



Evaluation of graphene as an advantageous adsorbent for solid-phase extraction with chlorophenols as model analytes

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ABSTRACT

Graphene, a novel class of carbon nanostructures, possesses an ultrahigh specific surface area, and thus has great potentials for the use as sorbent materials. We herein demonstrate the use of graphene as a novel adsorbent for solid-phase extraction (SPE). Eight chlorophenols (CPs) as model analytes were extracted on a graphene-packed SPE cartridge, and then eluted with alkaline methanol. The concentrations in the eluate were determined by HPLC with multi-wavelength UV detection. Under the optimized conditions, high sensitivity (detection limits 0.1–0.4 ng/mL) and good reproducibility of CPs (RSDs 2.2–7.7% for run-to-run assays) were achieved. Comparative studies showed that graphene was superior to other adsorbents including C18 silica, graphitic carbon, single- and multi-walled carbon nanotubes for the extraction of CPs. Some other advantages of graphene as SPE adsorbent, such as good compatibility with various organic solvents, good reusability and no impact of sorbent drying, have also been demonstrated. The proposed method was successfully applied to the analysis of tap and river water samples with recoveries ranging from 77.2 to 116.6%. This work not only proposes a useful method for environmental water sample pretreatment, but also reveals great potentials of graphene as an excellent sorbent material in analytical processes.

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1. Introduction

Sample pretreatment is an important step in chemical analysis. Especially in environmental analysis, sample pretreatment is usually the most important and laborious step due to the complex matrices of environmental samples and the extremely low concentration of contaminants. Solid-phase extraction (SPE) is a widely used technique for environmental sample pretreatment due to its high recovery, short extraction time, high enrichment factor, low consumption of organic solvents, and ease of automation [1]. The core of SPE is the sorbent material that determines the selectivity and sensitivity of the method. However, the commonly used SPE sorbents, such as C18 silica and graphitic carbon, are often only applicable for a limited number of analytes. Reusability of the SPE cartridges is also a problem. Thus, developing new SPE adsorbents is of high value.

Carbon nanomaterials represent a novel type of adsorbents, including fullerenes [2,3], carbon nanotubes (CNTs) [4,5], carbon nanohorn [6], and carbon nanocones/disks [7]. Fullerenes can be used as chromatographic stationary phases to offer high selectivity for specific compounds [8,9] or as sorbent materials for on-line clear

up and preconcentration [10,11]. In recent years, CNTs have been shown to be excellent kinds of sorbent materials for SPE [5]. Since the first application of multi-walled carbon nanotubes (MWCNTs) in SPE by Cai et al. [12], many reports have been published in recent years focusing on development of CNTs-based SPE methods for a great variety of analytes, including phenolic compounds [13–15], pesticides [16,17], pharmaceuticals [18,19], inorganic ions [20], organometallic compounds [21], etc. The primary advantage of CNTs for SPE adsorbents is their high surface areas, which endue CNTs with high sorption capacities. Then, the selectivity of extraction can be controlled by covalently or non-covalently modifying the CNTs with functional groups. Furthermore, intrinsic properties of CNTs such as fine chemical and thermal stability also make them suitable to be used as SPE adsorbents. Other carbon allotropes, such as graphite fiber and diamond, have also been demonstrated as adsorbents in SPE or micro-SPE [22,23].

Graphene, a new class of carbon nanomaterial, has recently sparked much interest due to its unique strict two-dimensional nanostructure [24–26]. Graphene possesses extraordinary electronic, thermal and mechanical properties, such as ultrahigh specific surface area, good thermal conductivity, fast mobility of charge carriers, high values of Young's modulus and fracture strength [27–30]. These properties hold great promise for its applications in chemical analysis [31]. For instance, solid-state gas sensors made from graphene are capable of detecting individual

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gas molecules due to its exceptionally low electronic noise [32,33]. Because of the remarkable electronic properties, graphene appears to be a good component for fabricating electrochemical sensors [34–37]. Generally, in the field of chemical sensors, graphene has shown a bright future. However, in other fields of analytical chemistry, its full potential has yet to be realized.

Taking into account the exceptional properties of graphene, it is rational to expect graphene to be a superior adsorbent for SPE. Firstly, graphene has a large specific surface area (theoretical value $2630 \text{ m}^2/\text{g}$ [27]), suggesting a high sorption capacity. Specifically, both sides of the planar sheets of graphene are available for molecule adsorption; while for CNTs and fullerenes, steric hindrance may exist when molecules access their inner walls. Secondly, graphene can be easily modified with functional groups, especially via graphene oxide (GO) that has many reactive groups [38]. The functionalization may further enhance the selectivity of SPE. Thirdly, CNTs usually contain trace amounts of metallic impurities that come from the metal catalysts used in the synthesis process. These impurities may have negative influences on the applications of CNTs [39–41]. While for graphene, it can be synthesized from graphite without use of metal catalysts, thus it is easier to obtain pure material. Despite these potential advantages, less attention has been paid to the SPE applications of graphene. Dong et al. [42] and Tang et al. [43] recently reported the use of graphene as matrix or probe for matrix-assisted or surface enhanced laser desorption ionization time-of-flight mass spectrometry (MALDI- or SELDI-TOF MS). In these reports, the graphene sheets were dispersed in sample solutions to preconcentrate the analytes, and then the analyte–graphene complexes were collected by centrifugation and directly analyzed by the MS techniques. However, we found that the well-dispersed graphene sheets were difficult to completely isolate from the dispersions even by high-speed centrifugation due to the presence of miniscule sheets of graphene. Furthermore, these methods involved no elution steps, thus they seemed not to be intact SPE methods.

In this work, we demonstrate a novel SPE method using graphene powder as adsorbent. Chlorophenols (CPs) were selected as model analytes for their high toxicity and widespread environmental occurrence [44]. Eight CPs were extracted by graphene-packed SPE cartridges, and then the cartridges were eluted by alkaline methanol. The eluates were analyzed by high-performance liquid chromatography (HPLC) with multi-wavelength ultraviolet (UV) detection. The performance of graphene was compared with several other adsorbents including C18 silica, graphitic carbon and CNTs. Finally, the proposed method was applied to the analysis of environmental water samples.

