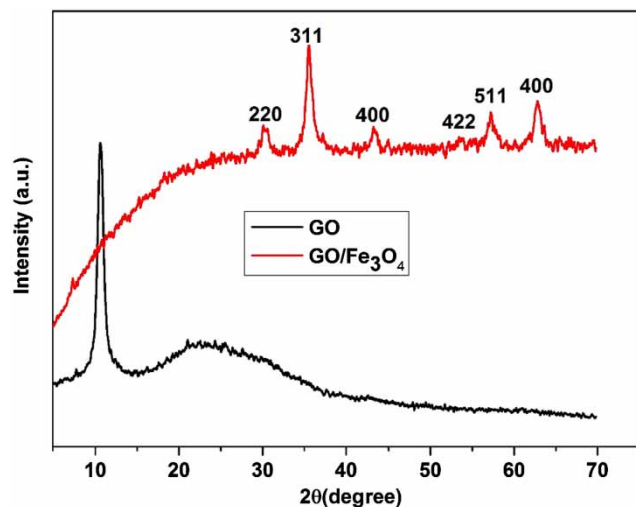


Figure 3 | XRD pattern of GO and Fe₃O₄/GO.

parameters, including the amount of adsorbent, the extraction time, the pH and the elution conditions, were investigated in detail. Each variable was optimized independently to obtain the best conditions for the MSPE procedure. All experiments were performed in triplicate.

Effect of the amount of adsorbent

In order to investigate the optimum amount of adsorbent needed for the extraction of target analytes, the amount of Fe₃O₄/GO nanocomposite in the solution was varied from 10 to 50 mg. As is shown in Figure 4, the results revealed that the extraction recoveries were increased by increasing the adsorbent amount and reached a maximum at 20 mg, and further increasing the amount of the adsorbent gave no significant improvement for the recoveries of the three

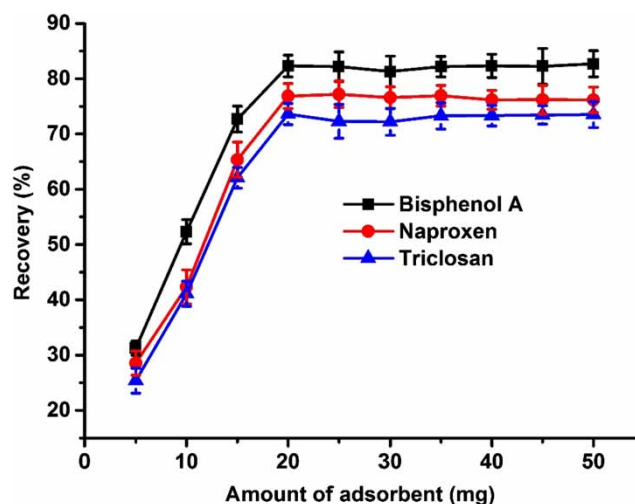


Figure 4 | Effect of the amount of adsorbent on the recovery of the analytes. Extraction conditions: sample volume, 50 mL; adsorption time, 5 min; eluent, 2 mL methanol; sample pH, 6.

PPCPs. So, 20 mg of the Fe₃O₄/GO was selected for all subsequent experiments.

Effect of pH

The pH of sample solution plays a key role for the adsorption of the analytes by affecting the existing forms of the target compounds. To evaluate the effect of pH on the extraction efficiency of the analytes, pH of the sample solutions was changed in the range of 4–12 with appropriate amounts of HCl or NaOH solutions. The recovery of naproxen was generally highest at pH 4–5, and there was a decrease in the recoveries of bisphenol A and triclosan at pH values higher than 10 (Figure 5). This was because the naproxen ($pK_a = 4.2$) molecules at pH 4.0 and 5.0 were mainly in the non-dissociation form, and as the pK_a values of bisphenol A and triclosan were between 8.1 and 9.6, these compounds exist in a neutral form between pH 4.0 and 8.0. Based on the above findings, a pH of 7.0 was selected for the following experiments, and it is also close to the wastewater pH.

