CALCIUM ALGINATE CAGED MULTIWALLED CARBON NANOTUBES FOR THE PRE-CONCENTRATION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM ENVIRONMENTAL WATER SAMPLES

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THIS THESIS IS DEDICATED TO MY PARENTS, WIFE AND SIBLING FOR THEIR LOVE, ENDLESS SUPPORT AND ENCOURAGEMENT

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ABSTRACT

Monitoring of polycyclic aromatic hydrocarbons (PAHs) in water samples is important for human protection due to the carcinogenicity and mutagenicity of these compounds. A new technique termed dispersive micro solid phase extraction (D-µ-SPE) based on multiwalled carbon nanotubes (MWCNTs) caged in calcium alginate (Ca^{+2}-Alg) was developed and applied for efficient extraction of PAHs from environmental water samples. The prepared adsorbent (Ca-Alg-MWCNTs) was characterized by Fourier transform infrared spectroscopy, scanning electron microscopy and thermal gravimetry analysis. The hydrophilicity of the Ca^{+2}-Alg cage enhances the dispersibility of the adsorbent in water samples and the MWCNTs core facilitates separation of PAHs. The composite beads not only make full use of the good PAHs adsorption properties of alginate and MWCNTs, but also prevent MWCNTs from breaking off from the composites to cause secondary micro-pollution to water. The proposed D-µ-SPE method was applied successfully for the extraction of selected PAHs from environmental water samples. The D-µ-SPE technique provides reasonable extraction time (30 min) to extract trace levels of PAHs from 100 mL of water samples with 100 mg of adsorbent. The extracted PAHs were desorbed by 0.1 mL of ethyl acetate to give enrichment factor of 1000. Under the optimized conditions, the detection limits for fluorene, phenanthrene and fluoranthrene were 0.42 ng mL^{-1}, 0.3 ng mL^{-1} and 0.22 ng mL^{-1}, respectively. The recoveries of several spiked real water samples for PAHs were in the range of 71.2-104.2% with good relative standard deviations (1.2% - 7.2%), showing good reproducibility of the method. The potential benefits of the D-µ-SPE using Ca-Alg-MWCNTs include high extraction efficiency, short analysis time and convenient extraction procedure. Thus D-µ-SPE method based on Ca-Alg-MWCNTs is a suitable candidate for use as an alternative adsorbent in the simultaneous pre-concentration of PAHs from environmental water samples.

ABSTRAK

Pemantauan berterusan hidrokarbon aromatic polisiklik (PAH) sangat penting bagi memastikan perlindungan manusia daripada kesan karsinogen dan mutasi sebatian ini. Satu kaedah baru disebut sebagai fasa pengekstrakan pepejal secara serakan (D- μ-SPE) menggunakan tiub nanokarbon dinding berganda (MWCNTs) disalut dengan kalsium alginate telah dibangun dan digunakan sebagai pengekstrak berkesan PAH daripada air alam sekitar. Pencirian bahan penjerapan baru telah dianalisis menggunakan spektroskopi infra merah (FTIR), Imbasan Electron mikroskopi (SEM) dan termogravimetri. Ciri-ciri hidrofilik kurungan Ca^{+2}-Alg telah meningkatkan lagi daya serakan bahan penjerap dalam air, manakala teras tuib nano karbon dinding berganda berfungsi untuk penjerap PAH. Butiran komposit ini bukan sahaja menggunakan kelebihan MWCNTs untuk menyerap PAH, malah alginat telah berjaya menghalangnya daripada menjadi bahan pencemar sekunder kepada air. Kaedah D-uSPE telah berjaya diaplikasikan dalam pengekstrakan beberapa PAH terpilih dalam sampel air alam sekitar. D-uSPE memberikan masa pengekstrakan yang baik (30 minit) untuk mengekstrak PAH dalam 100 mL sampel air menggunakan 100 mg bahan penjerap. PAH telah dinyahjerap menggunakan 0.1 mL etil asetat bagi menghasilkan faktor pengkayaan 1000. Di bawah keadaan optimum, had pengesanan bagi fluorena, fenantrena dan fluorantena adalah masing-masing 0.42 ng mL^{-1}, 0.3 ng mL^{-1} dan 0.22 ng mL^{-1}. Pengembalian semula PAH dalam beberapa sampel air adalah dalam julat 71.2 - 104.2% dengan sisihan piawai relatif yang baik dalam julat 1.2% - 7.2% yang menunjukkan kebolehulangan yang baik. Justeru, kaedah D-μ-SPE menggunakan alginat-MWCNTs merupakan kaedah alternatif yang sesuai bagi pra-pemekatan PAH di dalam sampel air alam sekitar.