2. Experimental

2.1. Chemicals

Graphite powder (-325 mesh, 99.9995%) was purchased from Alfa Aesar (Ward Hill, MA). Hydrazine hydrate (85%) and P_2O_5 were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). H_2O_2 , KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$ and concentrated H_2SO_4 were from Beijing Chemical Works (Beijing, China). 2-Chlorophenol (2-CP, 98+%), 3-chlorophenol (3-CP, 99%), 2,4-dichlorophenol (2,4-DCP, 99%), 3,4-dichlorophenol (3,4-DCP, 99%), and 2,4,6-trichlorophenol (2,4,6-TCP, 98%) were from Acros Organics (Geel, Belgium). 4-Chlorophenol (4-CP, 100%) and 2,3,5-trichlorophenol (2,3,5-TCP, 98.3%) were from AccuStandard (New Haven, CT). 2,3-Dichlorophenol (2,3-DCP, 98%) was from Alfa Aesar. The standard stock solutions of CPs ($2000 \mu\text{g}/\text{mL}$) were prepared in methanol (MeOH) and stored in the dark at 4°C . The working solutions were freshly prepared by diluting the stock solutions with water.

Single-walled CNTs (SWCNTs, >90%, outer diameter <2 nm, length 5–15 μm) and MWCNTs (>98%, outer diameter 20–40 nm, length 5–15 μm) were obtained from Nanotech Port Co. Ltd. (Shenzhen, China). Organic solvents used in this work were all from J.T. Baker (Phillipsburg, NJ) and of HPLC grade. Ultrapure water from a Milli-Q system (Millipore, Billerica, MA) was used throughout. All reagents were of analytical grade unless otherwise noted.

2.2. Apparatus

The SPE experiments were performed on an Agilent vacuum manifold processing station (Santa Clara, CA) with a Gast vacuum pump (Benton Harbor, MI). The empty SPE cartridges (3 mL) and SPE frits were purchased from Agilent. The HPLC experiments were performed on a Dionex Ultimate 3000 HPLC system (Sunnyvale, CA) consisting of a DGP-3600SD pump, a WPS-3000SL autosampler, a TCC-3000SD column compartment, and a DAD-3000 diode array detector (DAD). The system was controlled by Chromeleon software. Separations were performed on a Dionex Acclaim PolarAdvantage C16 column (5 μm , 150 mm \times 4.6 mm) with an Inertsil ODS-SP guard column (5 μm , 10 mm \times 4.0 mm; GL Sciences Inc., Tokyo, Japan).

2.3. Synthesis and characterization of graphene

Graphite oxide was synthesized by a modified Hummers method [45,46]. Graphite powder (3 g) was added into an 80°C solution of concentrated H_2SO_4 (12 mL) containing 2.5 g of $\text{K}_2\text{S}_2\text{O}_8$ and 2.5 g of P_2O_5 , and kept at 80°C for 4.5 h. Then, the mixture was diluted with 0.5 L of water and left overnight. After that, the mixture was filtered through a 0.20 μm Millipore nylon membrane and washed with 1 L of water. The product was dried under ambient condition. This pre-oxidized graphite was added into 120 mL of concentrated H_2SO_4 in an ice-bath, and 15 g of KMnO_4 was gradually added into the mixture under stirring. Note that the rate of addition must be carefully controlled to prevent the temperature from exceeding 20°C . Consequently, the mixture was stirred at 35°C for 2 h and then slowly diluted with 250 mL of water in an ice-bath to keep the temperature below 50°C . Then, the mixture was stirred for another 2 h and diluted with 0.7 L of water. Shortly after the addition of water, 20 mL of H_2O_2 (30%, v/v) was added, causing the color turning to yellow along with bubbling. The mixture was filtered and washed with 1 L of HCl (1:10, v/v) and 1 L of water. The obtained solid was dialyzed against water for 1 week, and then dried under ambient condition.

Graphene was synthesized by hydrazine reduction of graphene oxide (GO) [47,48]. The dispersion of graphite oxide (1 mg/mL) was ultrasonicated for 1 h to exfoliate graphite oxide to GO. Then, hydrazine hydrate was added to the dispersion with the weight ratio of hydrazine to GO being 7:10. This dispersion was heated at 95°C for 24 h, and the reduced GO gradually precipitated as black solid. The final product of graphene was collected by filtration through a fritted glass funnel, washed thoroughly with water and MeOH, and freeze-dried under vacuum.

The TEM images of graphene sheets were captured on a Hitachi H-7500 transmission electron microscope (Tokyo, Japan). The samples for TEM were prepared by placing a drop of GO dispersion on a carbon-coated copper grid and dried at room temperature. The AFM images were taken in tapping mode on a Veeco Dimension 3100 scanning probe microscope (Plainville, NY). The AFM samples were prepared by drop-casting a GO dispersion onto a fresh mica wafer and then dried under room temperature. The SEM images were obtained on a Hitachi S-5500 field-emission scanning electron microscope. The samples for SEM were prepared by placing a drop of MeOH dispersion of graphene on a silicon wafer and then dried at room temperature. Specific surface area of graphene was character-

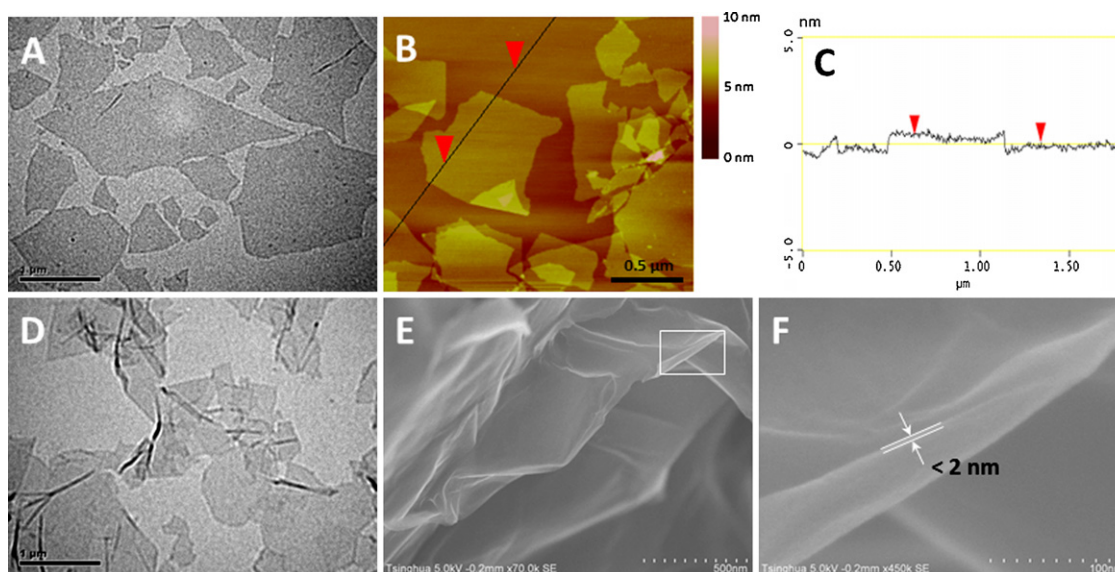


Fig. 1. (A) A typical TEM image of GO sheets. (B) A typical tapping-mode AFM image of GO sheets deposited on a mica substrate. (C) Height profile taken along the solid line in (C) indicates a sheet thickness of 0.353 nm. (D) A typical TEM image of chemically reduced graphene sheets. (E) SEM image of graphene adsorbent. (F) A high magnification SEM image of (E) shows a graphene sheet having an upper bound thickness less than 2 nm.

