Feasibility Study of Glass Slide Extraction Device Coated with Molybdenum Disulfide@graphene Oxide/polystyrene as Sorbent for the Extraction of Polycyclic Aromatic Hydrocarbons

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Abstract

This work is a possibility study of a molybdenum disulfide@graphene oxide/polystyrene (MoS_2@GO/PS) coated on glass slide as an extraction device for the extraction and preconcentration of polycyclic aromatic hydrocarbons (PAHs) prior to analysis with high performance liquid chromatography coupled with diode array detector (HPLC-DAD). Chrysene (Chr), benzo(b)fluoranthene (BbF), and benzo(a)pyrene (BaP) were used as model compounds. Under the optimum conditions of chromatographic separation, linearity (R^2 > 0.999) at concentrations of 2 µg L^{-1}–100 mg L^{-1}, with the limits of detection of 1.881 ± 0.004, 3.396 ± 0.012 and 5.695 ± 0.029 µg L^{-1} for Chr, BbF, and BaP were achieved, respectively. Along with the preliminary extraction and desorption of Chr, BbF, and BaP at a concentration of 100 µg L^{-1}, this developed extraction device could adsorb at a yield of 77 to 87% and the recovery of 15 to 26%. Further investigation is needed and the effective parameters on the extraction performance of the MoS_2@GO/PS coated on glass slide must be optimized to obtain the acceptance recovery before applying for the determination of Chr, BbF and BaP in food samples.

Keywords: Molybdenum Disulfide@Graphene Oxide; Polystyrene; Polycyclic Aromatic Hydrocarbon; HPLC-DAD; Extraction Device

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds composed of two or more fused benzene rings. PAHs are normally generated by pyrolysis processes using high thermal, high pressure, and incomplete combustion of, for example, organic substance, petroleum, coal, and wood as well as by commercial or home preparation using intense heat processing for instance, grilling, smoking, baking, frying, drying, and roasting (Chen et al., 2020; 2018). PAHs are raising concern because they can diffuse and contaminate into the environment (air, surface water, water, and soil) and food (Jesus et al., 2022; K. Sun et al., 2021). PAHs are known as potential genotoxic and possible carcinogenic causing cancer in humans (Binello et al., 2021; Li et al., 2018; Myint Zaw et al., 2022). In this work, the focus is on the determination of chrysene (Chr), benzo(b)fluoranthene (BbF) and benzo(a)pyrene (BaP) which are grouped as heavy PAHs leading to the rising of hazards and toxicity. Accordingly, the International Agency for Research on Cancer (IARC) has classified BaP as group 1 (carcinogenic to humans), BbF and Chr as group 2B (possibly carcinogenic to humans) (Lee et al., 2019). The Agency for Toxic Substances and Disease Registry has limited a maximum contamination level of BaP at 0.2 µg L^{-1} in drinking water (ASTR, 2009).

Chromatographic techniques have been developed to determine the PAHs compounds, especially high-performance liquid chromatography (HPLC). HPLC is useful due to its high selectivity and high resolution. Also, HPLC coupled with diode array detector (DAD) provides good detection sensitivity. However, the contamination of PAHs in the sample was typically presented at low concentration and may be interrupted from matrix interference. Therefore, sample preparation techniques are required for preconcentration and matrix elimination.

Solid phase extraction (SPE) is a popular sample preparation technique because it is simple to prepare, uses less solvent, and has a high extraction efficiency for a variety of target compounds (Critto et al., 2022; Wang et al., 2023; Xiao et al., 2023). However, to increase the efficiency of SPE for the extraction of target analyte, therefore, the development of SPE material is necessary. In this work, molybdenum disulfide@graphene oxide/polystyrene (MoS_2@GO/PS) was developed as a composite sorbent for the extraction of PAHs.

A composite sorbent with a lot of surface area, thermal stability, and strong - interaction is frequently prepared using GO (Fan et al., 2015). Nevertheless, GO can easily aggregate when strong bonds are present, which reduces the surface area or active area. To resolve the GO aggregation, MoS_2 is added as interval material. As a result, MoS_2@GO is an outstanding and prospective sorbent with a large specific surface area for the extraction of PAHs via the π- π interaction (W. Sun et al., 2021). Together with polystyrene (PS), it has a phenyl group and a single C-C bond in its structure. It is appropriate to employ as a sorbent for the extraction of PAHs because it can also interact with PAHs via π- π and hydrophobic interactions (Andrade et al., 2019).