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LIST OF ABBREVIATIONS

Alg	-	Alginate
Ca-Alg-MWCNTs	-	Calcium alginate Multiwalled carbon nanotubes beads
AU	-	Arbitrary Unit
CA	-	Calcium alginate
DLLME	-	Dispersive liquid-liquid microextraction
DSPE	-	Dispersive solid phase extraction
D-μ-SPE	-	Dispersive micro-solid phase extraction
EF	-	Enrichment factor
EU	-	European Union
FID	-	Flame ionization detector
FTIR	-	Fourier transform infrared
FLA	-	Fluoranthene
FLU	-	Fluorene
GC	-	Gas chromatography
HF	-	Hollow fiber
HF-LPME	-	Hollow fiber liquid phase microextraction
HPLC	-	High performance liquid chromatography

IUPAC	-	International Union of Pure and Applied Chemistry
LOD	-	Limit of detection
LOQ	-	Limit of quantification
LPME	-	Liquid phase microextraction
MCM-41	-	Mobil composition of matter no. 41
MIP	-	Molecularly imprinted polymer
MRL	-	Maximum residue limit
MS	-	Mass spectrometry
MS/MS	-	Tandem mass spectrometry
MWCNTs	-	Multiwalled carbon nanotubes
NaCl	-	Sodium chloride
PAHs	-	Polycyclic aromatic hydrocarbons
PHE	-	Phenanthrene
R	-	Recovery
RSD	-	Relative standard deviation
SBSE	-	Stir bar sorptive extraction
SDME	-	Single drop microextraction
SEM	-	Scanning electron microscope
SFE	-	Supercritical fluid extraction
SPE	-	Solid phase extraction
SPME	-	Solid phase microextraction
SPMTE	-	Solid phase membrane tip extraction

USEPA	-	United States Environmental Protection Agency
UV	-	Ultraviolet
WHO	-	World Health Organization
µ-SPE	-	Micro solid phase extraction

LIST OF SYMBOLS

pKa	-	Acid dissociation constant
Å	-	Angstrom
cm^3g^{-1}	-	Centimeter cubed per gram
R^2	-	Coefficient of determination
°	-	Degree
°C	-	Degree celsius
eV	-	Electronvolt
g	-	Gram
$g\ mol^{-1}$	-	Gram per mol
h	-	Hour
m/z	-	Mass to charge ratio
m^2g^{-1}	-	Meter square per gram
$\mu g\ kg^{-1}$	-	Microgram per kilogram
$\mu g\ L^{-1}$	-	Microgram per liter
µL	-	Microliter
Mg	-	Milligram
mL	-	Milliliter
Mm	-	Millimeter

Min	-	Minute
ng	-	Nanogram
ng L^{-1}	-	Nanogram per liter
N_2	-	Nitrogen
n	-	Number of replicate
ppb	-	Part per billion
Log P	-	Partition coefficient
%	-	Percent
pg/g	-	Picogram per gram
rpm	-	Rotation per minute
s	-	Second
t_R	-	Retention time
v/v	-	Volume per volume
w/w	-	Weight per Weight

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polycyclic aromatic hydrocarbons (PAHs) are notorious environmental persistent pollutants with toxic, carcinogenic and mutagenic properties (Menezes and de Lourdes Cardeal, 2011). So far, over 100 PAHs have been known to occur naturally and 16 of them have been included in the list of priority pollutants (EPA, 1995). PAHs are non-polar and hydrophobic compounds with low water solubility. PAHs are considered as very significant environmental pollutants since they are restrict biodegrade due to their high stability and complex molecular structures (Anyakora and Nollet, 2007). PAHs are a set of organic compounds with two or more fused aromatic rings. They are mainly produced by human activities such as incomplete combustion of fossil fuels or carbon-containing organic substances, industrial processes, and domestic burning (Hii *et al.*, 2009). Therefore, PAHs can easily mobile into aquatic environments that lead to human risk. However, US Environmental Protection Agency (EPA) have set a maximum residual levels (MRLs) is 0.2 ng mL^{-1} for specified PAHs in drinking water (EPA, 2009)

