Carbonaceous nanomaterials immobilised mixed matrix membrane microextraction for the determination of polycyclic aromatic hydrocarbons in sewage pond water samples[☆]

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HIGHLIGHTS

- Carbonaceous nanomaterials were incorporated into MMM for micro-extraction approach.
- SLG-MMM was found comparable or even better than standard SPE technique.
- New approach was successfully applied to monitor PAHs content in sewage water samples.

GRAPHICAL ABSTRACT
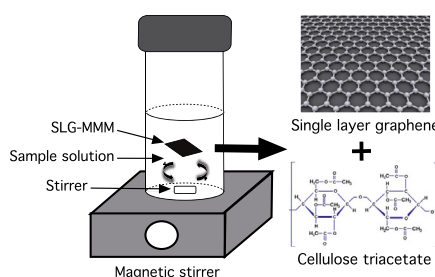
ABSTRACT

In this study, the potential for carbonaceous nanomaterials to be used as adsorbents for the mixed matrix membrane (MMM) microextraction and preconcentration of organic pollutants was demonstrated. For this method, multiwall carbon nanotubes (MWCNT) and single layer graphene (SLG) nanoparticles were individually incorporated through dispersion in a cellulose triacetate (CTA) polymer matrix to form a MWCNT-MMM and SLG-MMM, respectively. The prepared membranes were evaluated for the extraction of selected polycyclic aromatic hydrocarbons (PAHs) present in sewage pond water samples. The extraction was performed by dipping a small piece of membrane (7 mm × 7 mm) in a stirred 7.5 mL sample solution to initiate the analyte adsorption. This step was followed by an analyte desorption into 60 µL of methanol prior to high performance liquid chromatography (HPLC) analysis. When the optimum SLG-MMM microextraction technique was applied to spiked sewage pond water samples, the detection limit of the method for the PAHs were in the range of 0.02–0.09 ng/mL, with relative standard deviations of between 1.4% and 7.8%. Enrichment factors of 54–100 were achieved with relative recoveries of 99% −101%. A comparison was also made between the proposed approach and standard solid phase extraction using polymeric bonded octadecyl (C_{18}) cartridges.

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1. Introduction

When dealing with environmental water samples that have considerable matrices, many analytical approaches generally involve a pretreatment step prior to instrumental analyses.

Although conventional extraction techniques such as liquid-liquid extraction (LLE) and solid phase extraction (SPE) are favoured, the organic waste produced and the use of multistep procedures remain open issues. Recently, several microscale membrane based methods (e.g., hollow fibre liquid phase microextraction (HF-LPME) [1,2], micro-solid phase extraction (μSPE) [3], electromembrane extraction (EME) [4,5], solid phase membrane tip extraction (SPMTE) [6], and thin-film microextraction (TFME) [7,8]) have been introduced to speed up and simplify the sample preparation procedure as well as minimise organic solvent usage. In these reported approaches, the membrane being used can act as a solid matrix support in the form of a supported liquid membrane, a porous solid protected sheet for an adsorbent/organic solvent, or a homogenous thin film.

We recently developed another variation on the thin-film extraction approach based on an adsorbent-immobilised mixed matrix membrane (MMM) [9]. In this method, the membrane, which consisted of 15% commercial octadecyl (C_{18}) bonded on silica particles dispersed in a cellulose triacetate (CTA) polymer matrix, demonstrated superior mechanical robustness and was proven to be suitable for solid-liquid phase microextraction. The membranes were prepared by dispersing the adsorbents in volatile dichloromethane containing CTA and casting the well-dispersed suspension as a thin film. The membranes could then be used as disposable, single-use membranes, thereby avoiding any possible analyte carry-over effects. The approach we developed is also beneficial in terms of simplicity, cost, and ease of experimental setup. Nevertheless, the developed microextraction approach only demonstrated the feasibility of using silica-based particles in the micrometre size range as adsorbent filler, and thus we are interested in exploring alternative nanoparticle adsorbents with greater selectivity and adsorption affinity against organic compounds for a wider range of potential chemical and biochemical applications.