ized by BET method using an adsorption instrument (Autosorb-1, Quantachrome, USA). The UV–vis spectra were scanned on a DU800 UV/vis spectrophotometer (Beckman Coulter, Brea, CA). The X-ray photoelectron spectra (XPS) were obtained on an AXIS Ultra DLD X-ray photoelectron spectrometer (Kratos, Manchester, UK) with Al K α X-ray radiation as the X-ray source excitation.

2.4. Solid-phase extraction cartridges and procedures

Graphene (20 mg) was placed in a 3 mL SPE cartridge using an upper frit and a lower frit to avoid adsorbent loss. Prior to extraction, the cartridge was preconditioned with 9 mL of MeOH and 9 mL of water, respectively. The sample solution (50 mL) was passed through the cartridge at a flow rate of 1.5 mL/min. Then, the cartridge was washed with 1 mL of 10% (v/v) MeOH aqueous solution to remove the co-adsorbed matrix materials from the cartridge. The analytes retained on the cartridge were eluted with 1 mL of alkaline MeOH, and then the excess base in the eluate was neutralized by 30 μ L of 1 M HCl aqueous solution. Finally, 20 μ L of the eluate was injected into the HPLC system. After extraction, the cartridge was washed with 1 mL of alkaline MeOH, 9 mL of MeOH and 9 mL of water. In this way, the cartridge was available for a next extraction immediately. *Note:* the alkaline MeOH was prepared by adding 1.5 mL of 1 M NaOH aqueous solution into 50 mL of MeOH.

2.5. HPLC analysis

The mobile phase consisted of (A) 25 mM HAc/25 mM NH $_4$ Ac (1.45:1, v/v) and (B) acetonitrile (ACN). The gradient elution program was as follows: starting at 35% B, increasing B to 62% in 18 min, then decreasing B to 35% in 1 min, and keeping constant for 2 min to equilibrate the column. The flow rate was 1 mL/min. The column was thermostated at 30 $^{\circ}$ C. Multiple wavelength UV detection was used for the quantification of CPs: 276 nm for 2-CP and 3-CP, 282 nm for 4-CP and 2,3-DCP, 286 nm for 2,4-DCP and 3,4-DCP, and 290 nm for 2,4,6-TCP and 2,3,5-TCP. The samples were filtered through a 0.20 μ m Millipore nylon membrane before injection.

2.6. Tap and river water samples

Tap water samples were collected from a water tap in our lab (Beijing). River water samples were collected from the section of

Beijing in the Xiaoqing River. The collected water samples were filtered through a 0.45 μ m Millipore cellulose membrane immediately after sampling and stored in amber glass bottles at 4 $^{\circ}$ C.

3. Results and discussion

3.1. Characterization of graphene and graphene-packed SPE cartridges

The graphene was synthesized from its oxide form. The TEM (Fig. 1A) and AFM images (Fig. 1B) show that the as-prepared GO was completely exfoliated to individual nanosheets with no bulk aggregates. The size of the sheets ranged from dozens of nanometers to several micrometers. Noteworthy, from Fig. 1C, the corresponding section analysis of the AFM image shows that the thickness of the obtained GO sheets could be less than 0.5 nm, indicating the generation of single layer of GO sheets. After reduction by hydrazine, as shown by the TEM image in Fig. 1D, the graphene maintained its morphology of nanosheets. From the SEM image (Fig. 1E), the reduced graphene consisted of randomly aggregated and crumpled sheets to form a disordered solid. A high-resolution SEM image (Fig. 1F) indicates that the folded regions of the graphene sheets were thinner than 2 nm. Surface area measurement of the graphene sheets via N $_2$ gas adsorption yielded a BET value of 433.1 m 2 /g, which is close to a previously reported value (466 m 2 /g) [47]. However, this value is lower than the theoretical specific surface area of completely exfoliated and isolated graphene (2630 m 2 /g [27]) probably due to the partial aggregation of GO during the reduction process. Despite this, the specific surface area is sufficiently high for a SPE adsorbent. For comparison, we also measured the specific surface areas of commercially available SWCNTs and MWCNTs. The obtained values are lower than that of graphene: 211.9 m 2 /g for SWCNTs and 89.8 m 2 /g for MWCNTs.

The chemical reduction of GO to graphene was confirmed by UV–vis absorption spectroscopy and XPS. In UV–vis spectra, GO dispersion showed an absorption peak at 229 nm (data not shown). After being reduced with hydrazine, the peak at 229 nm shifted to 262 nm, and the absorption in the whole spectral region increased. This phenomenon suggests that hydrazine reduction cause the restoration of the electronic conjugation in the graphene sheets [48]. Fig. 2 shows the high-resolution C 1s XPS spectra of GO

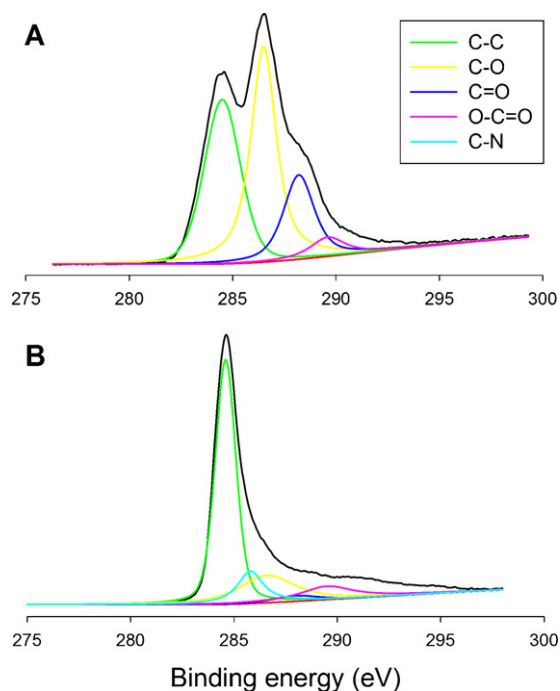


Fig. 2. The C 1s XPS spectra of GO (A) and chemically reduced graphene (B).

