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Introduction of a bio-waste/reduced graphene oxide nanocomposite as a new bio-sorbent for the solid-phase extraction of some polycyclic aromatic hydrocarbons

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Abstract

The current study introduces a high-performance green bio-waste nanocomposite made of chicken feet yellow membrane mixed with reduced graphene oxide (CFYM/rGO). The synthesized nanocomposite as a bio-sorbent of an SPE cartridge has been utilized for the extraction and pre-concentration of commonly seen PAHs in some food samples before their HPLC-UV examination. Wide linear ranges (LR, 0.01–184 µg L^{-1}), low detection limits (LOD, 0.01–0.25 ng L^{-1}), low quantification limit (LOQ, 0.06–0.83 ng L^{-1}), and adequate recoveries (92.30–102.30 %) were achieved under the optimum conditions. The employed raw materials are low-priced, easily accessible and a good alternative to the expensive commercially sorbents. Simple synthesis, a high-long service lifetime, and excellent extraction capability are some of the other advantages of the suggested sorbent. Therefore, the presented approach can be employed satisfactorily for the simultaneous determination of PAHs in complex matrixes.

Keywords: chicken feet yellow membrane; polycyclic aromatic hydrocarbons; reduced graphene oxide; solid-phase extraction.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the main groups of global pollutants that are generally formed during different imperfect thermal procedures and human activities [1]. PAHs can contaminate the foodstuffs from the air, soil, and water and also within the preparing, conservation, storage, and cooking procedures [2]. Most of the PAHs are carcinogenic and mutagenic and possess highly toxic impacts on the human organism. Therefore, the PAHs monitoring in foodstuffs and designing proper analytical techniques for their trace measurement are strongly recommended [3]. So far, various analytical techniques (including liquid-based and solid-based extraction methods) have been documented for the extraction and determination of PAHs from different samples. Among them, the solid-phase extraction (SPE) technique coupled with high-performance liquid chromatographic (HPLC) and gas chromatographic (GC) systems has evolved more widely employed in recent years [4].

SPE or liquid-solid extraction is a practical technique utilized in the isolation and separation of different micro-pollutants from liquid matrices [5]. SPE columns are usually packed with small quantities of various polar or non-polar commercially sorbents [6]. The Sophisticated preparation methods, high prices, no environment-friendliness, instability, incomplete adsorption and desorption, poor extraction capacity, and low selectivity are some of the main weaknesses of these sorbents [7]. Therefore, nowadays, natural materials and green synthetic chemicals have attracted great attention to conceivably overcome some of these disadvantages. So far, numerous raw materials

and bio-material wastes (bio-waste) have been used to prepare low-cost, eco-friendly, and high-capacity bio-sorbents [8]. These kinds of sorbents can utilize for the extraction and removal of organic and inorganic pollutants from the different matrices. However, large quantities of natural by-products and wastes are still produced yearly through industrial and household activities [9]. Many of these wasted such as chicken feet yellow membrane (CFYM) can be a good source for the production of new bio-sorbents. Moreover, adding a carbonaceous material (such as graphene oxide (GO) or reduced graphene oxide (rGO)) into the bio-sorbents matrix can improve their elasticity, conductivity, and adsorption characteristics [10].

This study reports a new SPE-sorbent of chicken feet yellow membrane bio-waste/reduced-graphene oxide (CFYM/rGO) nanocomposite for the first time. The proposed bio-sorbent coupled with HPLC-UV was successfully employed for the simultaneous extraction and measurement of some PAHs as the model analytes in different food samples.

Experimental

Chemicals and materials

Reduced graphene oxide (rGO), naphthalene, phenanthrene, anthracene, fluoranthene, and pyrene were purchased from Merck (Darmstadt, Germany). A stock solution of PAHs (100 mg L–1) was prepared in the HPLC-grade methanol and then the working solutions were prepared by proper dilution with deionized water. All the solutions were stored in a refrigerator below 4 C. HPLC grade acetonitrile and methanol were obtained from Carlo Erba (Valde Reuil, France). All Other chemicals and reagents with analytical grades were obtained from Merck (Darmstadt, Germany). The real samples were bought from Refah Chain Store (Tabriz, Iran). The CFYM wastes were supplied from a hen slaughterhouse (Tehran, Iran).

