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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.

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 m^2/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, $KMnO_4$, $K_2S_2O_8$ 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 μg/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 × 4.6 mm) with an Inertsil ODS-SP guard column (5 μm, 10 mm × 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 $K_2S_2O_8$ 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 (Plainview, 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-