and graphene. Peak fitting of the C 1s bands of GO yields several components corresponding to different functional groups: non-oxygenated ring C (C–C), C–O bonds, carbonyl (C=O) and carboxylate C (O–C=O) [47]. Upon hydrazine reduction, the peak intensities of the oxygen functionalities significantly decrease, indicating that GO has been successfully reduced to graphene. A new component appears at 285.8 eV, probably corresponding to C–N bonds [47,49]. In addition, it should be noted that the oxygen functionalities still exist in Fig. 2B, clearly indicating that the chemically reduced graphene used in this work still contains some polar and hydrophilic groups. This result is also consistent with the previously reported literature [38,47,50].

We then tested whether or not the graphene-packed SPE cartridges could be kept intact upon rinsing with various solvents, because small sheets of graphene were present in the adsorbent, and adsorbent loss would reduce the reusability of SPE cartridge and precision of the method. As indicated by Fig. 2, GO contains a large amount of hydrophilic groups and can be soluble in water and some polar solvents [38]. Thus, GO is unsuitable for direct use as SPE adsorbent because it can be easily rinsed out of the cartridge. However, after chemical reduction by hydrazine, the hydrophilic groups in GO sheets are greatly reduced, and the yielded graphene is difficult to be dispersed in water or some organic solvents [47]. Herein, the graphene-packed cartridges were washed thoroughly with water and various organic solvents, and no visible adsorbent losses were observed in all cases with commercial SPE frits. The tested organic solvents included MeOH, ACN, ethanol, 2-propanol, tetrahydrofuran (THF), acetone, ethyl acetate, hexane, cyclohexane, dichloromethane, chloroform, and methyl *t*-butyl ether. The good compatibility with various organic solvents may be benefited from the partial aggregation of graphene mentioned above. This result shows the robustness of graphene-packed SPE cartridges for different applications.

3.2. Optimization of HPLC conditions

HPLC–UV was used for quantification of CPs in both standard solutions and real water samples. Therefore, the HPLC conditions

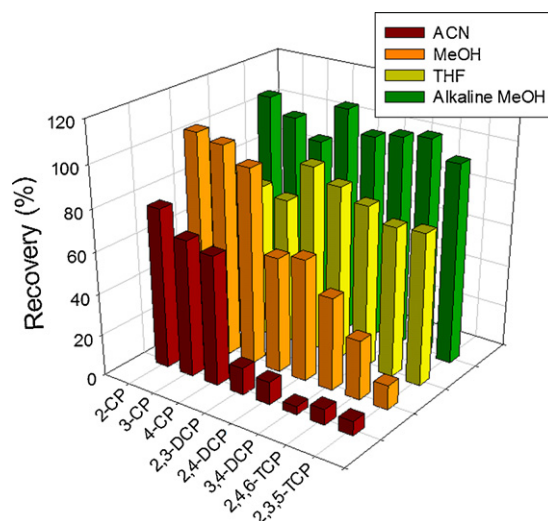


Fig. 3. Effect of eluent type on the recoveries of eight CPs. Volume of eluent: 1 mL. The alkaline MeOH was prepared by adding 1.5 mL of 1 M NaOH aqueous solution in 50 mL MeOH. Other experimental conditions are stated in Section 2.

were optimized before the SPE experiments. A polar-enhanced reversed-phase C16 silica column was used to facilitate the separation of the polar CP analogues. Specifically, we noticed that the maximum absorption peaks of the eight CPs were different from each other. Since a DAD was used here, the eight CPs were determined simultaneously at four different UV wavelengths to reach the maximum sensitivity for each analyte: 276 nm for 2-CP and 3-CP, 282 nm for 4-CP and 2,3-DCP, 286 nm for 2,4-DCP and 3,4-DCP, and 290 nm for 2,4,6-TCP and 2,3,5-TCP. Other detailed optimized HPLC conditions are presented in Section 2.5.

3.3. Optimization of SPE procedures

The sorption of CPs on the graphene-packed SPE cartridges was examined. Aqueous standard solutions (1 mL) of the eight CPs at concentrations up to 10 $\mu\text{g}/\text{mL}$ were passed through the cartridges, and no analytes were detected in the flow-throughs, indicating that the graphene-packed cartridges have a good sorption capacity for the CPs. Then, the cartridge was washed with 1 mL of 10% MeOH aqueous solution. The collected washing solution was also analyzed and found to contain no CPs, indicating that 10% MeOH solution cannot elute the analytes from the cartridge and thereby was suitable to be used as a washing solution.

Although the graphene-packed SPE cartridges are applicable for various organic solvents, only several solvents that are compatible with reversed-phase LC column were tested as eluent solvents, including MeOH, ACN and THF, because a reversed-phase LC was used for the quantitative analysis. In all cases, the SPE cartridges were loaded with 2 μg of each CP in aqueous solution, and then 1 mL of different eluents was passed through the cartridge. The recoveries of the analytes were calculated based on their concentrations in the eluates. As shown in Fig. 3, ACN had a poor eluting power toward CPs; especially for DCPs and TCPs, their recoveries were lower than 15%, indicating the strong affinity of CPs for graphene. MeOH yielded higher recoveries than ACN, because protic solvent (i.e., MeOH) can elute the polar CPs that may have hydrogen bonding with the hydroxyl groups on the graphene surface more effectively than aprotic solvent (i.e., ACN). However, MeOH failed to effectively elute DCPs and TCPs (recoveries less than 60%). THF also could not satisfactorily elute CPs, with the recoveries ranging from 72.0 to 90.0%. The satisfactory results were achieved in the case of alkaline MeOH, with the recoveries of 91.0–109.4%. This was probably because the alkaline condition was favorable for the