Instruments

A JASCO (Japan) high performance liquid chromatographic (HPLC) system equipped with a PU-1580 pump, a Rheodyne 7725i injector with a 20 µL manual six-port valve (Rheodyne, Cotati, CA, USA), a UV–1575 detector (JASCO-1575), HSS-2000 (JASCO) package, a LC-Net II/ADC interface, and a BORWIN software (version 1.50) was used for the main chromatographic analysis. The analytical separations were performed employing an ODS-3 column (250 mm X 4.6 mm ID, 5 lm (MZ-Analysentechnik, Germany) with an ODS-3 pre-column (10 mm X 4 mm ID, 5 µm). A Hamilton micro-syringe (25 µL, zero dead volume, Switzerland) was applied for injection of the samples into the septum of the HPLC valve. A Tescan electron microscope model mira3 (Brno-Czech Republic) for field emission scanning electron microscopy (FESEM), a pH meter (Metrohm-744, Switzerland), an IKA-RCT basic magnetic stirrer (Germany), a Beckman-GS6 centrifuge (USA), a Falc ultrasonic device (Italy), and an oven were also applied. The chromatographic investigations were accomplished in isocratic mode at the wavelength of 254 nm. All the analyses were performed at room temperature.

Preparation of CFYM powder

CFYM powder was prepared as explained in our previous work [11]. Briefly, the removed yellow thin skin of the chicken feet was washed with hot deionized water to remove all the contaminants and fatty wastes from the surface. The cleaned membranes were completely dried at 90°C for 24 h. Then, the dried membranes were ground and the obtained yellow powder was stored at laboratory temperature.

Preparation of CFYM/rGO

At first, 0.75 g CFYM powder was added to 10 mL thioglycolic acid solution. Then, the reaction mixture had been heated at 90 °C until the yellow powder was completely dissolved and a homogeneous gel appeared [12]. Then, the heater was switched off, 0.25 g rGO was dispersed into the mixture, and a sufficient concentrated gel was obtained. Then the achieved homogeneous gel was oven-dried at 60°C for 24 h. Next, the solid product was crushed into the fine particles. The obtained powder was sieved to get a powder of about 90 µm in size.

SPE-HPLC procedure

In the beginning, 50 mg of the synthesized bio-sorbent was filled into an empty polypropylene SPE-cartridge and equilibrated with 2 mL of acetone and 5 mL of deionized water. Then, 200 mL of a PAHs standard/sample solution was loaded into the cartridge (flow rate= 2 mL min^{-1}). In the following and after a washing step with deionized water (5 mL), the analyte was eluted utilizing 2 mL of acetone. To finish, 100 µL of the obtained solution was injected into an HPLC-UV system for the analysis of the target analytes and evaluation of the extraction efficiency.

Sample preparation

Wheat, smoked rice, tomato and potato were selected as the real samples to estimate the proposed technique efficiency. The samples were prepared exactly as the same as reported in our previous works [8,11].

Results and discussion

FESEM studies of the prepared bio-sorbent

The FESEM spectroscopy was employed for the examination of the surface morphology of the prepared sorbent. Figure 1A demonstrates that the CFYM gel material has a fairly homogeneous media containing irregular groups of fine spherical bumps without any clear structure and porosity. However, the addition of rGO into the CFYM gel was created a rough and porous media (Figure 1B). These conversions prove the positive influence of rGO on expanding the adsorbent porosity and improving its extraction capacity.