Effect of extraction time

The effect of the extraction time was examined by varying the stirring time from 2 to 10 min. The results indicated that the recoveries of the target compounds increased with increasing extraction time, and then kept in balance when the extraction time exceeded 5 min. The fast adsorption of the analytes may be attributed to the π - π stacking between the benzene rings of the analytes and the GO, as well as the hydrogen bonds

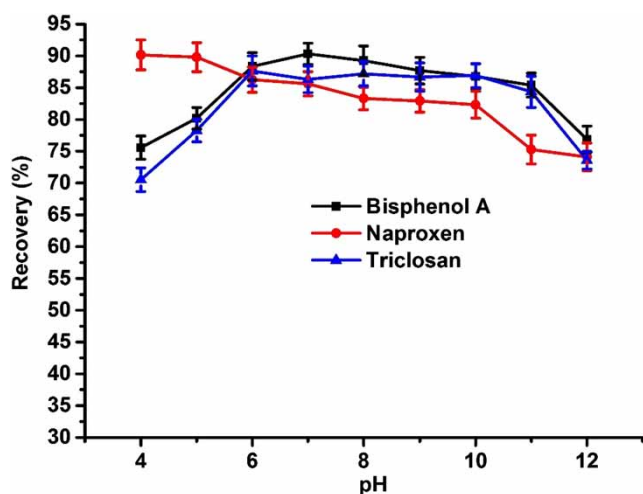


Figure 5 | Effect of the pH on the recovery of the analytes. Extraction conditions: sample volume, 50 mL; adsorbent, 20 mg; adsorption time, 5 min; eluent, 2 mL methanol; sample pH, 5.

between the oxygen functional groups contained in analytes and GO (Wang *et al.* 2015). Thus, the optimum extraction time of 5 min was selected for further studies.

Effect of desorption conditions

In order to achieve optimum desorption conditions, different organic solvents were used for the desorption of analytes from Fe₃O₄/GO including methanol, ethanol, propanol, acetone, and acetonitrile. It was found that the best recovery was obtained with methanol.

The effect of eluent volume (1.0–10.0 mL) on the recovery was investigated. Results showed that with increasing volume of the eluting solvent the recoveries of the target compounds increased and reached a maximum (85.9–96.8%) when 6.0 mL of methanol was used. The sonication time (1–5 min) was also studied, and satisfactory recoveries were obtained when 3 min sonication was used.

Analytical performance

In order to evaluate the method performance, the linearity, repeatability, limits of detection (LODs) and enrichment

factors (EFs) were studied using spiked ultrapure water samples under the optimized extraction conditions. Calibration curves for each analyte were obtained by extracting three spiked levels (1–200 µg/L) of sample solutions in three parallel experiments. The results are listed in Table 1. Good linearity was achieved over a wide concentration range of 1–200 µg/L with correlation coefficients (R) ranging from 0.9997 to 0.9999. The repeatability of the method, expressed as relative standard deviation (RSD), varied from 3.36% to 4.18% for five repeated experiments. The LODs of the proposed method, based on the ratios of the three times of the standard deviations of the blank signals over the slope of the calibration curves, ranged between 0.5 and 0.8 µg/L. The EFs values with a range of 81–89 were obtained under optimal conditions. EF was calculated as follows: $EF = C_m/C_{in}$, where C_m is the analyte concentration after MSPE procedure, and C_{in} is the initial concentration of the analyte in the aqueous sample.

Real samples analysis

To evaluate the feasibility of the proposed method for analysis of real samples, the method was applied to the extraction of bisphenol A, naproxen, and triclosan from wastewater samples derived from two large WWTPs. The reliability was checked through the recovery experiment of spiked samples at three concentrations of the analytes. The results of the feasibility and recovery studies for the spiked samples are summarized in Table 2. The recoveries of the target compounds were 73.2–89.87% with the RSDs 1.79–4.28%. Figure 6 shows the typical chromatograms of the three PPCPs for spiked and blank wastewater, which indicate that sample matrix had no significant interferences. The results demonstrated that the present method was suitable for the determination of trace level of PPCPs in real environmental water samples.

Comparison of the MSPE method with other methods

A comparison of the proposed method with other reported methods is provided in Table 3. The LODs and RSDs

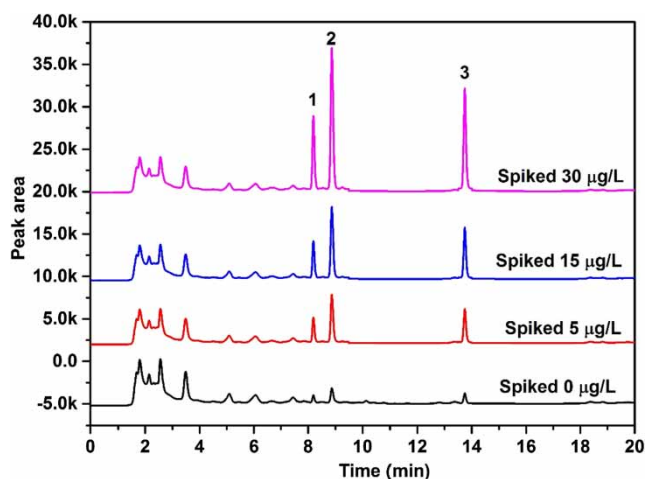
Table 1 | Linear range for the PPCPs obtained from proposed method