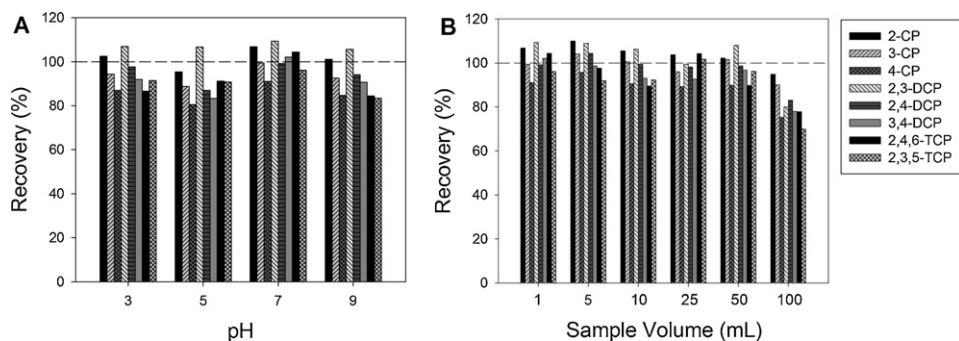


Fig. 4. Effect of sample pH (A) and volume (B) on the recoveries of eight CPs. Eluent: 1 mL of alkaline MeOH. The sample pH was adjusted by 1 M HCl or NaOH aqueous solution. Other experimental conditions are stated in Section 2.

ionization of CPs, thus reducing their affinity for graphene and facilitating the elution. The volume of eluent was also optimized, and the efficient elution could only be achieved with no less than 1 mL of alkaline MeOH. A sequential elution with another milliliter of alkaline MeOH revealed the absence of CPs in the adsorbent. Thus, 1 mL of alkaline MeOH was used as eluent. This complete elution of analytes also guarantees the reusability of the SPE cartridges. Between extractions, the cartridges were washed with alkaline MeOH, pure MeOH and water to ensure that the cartridge could immediately be available for a next extraction. It is noted that before injection into HPLC, 30 μ L of 1 M HCl aqueous solution must be added into the eluate to neutralize the excess base.

The effects of sample pH and volume on the recoveries were also investigated. The cartridge was loaded with 2 μ g of each CP in aqueous solution, and the sample pH was adjusted by 0.1 M NaOH or 0.1 M HCl aqueous solutions. As shown in Fig. 4A, no significant effects were observed with sample pH varying within 3–9. Note that CPs are ionizable at $\text{pH} > \text{pK}_a$ (the pK_a values are listed in Table 1). The less effect of sample pH suggests that non-electrostatic interaction such as π – π interaction plays an important role in the adsorption of CPs to graphene. To facilitate the extraction process, no adjustment of sample pH was performed in the following experiments. To optimize the sample volume, the cartridge was loaded with 1–100 mL aqueous standards containing 2 μ g of each CP in all cases. Generally, for SPE, satisfactory recoveries are required in as large volume of sample solution as possible to obtain a high enrichment factor. It is thus necessary to determine the breakthrough volume. As shown in Fig. 4B, the recoveries were acceptable with sample volume increasing up to 50 mL. Therefore, 50 mL was regarded as the breakthrough volume. This breakthrough volume is larger than that obtained with carbon nanocones/disks (10 mL) with the same amount of adsorbent [7], suggesting that graphene have a higher sorption capacity than carbon nanocones/disks.

3.4. Comparison with other sorbent materials

To evaluate the usefulness of graphene adsorbent, its performance was compared with several commonly used reserved-phase sorbent materials, including C18 silica, graphitic carbon, and CNTs. For this purpose, the same amount (20 mg) of different adsorbents was packed in 3 mL SPE cartridges. The cartridges were loaded with 50 mL of sample solutions containing 2 μ g of each CP. The C18 silica was evacuated from a Supelclean LC-18 SPE tube (Supelco, Bellefonte, PA). The CPs in the flow-through, washing solution and eluate were all determined.

We first optimized the extraction conditions with regard to different adsorbents. It was found that CPs adsorbed on C18 and graphitic carbon cartridges can be easily eluted with MeOH; while for graphene and CNTs cartridges, the adsorption was very stable, thus alkaline MeOH was used to effectively elute the CPs.

As shown in Fig. 5, graphene-packed cartridge yields the highest recoveries (89.8–102.2%) among these studied adsorbents. This result definitely justifies the worth of graphene as SPE adsorbent. For C18 silica, the elution was easier to be conducted than graphene, but the adsorption was poorer. The CPs could be detected in the flow-through and washing solution after loading on C18 cartridge, indicating that 20 mg of C18 silica is insufficient for retention of CPs. Especially for MCPs, their recoveries are much lower than DCPs and TCPs, suggesting that C18 has a poor sorption capacity for polar compounds. To obtain acceptable results with C18, more adsorbent should be packed in the cartridge to enhance the adsorption capacity. For instance, with a C18 cartridge packed with 500 mg of C18 silica, the recoveries of CPs can reach 98.8–107.5%. However, increasing the adsorbent amount will add the cost of analysis and is unfavorable for instrument miniaturization. For graphitic carbon, the performance was even poorer than C18, and its main problem is also the shortage of sorption capacity. For MWCNTs, the recoveries were in the range of 60.8–91.5%. These values were evidently inferior to those of graphene. For SWCNTs, the recoveries were better than MWCNTs, but still inferior to graphene. Notably, we found that no CPs were present in the flow-throughs and washing solutions for MWCNTs and SWCNTs, indicating that CNTs also have good sorption capacities for CPs. Thus, the lower recoveries on CNTs should be ascribed to too stable adsorption and incomplete elution. Increasing the volume of eluent solvent can improve the recoveries, e.g., with 2 mL of alkaline MeOH as eluent solvent, the recoveries of CPs on SWCNTs cartridge can reach 86.6–103.4%. Nevertheless, increas-

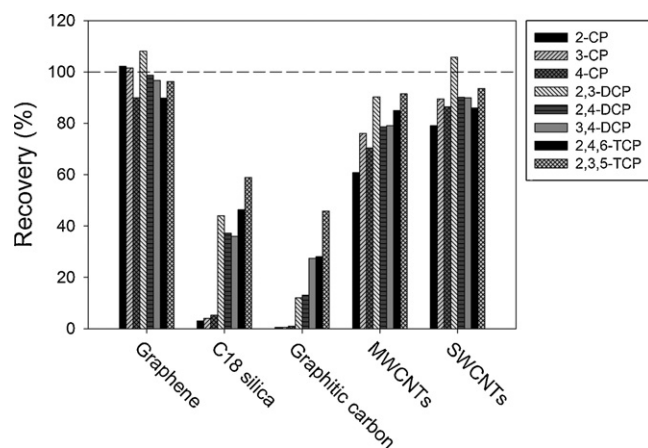


Fig. 5. Comparison of the performance of graphene with several other adsorbents (C18 silica, graphitic carbon, SWCNTs, and MWCNTs) for the SPE of eight CPs. The SPE cartridges were packed with 20 mg adsorbents in all cases. For graphene and CNTs, the eluent solvent was 1 mL of alkaline MeOH; for C18 and graphitic carbon, the eluent solvent was 1 mL of MeOH. Other experimental conditions are stated in Section 2.