This work thus focuses on the application of MoS_2@GO/PS composite sorbent for the extraction of Chr, BbF, and BaP coupled with the analysis using HPLC-DAD. To simplify the extraction process, the composited sorbent was coated on the surface of the glass slide. The extraction was performed by dipping this modified glass slide in the sample solution under the stirring.

Objective

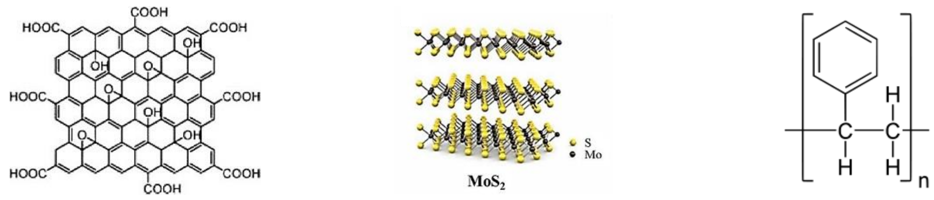
To develop a new extraction device with outstanding performance, a straightforward extraction process for the detection of polycyclic aromatic hydrocarbons in food samples.

Concept, theory, and conceptual framework

Graphene oxide (GO) (Fig. 1a) is a two dimensional (2D) layered material consisting of hydroxyl, epoxy, and carboxyl functional groups. Its large specific surface area, high adsorption efficiency, outstanding chemical and thermal stability, abundance of oxygen functional groups and π- π bond make it possible for GO to bind both polar and less polar analytes especially with PAHs. Nevertheless, the specific surface area, active sites may be reduced due to aggregation between the layers of GO. Molybdenum disulfide (MoS_2) (Fig. 1b), an interlayer material, is an option to prepare as an inserted material to address the issue of GO aggregation (Fan et al., 2015).

It has been observed that GO can effectively adsorb PAHs and is frequently utilized for adsorption and preparation as an adsorbent for sample preparation. MoS_2 can be used to improve the mechanical properties of material composites by being introduced into them (Liu et al., 2019; Lv et al., 2017). MoS_2 can be used to improve the mechanical properties of material composites by being introduced into them. As a result, applying MoS_2@GO as a composite sorbent for PAHs extraction is a good choice. However, to coat the material onto a solid substrate and make it as an extraction device, a good binder is needed.

From our previous work, solid polystyrene (PS) sorbent from recycled PS waste have been developed and used for the extraction of bisphenol A. The interaction was occurred via π- π and hydrophobic interaction (Myint Zaw et al., 2023). From PS structure shown in Fig. 1c, it can also interact with PAHs with π- π bonding of aromatic ring in structure together with hydrophobic interaction. Because it can serve as both a coating binder and an additional sorbent for PAH extraction, a PS solution made from recycled PS waste was employed.



(a) (b) (c)

Figure 1: The structure of (a) graphene oxide (GO) (Dreyer et al., 2010), (b) molybdenum disulfide (MoS_2) (Liu et al., 2019) and (c) polystyrene (PS).

The MoS_2@GO/PS composite material is intended to be coated on the glass slide and used as the extraction device by immersion in the sample solution. The extraction device has the benefits of being easy to use, convenient to prepare and durable as well as using less composite sorbent material (film coat).

Research Methods

1. Optimization of HPLC-DAD

Agilent 1200 series instruments were used for chromatographic separation (Agilent Technologies, California, USA) coupled with a reverse-phase VertiSep^{TM} UPS C18 column (150 mm 4.6 mm x 5 μm) (Vertical Chromatography Co., Ltd, Bangkok, Thailand) and a diode array detector. The flow rate and composition of the mobile phase, and the maximum detection wavelength must be tuned in the HPLC-DAD to achieve the best conditions for chromatographic separation. Good chromatographic separation, a high detection sensitivity, and a short analysis time were used to consider the optimum conditions.

2. Preparation of MoS_2@GO/PS coated on glass slide as an extraction device

The glass slide (7.60 x 1.25 cm) was etched using glass etching cream on both sides to create a rough surface that helps the composite coating adhere. The wasted PS foam was then weighed and dissolved in ethyl acetate to create a 10% PS solution. MoS_2@GO powder was weighed to achieve a concentration of 1.0% w/v in PS solution. After stirring the MoS_2@GO/PS composite solution, the etched glass slide was dipped for 2 seconds, 4 times. The coated glass slide was then dried in an oven at 60°C for 10 minutes (Fig. 2).

Figure 2: Schematic presentation of preparation of the MoS_2@GO/PS composite coated on etched glass slide.

