

# Evaluation of carbon foam as an adsorbent in stir-bar supported micro-solid-phase extraction coupled with gas chromatography–mass spectrometry for the determination of polyaromatic hydrocarbons in wastewater samples



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## ABSTRACT

In this work, a low-cost sorbent namely “carbon foam” was synthesized and calcined by a single step reaction. The mixture of precursors (sucrose and zinc nitrate) was heated under a nitrogen environment inside a furnace using a pre-defined temperature programming. The morphological features of the resulting material were revealed by field emission scanning electron microscopy. The material was further utilized for stir-bar supported membrane protected micro-solid-phase extraction (SB- $\mu$ -SPE) of polyaromatic hydrocarbons (PAHs) in water samples. The extracted analytes were quantified using gas chromatography–mass spectrometry. The performance of SB- $\mu$ -SPE was optimized by using a univariate approach. This method provided a good linear relationship for extraction of the PAHs, and  $R^2$  values ranged from 0.9986 to 0.9994. Detection limits were ranged from 0.29 to 8.4 ng/mL. Relative standard deviation values were calculated at various concentrations and ranged between 3.8 and 10.9%.

## 1. Introduction

Polyaromatic hydrocarbons (PAHs) represent a major class of hazardous organic pollutants, which consist of fused benzene rings in linear, angular or cluster arrangements. They are ubiquitous environmental pollutants and are therefore present in air, soil and water. They are released into environment from both natural and anthropogenic sources, and the major sources include incomplete combustion of fossil fuels, petrochemical cracking processes, degradation of plastics, dyes, lubricating oils and other products, and disposal and burning of coal and tar [1]. The major concern about their presence in environment arises from their carcinogenic and mutagenic properties that lead to serious health risks in human and other living organisms [2]. These health risks may include malfunction of immune system, kidneys, liver, and lungs; continuous exposure may also cause some skin related diseases [3].

The determination of PAHs in environmental matrices is highly challenging because of their low concentration levels and complexity of the matrices. In order to attain the required selectivity and sensitivity of analysis, it is necessary to develop the extraction and preconcentration methods of the selected PAHs before their analytical quantification. The

conventional methods for extraction of PAHs involve liquid–liquid extraction (LLE) and solid-phase extraction (SPE). Both classical methods have some serious disadvantages. For examples, LLE is tedious, time-consuming, and requires large volumes of organic solvents, which are not only expensive but also toxic in nature and cause many other environmental problems. On the other hand, SPE also consumes high volumes of toxic solvents [4]. Therefore, the research in the area of sample preparation is progressing toward the development of miniaturized extraction methods that can effectively utilize minimum amounts of hazardous solvents and accomplish the extractions in with desired precision and accuracy in short time durations. In this regard, some familiar methods include solid phase microextraction [5], dispersive liquid-liquid extraction [6], dispersive micro solid phase extraction [7], and many of their modified forms [8,9].

Membrane protected micro-solid-phase extraction ( $\mu$ -SPE) was introduced as an alternative to SPE in order to reduce the amount of required sorbent and hazardous eluents [10,11]. This method is based on packing of small amount of sorbent inside polypropylene (PP) bag via heat-sealing. This resultant device is efficiently utilized to extract the desired analytes from the sample solutions with varying matrix complexity. The one promising feature of  $\mu$ -SPE device is the protection

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of sorbent material from the complex sample matrix. It only allows target compounds to pass through the pores of the membrane and get adsorbed on the sorbent material.  $\mu$ -SPE and its modified versions are increasingly popular in extraction, and they are used for the extraction of environmental [12–18], food [19–23] and biological samples [23–28]. Recently, a new addition to the configuration of  $\mu$ -SPE device was introduced where a small stir bar was added to the  $\mu$ -SPE device and this new technique was named as stir-bar supported  $\mu$ -SPE (SB- $\mu$ -SPE). This makes the overall extraction process as more effective and efficient by solving the previously faced problems. Now, the weight of stir bar does not let the  $\mu$ -SPE device to float over the surface of sample solution and the device does not stick with the wall of vial during extraction process. The stir-bar supported  $\mu$ -SPE device keeps moving and rotating inside the sample matrix that not only enhances the exposure of target analytes toward the sorbent material but also provides an increase in effective surface area of sorbent [28,29].

In recent years, many important characteristics of carbon-based materials have taken the attention of scientific world for analytical extraction for a variety of analytes from varying sample matrix. Important carbon materials include graphite fiber, carbon nanotubes, pure and functionalized graphene, carbon soot and their modified forms. This prospective use of these materials is due to their enormously high surface areas and outstanding chemical, thermal, and mechanical stabilities. Moreover, they are capable of forming  $\pi$ - $\pi$  interactions with target compounds like PAHs [30]. In this regard, carbon foam is comparatively new material, and it is different from other forms of carbon due to its certain pore size. It has interconnected macropores (cells) and an open cell structure. Furthermore, carbon foam inherit features like light weight, thermally stable, hydrophobic and very high geometric surface area [31].

