Evaluation of graphene-based sorbent in the determination of polar environmental contaminants in water by micro-solid phase extraction-high performance liquid chromatography

Nyi Nyi Naing [a,b], Sam Fong Yau Li [a,b], Hian Kee Lee [a,b,*]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore
[b] National University of Singapore Environmental Research Institute, T-Lab #02-01, 5A Engineering Drive 1, Singapore 117411, Singapore

ARTICLE INFO

ABSTRACT

A facile method of extraction using porous membrane protected micro-solid phase extraction (μ-SPE) with a graphene-based sorbent followed by high performance liquid chromatography–ultraviolet detector was developed. The reduced graphene oxide (r-GO) (1 mg), synthesized from graphite oxide, was enclosed in a polypropylene bag representing the μ-SPE device, which was used for the extraction of estrogens such as estrone, 17β-estradiol, 17α-ethynylestradiol and diethylstilbestrol in water. The r-GO obtained was identified and characterized by Fourier transform infrared, transmission electron microscopy, scanning electron microscopy and thermogravimetric analysis. The sorbent was loaded with sodium dodecyl sulfate by sonication to prevent agglomeration in aqueous solution. With this method, low limits of detection of between 0.24 and 0.52 ng L^{-1} were achieved. For estrogen analysis a linear calibration range of 0.01–100 μg L^{-1} was obtained, with the coefficients of determination (r^2) higher than 0.992. This proposed method was successfully applied to determine estrogens in water.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the preparation of sorbents with specific characteristics and special interactions or selectivities toward particular target analytes has been the focus of much interest in the development of sample preparation on extraction approaches. Preparation of materials with high adsorption capacity and efficiencies is important for sorbent-based extraction [1–3]. This approach to sample preparation includes solid-phase extraction (SPE) [4–6], solid-phase microextraction (SPME) [7–10] and stir bar sorptive extraction (SBSE) [11–14]. Although these techniques have obvious advantages over classical extraction methods such as liquid–liquid extraction (LLE), they do have some drawbacks. For example, while SPE consumes much less solvent than LLE, it involves several steps, can be time consuming and can suffer from possible loss of analytes during the extraction process [15]. SPME is a widely practiced procedure but in general, its extraction fibers are expensive and fragile [16,17]. Moreover, the adsorption capacity of a fiber is limited by the low surface area of the sorbent phase. SBSE has a layer absorptive surface but only limited types of sorbents (polydimethylsilane, ethylene glycol-silicone and polyacrylate) are available commercially. Micro-solid phase extraction (μ-SPE), a relatively recent simple and fast sampling technique that requires minimal amount of solvents with good clean-up properties, was developed to overcome most of these problems [2]. The μ-SPE device consists of a porous polypropylene membrane envelope containing a few milligrams of sorbent. The membrane in the device can reduce significantly, if not eliminate, any interferences present in complex samples, and hence the extraction can be accomplished without additional sample clean-up. The major advantage of μ-SPE is that the clean-up and preconcentration during the extraction process take place in single step. Recently, various types of sorbents such as C_{18}, carbon nanotubes and polymer-based sorbents have been successfully applied for μ-SPE to investigate the extraction of different analytes in aqueous environment [18–20]. Indeed, any sorbent, whether commercial or synthesized in-house can be used for the procedure.

Graphene, a single-layer of sp^2 hybridized carbon atom, is a double-sided aromatic scaffold with a high specific surface area of 2630 m^2/g. The latter property suggests the material has a high sorption capacity. In fact, graphene possesses many extraordinary advantages, such as ultrahigh specific surface area, good thermal
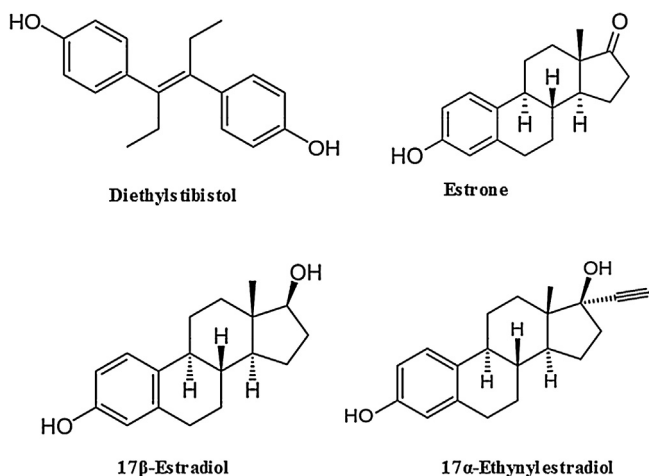
Fig. 1. Chemical structures of estrogens studied.

and chemical stability, ultra-high mechanical strength and low production cost. These properties represents great promise for its applications in the analytical chemistry field. Specifically, both sides of the planar sheet of graphene are available for molecule adsorption. Based on its large delocalized π-electron system, graphene can form strong π–π stacking interaction with the benzene ring [21,22]. This material thus has great potential to serve as sorbent for extraction of benzenoid compounds. Graphene oxide (GO), the oxidized counterpart of graphene contains functional groups such as epoxide, carboxyl and hydroxyl groups which can undergo covalent, electrostatic or hydrogen bonding with analytes.