Table 1
Analytical figures of merit via graphene-based SPE–HPLC–UV method.^a

Analyte	pK _a ^b	t _R (min) ^c	Regression equation ^d	R ² ^e	Linear range (ng/mL)	LOD (ng/mL) ^f	RSD (%)			
							Run-to-run ^g	Day-to-day ^h	Cartridge-to-cartridge ⁱ	Batch-to-batch ^j
2-CP	8.49	7.48	y = 0.0112x – 0.0141	0.9963	1–200	0.2	5.9	7.2	5.8	9.4
3-CP	8.85	8.59	y = 0.0092x – 0.0131	0.9964	1–200	0.2	4.6	7.0	5.4	9.8
4-CP	9.18	8.20	y = 0.0144x – 0.0246	0.9969	1–200	0.1	5.3	7.6	5.5	10.0
2,3-DCP	6.44	10.96	y = 0.0094x + 0.0290	0.9975	1–200	0.2	2.9	5.4	7.1	4.8
2,4-DCP	7.67	11.68	y = 0.0086x – 0.0197	0.9973	1–200	0.2	4.8	8.4	5.5	10.8
3,4-DCP	7.38	12.00	y = 0.0072x – 0.0240	0.9969	1–200	0.2	5.4	9.2	6.2	11.3
2,4,6-TCP	7.42	15.14	y = 0.0069x – 0.0198	0.9975	2–200	0.4	7.7	9.5	8.3	10.5
2,3,5-TCP	7.36	16.02	y = 0.0073x + 0.0584	0.9714	2–200	0.4	2.2	6.5	7.7	9.9

^a The experimental conditions are stated in Section 2.^b The pK_a values of CPs are adopted from Ref. [56].^c t_R, retention time.^d y = peak area in mAU min and x = concentration in ng/mL.^e R, correlative coefficient.^f LODs were estimated as the concentrations where s/n = 3.^g The run-to-run RSDs were calculated based on six extractions.^h The day-to-day RSDs were obtained over 3 days and nine extractions.ⁱ The cartridge-to-cartridge RSDs were tested with four graphene-packed SPE cartridges.^j The batch-to-batch RSDs were obtained with three batches of graphene.

ing the volume of eluent solvent will reduce the preconcentration factor.

From the above comparison, we can realize that the advantage of graphene over C18 and graphitic carbon mainly lies in the higher sorption capacity; while compared with CNTs, it is more facile to achieve complete elution with graphene. Therefore, we ascribe the advantages of graphene not only to its large surface area but also to its unique chemical structure. First, the hexagonal arrays of carbon atoms in the graphene sheets may have a strong π – π interaction with the target molecules. Second, although being chemically reduced, the graphene sheets still have some hydrophilic groups such as hydroxyl and carboxyl groups (as illustrated in Fig. 2). These hydrophilic groups can improve the water-wettability of graphene and enhance the retention and elution of polar compounds. Third, the molecules can readily access both the surfaces of graphene sheets, and this is favorable for both the adsorption and elution

process of SPE. While for CNTs, their tube-like structures may sterically hinder the access of target molecules into the inner structure of CNTs. These features make graphene very attractive as an adsorbent material. It is therefore believed that graphene has a potential to replace CNTs as a superior SPE adsorbent. Since the specific surface area of the graphene used in this work was still much lower than its theoretical value, future improvements in the synthesis process will certainly further improve the performance of graphene in SPE.

3.5. Analytical figures of merit

Table 1 summarizes the analytical performance obtained via this graphene-based SPE–HPLC–multi-wavelength UV method. SPE was carried out with 50 mL aqueous standards. All linear ranges were based on the average peak areas of at least five CP concentrations.

Table 2
Recoveries from tap and river water samples (n = 3).^a

Analyte	Tap water samples		River water samples	
	Concentration added (ng/mL)	Recovery (%)	Concentration added (ng/mL)	Recovery (%)
2-CP	10	87.8 ± 2.0	10	95.5 ± 2.2
	40	105.5 ± 3.8	40	91.5 ± 4.4
	100	99.1 ± 4.3	100	81.6 ± 4.5
3-CP	10	101.2 ± 4.8	10	101.2 ± 1.1
	40	104.3 ± 8.2	40	100.2 ± 6.2
	100	98.9 ± 5.0	100	88.5 ± 6.2
4-CP	10	89.0 ± 9.9	10	104.3 ± 3.5
	40	109.3 ± 2.8	40	100.0 ± 6.4
	100	104.2 ± 5.8	100	91.6 ± 4.9
2,3-DCP	10	98.2 ± 5.1	10	104.9 ± 8.4
	40	104.5 ± 4.1	40	101.5 ± 9.3
	100	107.7 ± 5.5	100	86.0 ± 7.3
2,4-DCP	10	99.0 ± 3.6	10	100.2 ± 2.5
	40	106.3 ± 3.1	40	99.3 ± 1.5
	100	108.6 ± 5.2	100	87.9 ± 2.1
3,4-DCP	10	96.7 ± 5.7	10	108.9 ± 7.1
	40	107.4 ± 2.9	40	103.6 ± 6.9
	100	110.3 ± 3.3	100	100.9 ± 3.1
2,4,6-TCP	10	103.4 ± 9.8	10	89.0 ± 3.5
	40	102.6 ± 9.4	40	79.8 ± 3.4
	100	95.8 ± 7.0	100	77.2 ± 3.5
2,3,5-TCP	10	106.2 ± 4.2	10	95.8 ± 6.7
	40	97.2 ± 9.3	40	92.5 ± 6.0
	100	116.6 ± 5.1	100	84.5 ± 7.5

^a The experimental conditions are stated in Section 2.