3. Extraction and desorption procedures

The extraction device was immersed into 4.0 mL of a standard solution containing 100 μg L^{-1} of Chr, BbF, and BaP for the preliminary extraction operation. Stirring for 30 minutes at 300 rpm was used to extract the target analytes. Afterwards, using hexane as a desorption solvent, the desorption procedure was carried out. Desorption was achieved by dipping the extraction device from the previous stage into the 4.0 mL of hexane and stirring it there for 30 minutes at 300 rpm. The desorbed solution was then evaporated to dryness and re-dissolved in 1.0 mL of acetonitrile. The final analysis was performed under the optimum conditions using HPLC-DAD (Fig. 3).

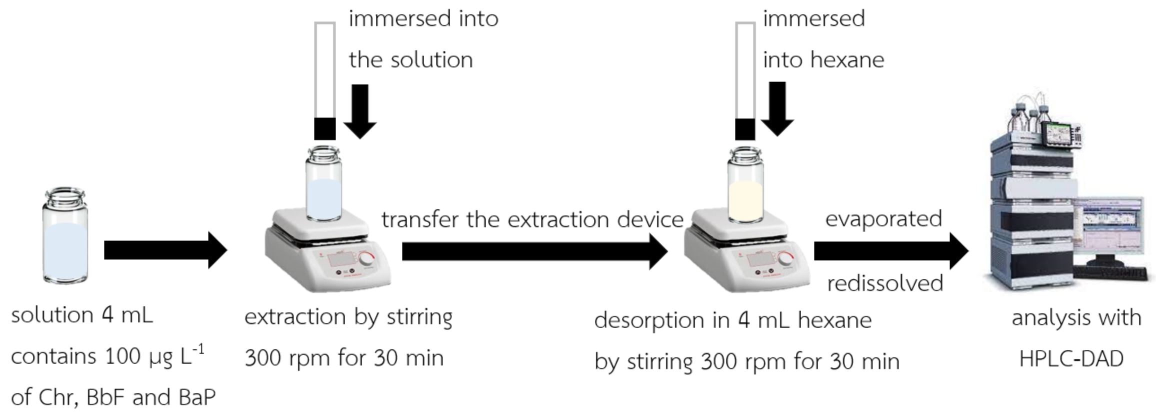


Figure 3: Schematic presentation of extraction and desorption procedures of the extraction device at 100 μg L^{-1} of Chr, BbF and BaP standard solution.

Results

1. Optimum conditions of HPLC-DAD

Table 1: Conditions for HPLC-DAD: flow rate, mobile phase composition, and detection wavelength

Parameters	Study range	Optimum condition
Flow rate ($mL\ min^{-1}$)	0.4, 0.6, 0.8, 1.0, 1.2	0.6
Mobile phase composition (%)	acetonitrile : water (95 : 5) acetonitrile (100) acetonitrile : methanol (95 : 5)	acetonitrile (100)
Detection wavelength (nm)	254, 256, 266, 270, 298	256 for BbF 266 for Chr and BaP

The optimum conditions for Chr, BbF and BaP chromatographic separation were summarized in Table 1. Under the optimum conditions linearity, limits of detection (LODs), and limits of quantitation (LOQs) were achieved in Table 2.

Table 2: Linearity, LODs, and LOQs of Chr, BbF, and BaP under the optimum condition of the HPLC-DAD

PAHs	Linearity	LODs ($\mu g\ L^{-1}$)	LOQs ($\mu g\ L^{-1}$)	R^2
Chr	2 $\mu g\ L^{-1}$ - 10 $mg\ L^{-1}$	1.881±0.004	6.270±0.013	1.0000
BbF	5 $\mu g\ L^{-1}$-100 $mg\ L^{-1}$	3.396±0.012	11.319±0.041	0.9999
BaP	10 $\mu g\ L^{-1}$-100 $mg\ L^{-1}$	5.695±0.029	18.983±0.095	0.9997

2. The surface morphology of the developed extraction device

The surface morphology of the glass slide is smooth and clear, as shown in Fig. 4a. The surface of the glass slide after the etching process provided a rough texture, thus increasing the surface area for sorbent coating, Fig. 4b. The SEM image of the MoS_2@GO/PS composite coated on the etched glass slide is observed as shown in Fig. 4c. The modified surface was fully covered with a high porosity composite material. Due to high porosity, it has a large quantity of active surfaces, resulting in a high adsorption capacity of PAHs via π- π and hydrophobic interactions.