Analyte	Linear range (µg/L)	Linear equation	R	LOD (µg/L)	LOQ ^a (µg/L)	EF	RSD (n = %)
Bisphenol A	1.0–200	$Y = 2,786.23X + 3,159.76$	0.9997	0.51	1.62	86	3.36
Naproxen	1.0–200	$Y = 2,958.88X + 2,699.57$	0.9999	0.82	2.48	89	4.26
Triclosan	1.0–200	$Y = 2,183.24X + 3,255.62$	0.9998	0.63	2.08	81	4.18

^aLOQ: limit of quantification.

Table 2 | Determination of the PPCPs and recovery in wastewater samples ($n = 5$)

Analyte	Spiked ($\mu\text{g/L}$)	WWTP 1			WWTP 2		
		Found ($\mu\text{g/L}$)	Recovery (%)	RSD (%)	Found ($\mu\text{g/L}$)	Recovery (%)	RSD (%)
Bisphenol A	0	3.36			1.31		
	5	7.41	81.00	4.28	5.19	77.60	3.16
	15	15.91	83.67	3.06	14.39	87.20	2.32
	30	29.33	86.57	2.16	28.19	89.60	2.17
Naproxen	0	5.65			3.15		
	5	9.51	77.20	3.18	7.09	78.80	3.19
	15	18.15	83.33	3.28	15.87	84.80	3.36
	30	31.17	85.07	2.61	30.11	89.87	3.45
Triclosan	0	1.76		1.79	1.29		
	5	5.53	75.40	2.31	4.95	73.20	3.09
	15	13.85	80.60	3.15	14.18	85.93	2.21
	30	27.97	87.37	3.63	26.95	85.53	3.52

**Figure 6** | The typical chromatograms of blank sample and spiked sample at various concentrations of target analytes. (1) Bisphenol A, (2) naproxen, (3) triclosan.

obtained from the method are comparable to or lower than those of the reported method. One reported SPE method (Lee *et al.*, 2005) has the lowest detection limit compared to other methods, but it is an exhaustive extraction process, is time consuming and is multi-step. In addition, SPE is

more expensive, and involves the use of large amounts of sorbent. In DLLME (Guo *et al.*, 2009), the method has a lower detection limit; however, the toxic organic solvent 1,3-dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$) was needed. Compared with other adsorbents, $\text{Fe}_3\text{O}_4/\text{GO}$ has excellent adsorption ability and can reach adsorption and desorption equilibrium in a short time. Moreover, the separation of adsorbent from sample solutions was rapid and convenient and the sorbent was easily reused.

CONCLUSIONS

In this work, magnetic GO was successfully prepared by means of a simple one-step chemical coprecipitation method, and then applied in an MSPE method as a highly efficient sorbent for isolation and enrichment of PPCPs from water samples. The magnetic separation greatly improved the separation rate while avoiding the time-consuming column passing or filtration operation, and the sorbent was easily reused. The proposed method is simple, rapid, inexpensive and environmentally friendly, requiring low operational

Table 3 | Comparison of the proposed method with other methods for determination of PPCPs in water samples

Methods	Linearity ($\mu\text{g/L}$)	LOD ($\mu\text{g/L}$)	Recovery (%)	RSD (%)	Extraction time	Reference
M-MSPD-HPLC/UV ^a	20–1,000	2–10	–	1.01–4.03	>1,000 min	Aguilar-Arteaga <i>et al.</i> (2010)
SPE-GC/MS ^b	0.01–10	0.01–0.1	75–115	<7	>60 min	Lee <i>et al.</i> (2005)
USAEME–UV–Vis	20–180	5	–	3.5	>16 min	Cabaleiro <i>et al.</i> (2011)
DLLME–UHPLC–TUV ^c	0.025–100	0.042–0.24	64.3–115	4.6–5.43	>5 min	Guo <i>et al.</i> (2009)
MSPE-HPLC-UV	1–200	0.51–0.82	79.8–108.6	2.09–4.85	5 min	This work

^aM-MSPD: magnetic matrix solid-phase dispersion; ^bGC/MS: gas chromatography/mass spectrometry; ^cUHPLC-TUV: ultra-high-pressure liquid chromatography–tunable ultraviolet detection.

time and a very low consumption of organic solvents. Under the optimized conditions, high extraction efficiency, low LODs, and good repeatability and recoveries were obtained. The results of this study indicate that the proposed method could be further applicable for determination of residues of different PPCPs in a variety of environmental water samples.

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