The lower concentration limits of the calibration curves correspond to the limits of quantitation (LOQs), which were estimated as the concentrations where $s/n = 10$. Excellent linear relationships were obtained in all cases (R^2 0.9714–0.9975). The LODs varied from 0.1 to 0.4 ng/mL. These values are below the legal tolerance level for each phenol in drinking water (0.5 ng/mL) according to the European Community Directive [51] and the maximum contaminant level for phenols in drinking water (5 ng/mL) according to the Japanese Ministry of Health, Labour and Welfare [52]. The LODs were also lower than those obtained by GC-FID or GC-ECD in U.S. EPA Method 604 for 2-CP, 2,4-DCP, and 2,4,6-TCP [53]. Compared with the previously reported methods regarding CPs, the sensitivity of the present method is somewhat better than those obtained with C18 and styrene divinylbenzene SPE disks [54] and liquid phase microextraction with back extraction [55]. Compared with the CNTs-based SPE [13] and carbon nanocones/disks-based SPE [7], the obtained LODs are at the same level.

Our initial concern was the reproducibility of this method because of the polydispersity of the graphene sheets. To our surprise, the observed reproducibility of the method was satisfactory (as listed in Table 1). Notably, the run-to-run assays were performed on a single SPE cartridge ($n=6$), and thus the result also demonstrates the good reusability of the graphene-packed SPE cartridges. In fact, we have found that the graphene-packed SPE cartridges can be reused for over 50 times with acceptable recoveries. In the day-to-day assays, the cartridges were stored at room temperature after dried by air between days. As known, sorbent drying usually deteriorates the recoveries for the commonly used C18 adsorbent. By contrast, the good day-to-day RSDs listed in Table 1 demonstrate that sorbent drying has no significant impact on the analytical performance of the graphene-packed SPE cartridges.

3.6. Analysis of tap and river water samples

The proposed method was applied to the analysis of eight CPs in real environmental water samples including tap and river water collected in Beijing. Aliquots of 50 mL of each sample were filtered

through a 0.45 μm cellulose membrane, and then spiked with the CPs at three different concentration levels (10, 40, and 100 ng/mL). The spiked samples were stored in the dark overnight, and analyzed by the proposed method ($n = 3$). Fig. 6 shows typical chromatograms obtained from unspiked water samples and water samples spiked with the eight CPs at a concentration of 40 ng/mL. As listed in Table 2, the recoveries were in the range of 87.2–116.6% for tap water samples and 77.2–108.9% for river water samples. These satisfactory recoveries indicate no significant effects from the matrix composition of the environmental water samples.

4. Conclusions

In conclusion, the proposed method reveals great potentials of graphene as an advantageous sorbent material in SPE. By using eight CPs as model analytes, the graphene-packed SPE cartridges showed reliable and attractive analytical performance in the analysis of environmental water samples. Higher recoveries were achieved with graphene than with other adsorbents including C18 silica, graphitic carbon and CNTs, owing to the large surface area and unique chemical structure of graphene. Some other advantages of graphene as SPE adsorbent have also been demonstrated, such as high sorption capacity, good compatibility with various organic solvents, good reusability, no impact of sorbent drying, and fine reproducibility. Therefore, we believe that graphene is a promising material for SPE. Future efforts should be made to further enhance the surface area of the graphene adsorbent and extend the applications of the method.

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References

- [1] E.M. Thurman, M.S. Mills, *Solid-Phase Extraction: Principles and Practice*, John Wiley & Sons, Hoboken, NJ, 1998.
- [2] J.R. Baena, M. Gallego, M. Valcarcel, *Trends Anal. Chem.* 21 (2002) 187.
- [3] R.M. Vallant, Z. Szabo, S. Bachmann, R. Bakry, M. Najam-ul-Haq, M. Rainier, N. Heigl, C. Petter, C.W. Huck, G.K. Bonn, *Anal. Chem.* 79 (2007) 8144.
- [4] M. Valcarcel, S. Cardenas, B.M. Simonet, Y. Moliner-Martinez, R. Lucena, *Trends Anal. Chem.* 27 (2008) 34.
- [5] L.M. Ravelo-Perez, A.V. Herrera-Herrera, J. Hernandez-Borges, M.A. Rodriguez-Delgado, *J. Chromatogr. A* 1217 (2010) 2618.
- [6] S. Zhu, W. Niu, H. Li, S. Han, G. Xu, *Talanta* 79 (2009) 1441.
- [7] J.M. Jimenez-Soto, S. Cardenas, M. Valcarcel, *J. Chromatogr. A* 1216 (2009) 5626.
- [8] P. Jinno, K. Yamamoto, J.C. Fetzer, W.R. Biggs, *J. Microcolumn Sep.* 4 (1992) 187.
- [9] A. Glausch, A. Hirsch, I. Lamparth, V. Schurig, *J. Chromatogr. A* 809 (1998) 252.
- [10] M. Gallego, Y.P. Depena, M. Valcarcel, *Anal. Chem.* 66 (1994) 4074.
- [11] E. Ballesteros, M. Gallego, M. Valcarcel, *J. Chromatogr. A* 869 (2000) 101.
- [12] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, *Anal. Chem.* 75 (2003) 2517.
- [13] Y.Q. Cai, Y.E. Cai, S.F. Mou, Y.Q. Lu, *J. Chromatogr. A* 1081 (2005) 245.
- [14] H.Y. Niu, Y.Q. Cai, Y.L. Shi, F.S. Wei, J.M. Liu, G.B. Jiang, *Anal. Bioanal. Chem.* 392 (2008) 927.
- [15] M. Abdel Salam, R. Burk, *J. Sep. Sci.* 32 (2009) 1060.
- [16] Q. Zhou, J. Xiao, Y. Ding, *Anal. Chim. Acta* 602 (2007) 223.
- [17] L.M. Ravelo-Perez, J. Hernandez-Borges, M.A. Rodriguez-Delgado, *J. Sep. Sci.* 31 (2008) 3612.
- [18] G.Z. Fang, J.X. He, S. Wang, *J. Chromatogr. A* 1127 (2006) 12.
- [19] B. Suarez, B. Santos, B.M. Simonet, S. Cardenas, M. Valcarcel, *J. Chromatogr. A* 1175 (2007) 127.
- [20] P. Liang, Y. Liu, L. Guo, J. Zeng, H.B. Lu, *J. Anal. Atom. Spectrom.* 19 (2004) 1489.
- [21] J. Munoz, M. Gallego, M. Valcarcel, *Anal. Chem.* 77 (2005) 5389.
- [22] L. Xu, H.K. Lee, *J. Chromatogr. A* 1192 (2008) 203.
- [23] G. Saini, L. Yang, M.L. Lee, A. Dadson, M.A. Vail, M.R. Linford, *Anal. Chem.* 80 (2008) 6253.

