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Cotton-supported graphene functionalized with aminosilica nanoparticles as a versatile high-performance extraction sorbent for trace organic analysis

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ABSTRACT

Cotton fibers were functionalized, following the coating of fibers with graphene oxide (GO), the covalent attachment of aminosilica nanoparticles and the reduction to the cotton-GR-aminosilica material. Employing the cotton-supported graphene (GR)-aminosilica material, a novel and easily applicable extraction mode was put forward. Several groups of analytes were employed such as PAHs, phthalates, musks, phenolic endocrine disrupters and haloacetic acids to test the applicability of the functionalized cotton for extraction purposes. The extraction yields ranged from 76% to 96% corroborating the high degree of affinity of the material for the above groups of compounds while the limits of detection were between 0.06 and 1.10 μg/L using gas chromatography-electron capture detection for haloacetic acids and gas chromatography–mass spectrometry for the rest of the analytes. The accuracy of the method was evaluated in fortified lake water at a spiking level of three to ten times the lowest quantifiable concentration and the recoveries varied from 86% to 104% for all the studied analytes. The π–π and hydrophobic interactions, the hydrogen bonding between the functionalized cotton and analytes and the electron polarizability and ionizability of the chemical structures justify the extraction behavior.

1. Introduction

Classical and modern modes of extraction, share in common many sorbing materials such as silica-based reversed phase sorbents with different functional groups, polymeric sorbents, polyurethane foam, graphitized carbon black, fullerenes and carbon nanotubes, which have been used to extract non-polar analytes from different water samples [1]. Carbon-based materials, such as graphitized carbon black, porous graphitic carbon and activated carbon, possess strong sorption ability but they may encounter desorption problems due to irreversible sorption of some analytes, when they are applied as SPE sorbents [2].

Graphene oxide (GO) sheets, consisting of intact graphitic regions interspersed with sp^3-hybridized carbons, contain hydroxyl and epoxy functional groups on the top and bottom surfaces of each sheet in addition to the sp^2-hybridized carbons with hydroxyl, carbonyl and carboxyl groups at the sheet edges [3]. Hence, GO is hydrophilic and readily disperses in water to form stable colloidal suspensions [4]. In contrast, graphene (GR), the reduced form of GO, is hardly suspended in water due to being hydrophobic, electron-rich nanomaterial in nature, with a large delocalized π-electron system [5,6]. This endows GR with a strong affinity for carbon-based ring structures, which are widely present in drugs, pollutants and biomolecules and it has been served as an adsorption/extraction material and wonder sorbent for small and medium-sized molecules [7–15]. The performance of GR has been compared to C18-silica, graphitic carbon and carbon nanotubes with the same sorbent amount [10]. Of the materials tested, only GR completely retained the analytes; however, its direct use as sorbent in SPE may cause the following concerns: (I) miniscule GR sheets may escape from the cartridge due to their polydispersity and (II) GR sheets are apt to form irreversible agglomerates because of their hydrophobic nature and the strong π–π interactions. Therefore, aggregation of GR sheets may occur during sample solution passing the cartridge, which may affect the efficiency and reusability of the cartridge. On the other hand, GR sheets are relatively soft and flexible so they can be attached onto a support more easily than carbon nanotubes and fullerenes.

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Placing a premium on the advantages of GR, researchers developed GR-bound and GO-bound silica as SPE sorbents [16] or in the form of magnetic materials [17–22].

Microcolumns filled with cotton have been applied to the retention of synthetic colorants [23] and enrichment of polycyclic aromatic hydrocarbons (PAHs) [24] as well as to the extraction–preconcentration of the hydrophobic ion-pair copper-chromazurol S-cethyltrimethylammonium bromide [25]. Cotton microfibrils are made of poly-D-glucose chains, usually arranged in crystalline or partially crystalline domains [26]. As such, they are amenable to modifications through physical (sorption) and chemical processes [27].

In this article, cotton fibers are functionalized, in three successive steps: (I) coating of microfibrils with GO, (II) covalent attachment of aminosilica nanoparticles on GO and (III) reduction–hydrophobization to produce a web of aminosilica-GR cotton microfibrils. Employing the synthesized cotton-supported GR-aminosilica material, a novel and straightforward cotton-based extraction mode is put forward, for the first time. Succinctly, a functionalized cotton piece is added to an aqueous sample with a magnetic bar. A stirrer is switched on and the piece tumbles freely in the sample solution for a certain period of time. The extraction of analytes on cotton fibers, which takes place via π–π, hydrophobic, hydrophilic and ionic interactions is followed by the facile collection of cotton piece, the elution and subsequently the injection into the gas chromatograph. To test the applicability of the functionalized cotton and figure out the mechanism of extraction, several groups of pollutants were successfully employed such as PAHs, phthalates, musks, phenolic endocrine disrupters and haloacetic acids.