In this work, carbon foam was prepared and calcined using a single step method where commonly available precursor materials (sucrose and zinc nitrate) were reacted. The synthesized carbon foam was effectively utilized for extraction of five model PAHs in water samples. To the best of our knowledge, this is the first time that the carbon foam is being employed as a sorbent in SB- $\mu$ -SPE of PAHs in wastewater samples.

## 2. Experimental

### 2.1. Materials and chemicals

The PAHs listed in Table 1 were selected to evaluate the performance of proposed analytical method. The PAHs standard mixture solution was made from five individual solid analytical standards (attained from Sigma-Aldrich). The stock solution was prepared in methanol.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and crystalline sucrose was acquired from Sigma Aldrich. A polypropylene membrane with pore size of 0.2  $\mu\text{m}$ , 157  $\mu\text{m}$  thickness was bought from Membrana (Wuppertal, Germany). High purity solvents including methanol, toluene, *n*-hexane, *n*-pentane and carbon tetrachloride were obtained from Fisher (Loughborough, UK). To compare the extraction performance, Multi-wall carbon nanotubes (MWCNTs) with diameter: 20–30 nm, length 10–30  $\mu\text{m}$  and

**Table 1**

List of analytes, their elution time and  $m/z$  of selected ions for SIM mode. Quantifier ions are presented in bold letters.

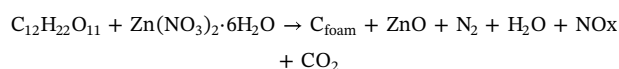
Analytes	Elution time (min)	$m/z$ of selected ions
Naphthalene	4.28	<b>128</b> , 102, 75
Biphenyl	5.22	<b>154</b> , 76, 128
Acenaphthene	5.82	<b>153</b> , 126, 76
Fluorene	6.41	<b>166</b> , 163, 139, 83
Phenanthrene	7.84	<b>178</b> , 89, 152

purity > 95% were purchased from Cheap Tubes Inc. (Cambridgeport, USA). Real samples were collected from a local wastewater treatment plant in Saudi Arabia.

### 2.2. Development of sorbent and its morphological characteristics

The previously reported methods [32,33] were modified to synthesize the carbon foam as a sorbent material. Briefly, sucrose and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were added to a crucible in ratio of 2:1 and heated in a tube furnace that was maintained under a constant supply of nitrogen by using a pre-defined temperature programming. The temperature was initially increased to 120 °C and held for 2 min, and then it was programmed to reach 180 °C and held for 5 min. Finally, it was increased to 1100 °C and held for 3 h. This procedure integrated synthesis and calcination in a single step, which had previously been carried out in two steps.

The following chemical equation represents the formation of carbon foam.



As the temperature increases, the mixture starts melting.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  being an important oxidizing agent, undergoes thermal decomposition which then cause it to simultaneously react with sucrose. This reaction with sucrose then leads to the production of different gases ( $\text{N}_2$ ,  $\text{NO}_x$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  vapors etc.). These gases while coming out of the melted reaction material blow the material and swell it up, resultantly making it foam like with high surface area. Unlike our previous work [33], a high temperature calcination for 3 h removed all the gases, Zn, and ZnO particles and resulted into a black, fluffy, and pure carbon foam.

The morphology of the synthesized material was studied by field emission scanning electron microscope (FE-SEM). Similar synthesis methods have reported the specific surface area of the carbon foam as high as 2340  $\text{m}^2/\text{g}$  [32].

### 2.3. Procedure and optimization of SB- $\mu$ -SPE

Fabrication of the SB- $\mu$ -SPE device is easy, cheap and simple [28]. In short, using the general pulse heat sealing, an envelope was made from PP sheet and a small stir-bar (7 mm  $\times$  2 mm) and 6 mg of the carbon foam material were packed inside. The overall estimated size of the SB- $\mu$ -SPE envelope was 2.2 cm  $\times$  1.0 cm. Since, carbon foam is a fluffy sorbent, it needs to be properly transferred to the bottom of the PP bag; presence of carbon particles under the heat-sealed area may lead to the opening of SB- $\mu$ -SPE device during the extraction process. Prior to extraction, the sorbent sealed in SB- $\mu$ -SPE device was aptly conditioned by ultrasonication in the presence of toluene for 3 min.

The SB- $\mu$ -SPE device was placed in a glass vial (25 mL) containing the sample solution (15 mL) and stirred at a rate of 800 rpm. After 40 min of extraction time, the SB- $\mu$ -SPE device was taken out with the help of tweezers, rinsed with water and dried using lint free tissue. Thereafter, analytes were desorbed by immersing SB- $\mu$ -SPE device in 300  $\mu\text{L}$  of desorption/elution solvent (*n*-pentane) in a desorption vial (1.5 mL), with the aid of sonication for 20 min. Subsequently, the desorption solvent containing the preconcentrated target analytes was injected into the injection port of GC-MS for quantification.

Ultrapure water spiked with 25 ng/mL of PAHs mixture was used to optimize the various parameters of extraction process. All experiments were carried out in triplicate. All parameters that affect the performance of the  $\mu$ -SPE, including type and quantity of sorbent, extraction and desorption times, desorption solvent and its volume, stirring speed, and salt addition were appropriately optimized by univariate approach.

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