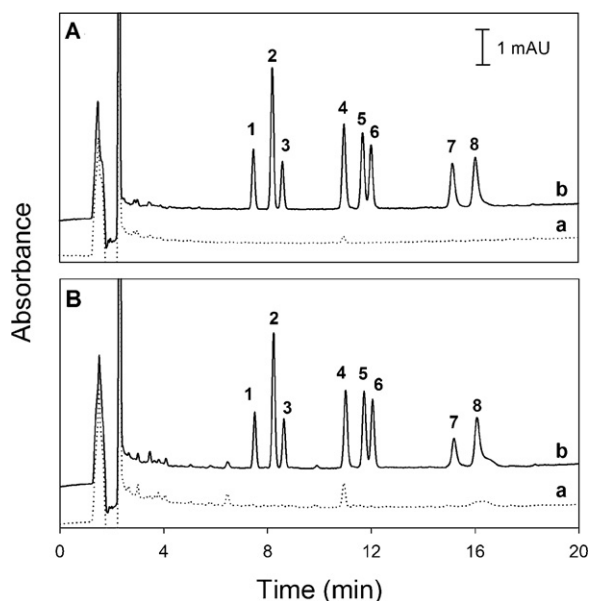


Fig. 6. Typical chromatograms from the analysis of tap water samples (A) and river water samples (B). (a) Unspiked samples and (b) samples spiked with the eight CPs at the concentration of 40 ng/mL. Peaks: (1) 2-CP; (2) 4-CP; (3) 3-CP; (4) 2,3-DCP; (5) 2,4-DCP; (6) 3,4-DCP; (7) 2,4,6-TCP; (8) 2,3,5-TCP. Detection wavelength, 286 nm. The chromatograms at other data channels (wavelengths) are not shown. Other experimental conditions are stated in Section 2.

- [24] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* 306 (2004) 666.
- [25] A.K. Geim, K.S. Novoselov, *Nat. Mater.* 6 (2007) 183.
- [26] A.K. Geim, *Science* 324 (2009) 1530.
- [27] M.D. Stoller, S.J. Park, Y.W. Zhu, J.H. An, R.S. Ruoff, *Nano Lett.* 8 (2008) 3498.
- [28] C. Lee, X.D. Wei, J.W. Kysar, J. Hone, *Science* 321 (2008) 385.
- [29] A.A. Balandin, S. Ghosh, W.Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, *Nano Lett.* 8 (2008) 902.
- [30] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H.L. Stormer, *Solid State Commun.* 146 (2008) 351.
- [31] W.R. Yang, K.R. Ratinac, S.P. Ringer, P. Thordarson, J.J. Gooding, F. Braet, *Angew. Chem. Int. Ed.* 49 (2010) 2114.
- [32] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K.S. Novoselov, *Nat. Mater.* 6 (2007) 652.
- [33] K.R. Ratinac, W.R. Yang, S.P. Ringer, F. Braet, *Environ. Sci. Technol.* 44 (2010) 1167.
- [34] M. Zhou, Y.M. Zhai, S.J. Dong, *Anal. Chem.* 81 (2009) 5603.
- [35] Y. Wang, Y.Y. Shao, D.W. Matson, J.H. Li, Y.H. Lin, *ACS Nano* 4 (2010) 1790.
- [36] Y. Liu, D.S. Yu, C. Zeng, Z.C. Miao, L.M. Dai, *Langmuir* 26 (2010) 6158.
- [37] D. Du, Z.X. Zou, Y.S. Shin, J. Wang, H. Wu, M.H. Engelhard, J. Liu, I.A. Aksay, Y.H. Lin, *Anal. Chem.* 82 (2010) 2989.
- [38] S. Park, R.S. Ruoff, *Nat. Nanotechnol.* 4 (2009) 217.
- [39] C.E. Banks, A. Crossley, C. Salter, S.J. Wilkins, R.G. Compton, *Angew. Chem. Int. Ed.* 45 (2006) 2533.
- [40] M. Pumera, Y. Miyahara, *Nanoscale* 1 (2009) 260.
- [41] L.P. Biro, N.Q. Khanh, Z. Vertesy, Z.E. Horvath, Z. Osvath, A. Koos, J. Gyulai, A. Kocsonya, Z. Konya, X.B. Zhang, G. Van Tendeloo, A. Fonseca, J.B. Nagy, *Mater. Sci. Eng. C* 19 (2002) 9.
- [42] X.L. Dong, J.S. Cheng, J.H. Li, Y.S. Wang, *Anal. Chem.* 82 (2010) 6208.
- [43] L.A.L. Tang, J. Wang, K.P. Loh, *J. Am. Chem. Soc.* 132 (2010) 10976.
- [44] U.G. Ahlborg, T.M. Thunberg, *Crit. Rev. Toxicol.* 7 (1980) 1.
- [45] W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.* 80 (1958) 1339.
- [46] Y.X. Xu, H. Bai, G.W. Lu, C. Li, G.Q. Shi, *J. Am. Chem. Soc.* 130 (2008) 5856.
- [47] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, *Carbon* 45 (2007) 1558.
- [48] D. Li, M.B. Muller, S. Gilje, R.B. Kaner, G.G. Wallace, *Nat. Nanotechnol.* 3 (2008) 101.
- [49] R.J. Waltman, J. Pacansky, C.W. Bates, *Chem. Mater.* 5 (1993) 1799.
- [50] M.J. Fernandez-Merino, L. Guardia, J.I. Paredes, S. Villar-Rodil, P. Solis-Fernandez, A. Martinez-Alonso, J.M.D. Tascon, *J. Phys. Chem. C* 114 (2010) 6426.
- [51] Drinking Water Directive 80/778/EEC, Commission of the European Communities, 1980.
- [52] Ministry Ordinance No. 15, Ministry of Health, Labour and Welfare, Tokyo, Japan, 2000.
- [53] Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 604 – Phenols, U.S. Environmental Protection Agency, Cincinnati, OH, 1984.
- [54] D. Puig, D. Barceló, *Chromatographia* 40 (1995) 435.
- [55] L. Zhao, H.K. Lee, *J. Chromatogr. A* 931 (2001) 95.
- [56] A.M. Nunez-Gaytan, L.E. Vera-Avila, M.D. Covarrubias-Herrera, *J. Mex. Chem. Soc.* 52 (2008) 185.