Some important environmental contaminants include endocrine disrupting compounds (EDCs). These natural and synthetic EDCs may affect human beings adversely, such as decreasing sperm count in man, increasing the possibility of causing breast cancer in woman and reproductive abnormalities in both man and woman and also detrimental effects on wildlife [23,24]. Among these EDCs, estrogens have received particular attention due to their high estrogenic potency. The classification of estrogens as natural hormones includes 17β-estradiol (E2), and its metabolites estrone (E1) and estriol whereas semi-synthetic and synthetic hormones include 17α-ethynylestradiol (EE2) and diethylstilbestrol (DES) (Fig. 1). DES was previously used for the treatment of high-risk pregnancies and was prescribed to millions of woman in the USA in the past. Estradiol has been used in the management of diverse cancers such as prostate and breast cancer and the menopausal syndrome [25,26]. The massive use of such drugs in daily life by the general population may cause cumulative residue of the drugs in the environment through the excretion, disposal of unused drugs and inadequate treatment of sewage treatment plant. These are the main sources of contamination [27,28]. Estrogens at ultratrace levels have been revealed to cause endocrine disruption in several varieties of fish. Determination of these compounds therefore requires highly-sensitive analytical methods. There have many sample preparation methods used in conjunction with the techniques. These include LLE, SPE, SPME and others [7,29]. Basheer et al. [30] reported a procedure that used a hollow-fiber coated with dihydroxylated polymethylmethacrylate to extract estrogens from water. Kanimozhi et al. [31] used μ-SPE with C_2-silica particles to extract these compounds from ovarian cyst fluid samples. Both of these extraction approaches were combined with gas chromatography–mass spectrometry (GC–MS) analysis with derivatization of the analytes either with N-methyl-N-(trimethylsilyl) trifluoroacetamide or N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA). Determination of trace estrogens in water using HLB SPE cartridge combined with two-dimensional

GC × GC–MS was reported by Gunatilake et al. [32]. In their procedure, BSTFA was used as derivatization agent. Thus, in these studies, an extra step was needed after extraction, before GC–MS or GC × GC–MS analysis.

Graphene-based sorbents have been used for the preconcentration of analytes containing benzenoid rings. Liu et al. [21] utilized graphene powder as a novel adsorbent in SPE. In their work, a graphene-packed SPE cartridge was used to extract eight chlorophenols in water. Zhang et al. [33] have applied sulfonated graphene sheets as a μ-SPE sorbent for the analysis of polycyclic aromatic hydrocarbons in water. A method to extract endocrine disrupting phenols from water using iron–ferric oxide-core shell nanowires on GO nano sheets in magnetic SPE was reported by Li et al. [34]. The adsorptive properties of graphene and GO and their applications in preconcentrating organic compounds and trace metal ions by SPE, SPME and magnetic SPE methods have been reviewed [35,36].

In this work, μ-SPE using reduced GO (r-GO) previously loaded with sodium dodecyl sulfate (SDS) surfactant by ultrasonication as sorbent was developed for the analysis of E1, E2, EE2 and DES present in trace levels in the aqueous phase using high performance liquid chromatography–ultraviolet (HPLC–UV) analysis. Various extraction parameters such as the extraction time, desorption time and effect of electrolytes were optimized to obtain maximum extraction efficiencies. The applicability of the proposed method was evaluated with genuine water samples from a local canal.

2. Experimental

2.1. Reagents and materials

Pure estrogen standards were purchased from Aldrich (Milwaukee, WI, USA). Stock solutions of these standards ($1000 \, \mu g \, L^{-1}$) were prepared individually in methanol. Solutions of mixtures containing $20 \, \mu g \, L^{-1}$ of each analyte were prepared by dilution with methanol from the stock solutions. SDS was obtained from Sigma–Aldrich (St. Louis, MO, USA). The graphite powder and hydrochloric acid (HCl 37%) were bought from Merck (Darmstadt, Germany). Potassium permanganate ($KMnO_4$) was purchased from Comak Chemicals Limited, (Hertfordshire, UK). Sodium nitrate ($NaNO_3$) was acquired from Strem Chemicals, Inc. (Newburyport, MA, USA). Sulfuric acid (H_2SO_4 95%) was supplied from BDH, Merck Ltd. (Poole, Dorset, UK). HPLC-grade mobile phase acetonitrile was obtained from Tedia (Fairfield, OH, United States). Ultrapure water was obtained from an ELGA Purelab Option-Q (High Wycombe, UK) system. All standard solutions were kept in the refrigerator at 4 °C. Q3/2 Accurel polypropylene (PP) membrane sheets (157 μm thickness, 0.2 μm pore size) were purchased from Membrana (Wuppertal, Germany). An alpha FT-IR Spectrometer (Bruker) (Karlsruhe, Germany) was used to characterize the synthesized sorbent, r-GO, by Fourier transform infrared spectroscopy (FTIR). Transmission electron microscope (TEM) images were taken using JEOL JEM-2010F & JEOL JEM-3010F systems (Tokyo, Japan). Field emission scanning electron microscope (FESEM) was conducted on a JEOL JSM-6701F system (Tokyo, Japan). The thermal properties of the composites were studied by thermogravimetric analysis (TGA) (Universal V3.9A, TA Instruments, New Castle, DE, USA). Genuine water samples were collected, from a canal in Singapore. Glass bottles previously rinsed with acetone were used to collect water samples. The bottle was fully filled without headspace. Each bottle was then wrapped with aluminum foil before being transported to the laboratory. They were kept in the refrigerator at 4 °C until use. Extraction was performed on unfiltered water samples.