2. Experimental

2.1. Chemicals and solutions

Pure hydrophilic, non-sterile cotton pads were purchased from a local pharmacy. Graphite powder (purity 99.9%), tetraethoxysilane (99%), 3-aminopropyltriethoxysilane and humic acid sodium salt were purchased from Aldrich (Sigma–Aldrich Ltd., Greece). Hydrazine for synthesis (about 100%) was obtained from Merck (Merck Chemicals, Darmstadt, Germany). Thirteen analytical standards of PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a*,*h*]anthracene) in methanol or acetone were obtained from Supelco (Bellefonte, PA, USA). Musks (phantolide, celestolide, tonalide, galaxolide, traseolide) were obtained from LGC Promochem (Promochem GmbH Wesel, Germany) and irgasan (triclosan) was obtained from Fluka (Buchs, Switzerland). Bisphenol A, β-estradiol, 4-*n*-octylphenol, 4-*tert*-butylphenol, pentachlorophenol, diethyl phthalate, dibutyl phthalate, dicyclohexyl phthalate, dioctyl phthalate and nonane were all obtained from Sigma–Aldrich. The haloacetic acids (HAAs) monochloroacetic, monobromoacetic, dichloroacetic, dibromoacetic, bromochloroacetic, trichloroacetic, bromodichloroacetic, dibromochloroacetic and tribromoacetic acids were purchased from Sigma–Aldrich (Madrid, Spain). The organic solvents employed (i.e. *n*-hexane, ethyl acetate, methyl-*tert*-butyl ether and methanol) were of GC grade and obtained from Labscan (Labscan, Dublin, Ireland).

Due to the presence of phthalates in many laboratory products including containers and glassware, high background may occur for the analysis of phthalates in real samples. To minimize contamination, all laboratory glassware used in the study was soaked in acetone for at least 30 min, rinsed with *n*-hexane, and then dried at 120 °C for at least 4 h, before use.

2.2. Instrumentation

Analyses were carried out on Shimadzu GC-17A gas chromatographs with electron capture detector (ECD) and QP 5000 mass spectrometer (MS) (Kyoto, Japan). The selective ion monitoring mode was adopted for the determination of the analytes grouping the fragment ions for PAHs, phthalates, musks and derivatized phenolic compounds (see Table S1). For detailed chromatographic conditions see Supplementary material.

2.3. Synthesis of GO and GR

Graphite powder was oxidized by a mixture of acids and $KMnO_4$, as described by Jabeen et al. [28] with modifications [17] and subsequently reduced with hydrazine. Details are given in Supplementary material.

2.4. Synthesis of aminosilica nanoparticles

Silica was prepared with hydrolysis of tetraethoxysilane using the well-known Stober's method, as reported elsewhere [29]. Details about the synthesis of aminosilica are given in the Supplementary material.

2.5. Modification of cotton fibers using GO

The coating of cotton fabrics with GO nanostructures was achieved using an approach, which comprised successive immersions assisted by ultrasonication and drying steps. Briefly, a cotton pad of ∼5 cm diameter weighing 0.56 g was rinsed with acetone and plenty of water. A GO 'ink'-dispersion was prepared by bath ultrasonication (120 W) of 200 mg of GO in 100 mL of double distilled water (DDW) for 10 min, followed by probe-ultrasonication at 250 W (MRC Scientific Instruments, Holon, Israel), for 30 min. The cotton pad was immersed in the GO ink under bath ultrasonication, for 10 min. After that, the GO-coated cotton was taken out of the solution and left drain on a net for 10 min. The resulting fabric was placed in an oven at 120 °C, for 20 min in order to complete the attachment. This process of coating was repeated six times to increase the GO loading on the cotton pad. Finally, it was washed with DDW for the removal of unretained GO and dried overnight, at 110 °C. The mass of the GO was obtained from the mass difference before and after the immersion and drying of the cotton pad.

2.6. Covalent attachment of aminosilica nanoparticles on cotton-GO

The GO-functionalized cotton was transferred to a beaker containing 100 mL ethanolic suspension of 0.5% aminosilica and placed in ultrasonic bath, for 60 min. At the end of the reaction, the cotton was removed from the suspension, washed several times with water and ethanol to remove completely any physically adsorbed reactants and loosely retained particles and then dried at 100 °C, for 1 h.

2.7. Cotton-supported GR-aminosilica

The reduction to cotton-GR-aminosilica was achieved by refluxing the cotton-GO-aminosilica in 100 mL of DDW containing 200 μL of hydrazine, at 90 °C, for 24 h. The final material was rinsed with plenty of water to remove minute amounts of detached GR and aminosilica nanoparticles and dried at 110 °C overnight. The color of the modified cotton turned dark gray.

Precaution: The use of hydrazine requires great care because it is both highly toxic and potentially explosive.