Carbonaceous nanomaterials have attracted great attention in the development of microextraction techniques over the past decade due to their unique physical and chemical properties [10]. Since then, large numbers of carbon-based nanoparticles have been investigated as sorbent materials in sample pretreatment. These carbon-based nanoparticles include graphene, carbon nanotubes, fullerenes, carbon nanofibres, nanodiamonds and their functionalised forms [11]. Among these materials, carbon nanotubes can be regarded as the most used carbonaceous nanomaterial in sample preparation. Both functionalised or non-modified carbon nanotubes have been widely employed as packing materials for the preconcentration of organic compounds, pesticides, pharmaceuticals, inorganic ions, etc (see reviews [12–16] for details). Recently, graphene and its oxide has once again modernised the trend of using carbon-based nanomaterials in microextraction techniques. Graphene is an allotrope of carbon present in a unique planar structure whereby carbon atoms are bonded together in a repeating pattern of hexagons [17]. This unusual characteristic of graphene has conferred it with outstanding electrochemical, mechanical and structural properties. Most importantly, graphene's large specific surface area and unique nanosheet morphology are beneficial for achieving rapid adsorption equilibrium and analyte elution [18]. These characteristics have made graphene an excellent choice as a sorbent material in SPE and solid phase microextraction (SPME) for the extraction of organic pollutants, drugs, heavy metals, and proteins [19,20].

Here, we conducted an exploratory study of the application of carbonaceous nanomaterial immobilised in mixed matrix membrane for the extraction of polycyclic aromatic hydrocarbons from environmental water samples. Nanoparticles, namely multiwall carbon nanotubes (MWCNTs) and single layer graphene (SLG), are evaluated as potential adsorbent filler to extract targeted analytes present in the sewage pond water samples. The membrane was prepared by casting a solution of the desired proportions of CTA polymer matrix and adsorbent nanoparticles in dichloromethane on a flat glass surface. The extraction efficiency of the membranes immobilised with MWCNT and SLG was comprehensively investigated. The performance of the optimised microextraction approach was evaluated by comparing the results of this method with the results of SPE, which is the standard protocol for PAHs analysis.

2. Experimental

2.1. Reagents and materials

Sodium hydroxide (NaOH), cellulose triacetate (CTA) and sodium chloride (NaCl) were obtained from Aldrich (Buchs, SG, Switzerland). Dichloromethane (DCM), methanol (MeOH), 2-propanol (2-PrOH), acetonitrile (ACN) and hydrochloric acid (HCl) were purchased from Merck (Darmstadt, Germany). The PAH standards (naphthalene (Nap), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr) and benz(a)anthracene (BaA)) were bought from Supelco (Bellefonte, PA) as a reagent kit. The MWCNTs with outer diameter of 10–30 nm and specific surface area of 100–250 m^2/g were obtained from Sun Nanotech Co. Ltd. (Nanchang, Jiangxi, China). SLG nanoparticles with average lateral size of 0.5–5 μm and surface area of 700–800 m^2/g were purchased from Nanjing XFNANO Materials Tech Co. Ltd (Nanjing, Jiangsu, China). Ultrapure deionised (DI) water was produced on a Direct-Q3 ultrapure water system (Merck Millipore, Darmstadt, Germany). All other reagents were of analytical grade and used without any further purification.

2.2. Mixed matrix membrane preparation

To prepare the MWCNTs-MMM, 0.5 mg of the MWCNT particles and 20 mg of CTA were weighed and dissolved in 600 μL of DCM. The mix solution was sonicated for 15 min to ensure the particles were well dispersed in the solution, which was then poured into a 2.5 cm I.D. glass ring that was fixed tightly on a flat glass plate with a rubber band. The solution was then solidified by allowing the solvent to gradually evaporate. The dried membrane was peeled off, and then it was conditioned by dipping it in methanol for 30 min prior to the microextraction approach in order to activate the sorbent surface. A similar approach was applied when preparing the SLG-MMM, except the optimum amount of SLG particles used was 0.1 mg. A Hitachi SU-70 field emission scanning electron microscope (Hitachi-Hitech, Tokyo, Japan) was used for the investigation of the surface morphology of the membrane. The membrane was fixed on the stub with double-sided tape and then coated with platinum for 15 s. The membrane thickness was measured with a digital micrometre (MDC-1, Mitutoyo Corporation, Kawasaki, Japan) and was determined to be approximately 50 μm.

2.3. Sample preparation

Stock solutions of PAHs (naphthalene, acenaphthene, fluorine, anthracene, phenanthrene, fluoranthene, pyrene and benz[a]anthracene) at a concentration of 2000 μg/mL in methanol was stored in the refrigerator. Standard solutions for elucidating the extraction performance were prepared by spiking the standard solutions with the PAHs at concentration of 50 ng/mL in deionised water. The sewage pond water sample was collected from the sewage pond of the Universiti Teknologi Malaysia, Johor, Malaysia. These were collected in bottles that were pre-cleaned with acetone. The sewage pond water samples were filtered through a PTFE membrane filter of 0.2 μm (Macherey–Nagel GmBH, Germany) and