Experimental optimization

Accomplishing a satisfactory extraction and sample preparation procedure is usually dependent on optimizing different experimental factors affecting the efficiency of the method [13]. Therefore, in the present study, the mass of the sorbent, washing and elution solvents, volume of washing and elution solvents, the flow rate of loading, washing and elution steps, sample volume, pH of sample solution, and sample solution was optimized. The optimum amounts of these parameters were: sorbent mass: 50 mg, loading flow rate= 2 mL min^{-1}, sample volume: 200 mL, washing solution: deionized water, washing solution volume: 5 mL, flow rate of washing solvent: 1 mL min^{-1},

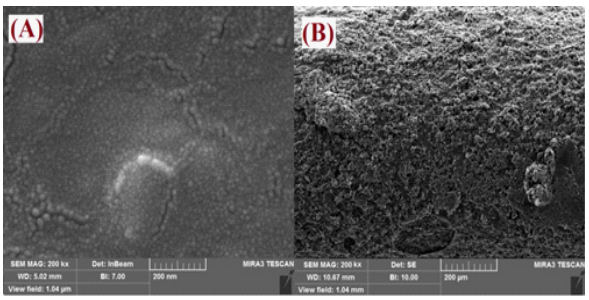

Figure 1: FESEM micrographs of the (A) CFYM gel and (B) CFYM/rGO nanocomposite.

elution solvent: acetone, elution solvent volume: 2 mL, elution flow rate= 1 mL min^{-1}, and sample pH=without control.

In addition, the highest chromatographic recovery and separation efficiency was obtained utilizing acetonitrile: deionized water (75:25 v/v) as the HPLC mobile phase.

Method validation

To examine the analytical performance of the developed SPE procedure, the figures of merit of the method were calculated. The wide linear ranges for the five target PAHs were located in the range of 0.01 to 184 µg L^{-1} with a determination coefficient of more than 0.99 in all cases. The limit of detection (LOD) and limit of quantification (LOQ) of the method (based on the four repeated analyses of blank samples) were in the range of 0.018–0.25 ng L^{-1} and 0.06–0.83 ng L^{-1}, respectively. The relative standard deviations (RSDs) of method repeatability and reproducibility were in the range of 2.10–3.70 % and 3.90–5.20 %, respectively (for eight-repeated analysis). In addition, the recycling and reusability study of the prepared SPE-column demonstrated that a single cartridge could be employed more than 50 cycles without any obvious decrease in its efficiency.

Real samples analysis

The suggested procedure was employed for the determination of the five selected PAHs in some real samples. The samples were spiked with 10 µg L^{-1} of the analytes and analyzed by the set SPE-HPLC procedure. Good recoveries (more than 92 %) in all cases point the high capacity of the proposed method for the routine analysis of PAHs in different food samples.

Conclusion

Due to the significance of the SPE technique in the sampling and sample preparation and also the necessity to produce new SPE sorbents with better attributes than commercial ones, a novel CFYM/rGO bio-sorbent was presented in this article for the first time. Cost-effective, safe and easy preparation procedure, affordable raw materials, environmental friendliness, high extraction capacity, and good precision are the major properties of the offered bio-sorbent. Good experimental results are promising to develop green high-efficiency technology for the simultaneous analysis of PAHs in different food samples.

Table 1: Determination of PAHs from some food samples with the developed SPE-HPLC technique (replicate= 3)

Analytes	Sample	Wheat		Smoked rice		Potato		Tomato	
	Added (µg L^{-1})	**Found (µg Kg^{-1})**	**RR[a] (%)**	**Found (µg Kg^{-1})**	**RR (%)**	**Found (µg Kg^{-1})**	**RR (%)**	**Found (µg Kg^{-1})**	**RR (%)**
Naphthalene	0.00	28.31	-	70.63	-	-	-	-	-
	10.00	38.19	98.80	80.73	101.00	9.20	92.00	9.40	94.00
Phenanthrene	0.00	-	-	50.18	-	17.63	-	-	-
	10.00	10.03	100.30	59.70	95.20	27.14	95.10	10.17	101.70
Anthracene	0.00	38.21	-	10.09	-	-	-	-	-
	10.00	47.46	92.50	20.00	99.10	10.23	102.30	10.02	100.20
Fluranthene	0.00	-	-	-	-	13.08	-	-	-
	10.00	9.95	99.50	10.03	100.30	22.19	102.30	9.23	92.30
Pyrene	0.00	-	-	31.17	-	-	-	-	-
	10.00	10.11	101.10	40.68	95.10	9.36	93.60	9.84	98.40

Declarations

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Competing interests: The author has declared no conflict of interest.

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