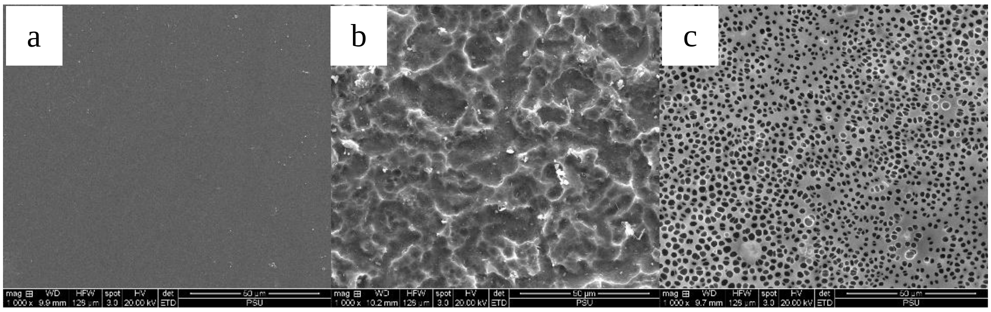
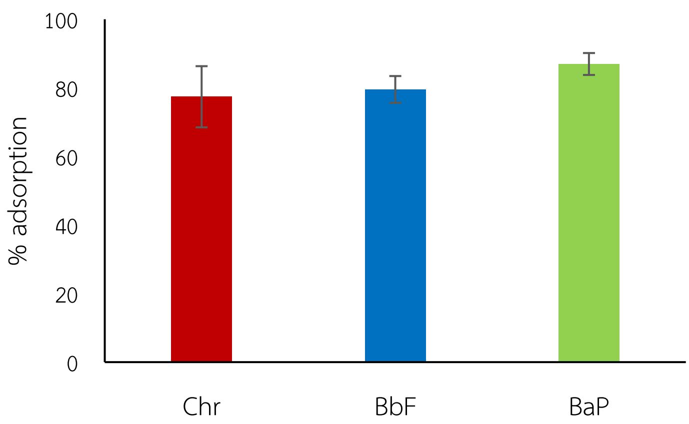


Figure 4: SEM images of the surface of glass slide (a), the surface of glass slide after etching (b), and the MoS_2@GO/PS composite coated on etched glass slide (c) at 50 μm, 1000x magnifications.

3. Extraction and desorption of 100 μg L^{-1} of standard solution

MoS_2@GO/PS coated on a glass slide was used as an extraction device, the preliminary test in Fig. 3 showed that the composite sorbent of MoS_2@GO/PS can adsorb Chr, BbF, and BaP (100 μg L^{-1}) with good adsorption efficiency for all three targets in the range of 77 to 87 % (Fig. 5a). However, their recoveries after desorption are still low ranging from 15 to 26 % indicating poor condition for the desorption of PAHs from the sorbent (Fig. 5b). Therefore, the optimization of the desorption condition must be performed to achieve better extraction-desorption efficiency. However, this is a promising result showing the possibility of using the MoS_2@GO/PS coated glass slide as a new extraction device for PAHs extraction.

(a)



(b)

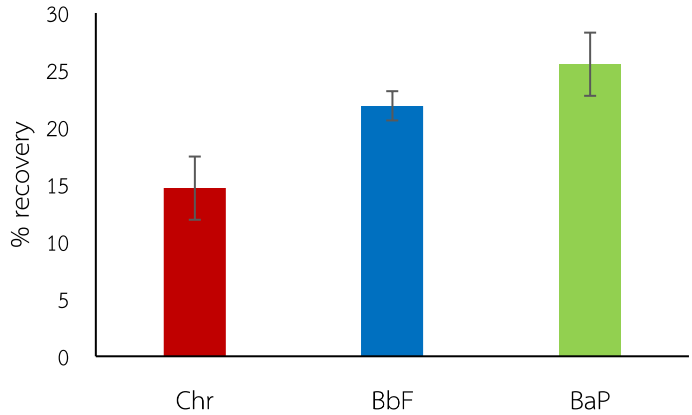


Figure 5: %Adsorption efficiency of the extraction device (a), and %recovery after desorption with hexane (b) of Chr, BbF and BaP (100 µg L^{-1}).

Conclusion

A MoS_2@GO/PS composite extraction sorbent coated on a glass slide has been created as a new extraction tool. According to preliminary results, the MoS_2@GO/PS composite can extract Chr, BbF, and BaP. However, the desorption efficiency is still moderate due to many parameters influencing the desorption efficiency still needing to be further investigated to achieve higher efficiency and ensure the precision and accuracy of Chr, BbF, and BaP determinations in food samples. Also, the analytical performance and the method validation are necessary to investigate.

Suggestion

The three PAHs were studied using this new methodology. We, however, anticipate that using this technology, other chemicals besides PAHs can also be extracted. The established method can also be used in a variety of contexts, including those involving food, water, and the environment.

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