Due to high toxicity of PAHs even at very low levels, development of methodologies for the monitoring of PAHs in environment is often necessary, thus one of the important aspects of environmental analytical chemistry (Li and Lee, 2001). The direct determination of PAHs by instrumental techniques is often limited due to the low concentration levels of the analytes and the presence of matrix interferences. Therefore, sample preparation is usually necessary to separate the

analytes from complex matrices or to pre-concentrate them in order to improve sensitivities and detection limits. Unfortunately, this step is considered the most time-consuming and error-prone step of the whole analytical procedure. Moreover, the classical sample pre-treatment techniques such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE) require high volumes of toxic reagents. In recent years, increased interest in the development of environmentally friendly analytical procedures according to the rules of green chemistry has been observed (Armenta *et al.*, 2008). The objectives of green analytical methods are replacing toxic reagents, minimizing waste in the laboratory and in consequence miniaturization of classical methods. Because of these trends, liquid-phase microextraction (LPME) and solid phase microextraction (SPME) have become the most valuable alternative techniques to classical LLE and SPE (Pena-Pereira *et al.*, 2010).

SPE has been extensively used for the pre-concentration of PAHs in environmental waters (Crozier *et al.*, 2001, Liang *et al.*, 2006, Ma *et al.*, 2010). In general, SPE is surface dependent processes since its kinetics depend directly on the contact surface between the analysts and the solid Adsorbent. This issue becomes critical when the amount of solid adsorbent reduced to the micro scale. In this context, dispersive-based procedures have gained importance as rapid and efficient sample treatment methodologies (Cruz-Vera *et al.*, 2011). In dispersive solid phase extraction (DSPE) and in dispersive micro solid-phase extraction (D-µ-SPE) the small amount of solid adsorbent promotes the immediate interaction between the analyst and adsorbent and shortens the time of sample preparation. After adsorption the analytes held in the solid adsorbent are eluted with suitable solvents (Fu *et al.*, 2012, Jiménez-Soto *et al.*, 2012).

The nature and properties of the solid adsorbent are of prime importance in D-µ-SPE. In practice, the main requirements for a solid adsorbent are: (a) fast and quantitative sorption and elution, (b) a high surface area and high capacity, and (c) high dispensability in liquid samples.

In this context, nanoparticles (NPs) seem to be perfect for use in D-µ-SPE. In general, NPs can be divided into two groups according to their chemical nature

carbon-based, such as fullerene (Hu *et al.*, 2008), carbon nanotubes (CNTs) (Bagheri *et al.*, 2011) and graphene (Luo *et al.*, 2011), and inorganic NPs (Wang and Campiglia, 2008) including magnetic NPs. Such NPs can be applied in organic (Ballesteros-Gómez and Rubio, 2009) and inorganic (Shin and Jang, 2007) analyses. Recently carbon based MWCNTs widely used as adsorbent for PAHs removal or pre-concentration (Wang *et al.*, 2007). Due to chemical structures of the PAHs are planar with benzene ring, which can form both hydrophobic interaction and strong π–π interaction with MWCNTs, the π–π bonding interaction is still strong enough to keep the analytes adsorbed onto them MWCNTs (Ding *et al.*, 2011).

However, widespread usage of MWCNTs will cause increased emissions to the aqueous environment and cause human health problem. Large numbers of *in vitro* and in *vivo* toxicology studies have shown that MWCNTs have an adverse effect on living organisms. They can enter into human pneumocytes and injure pulmonary functions (Davoren *et al.*, 2007, Firme and Bandaru, 2010), can be scavenged by the reticuloendothelial system from blood and accumulate in mouse liver and spleen and affect the immunity of spleen (Deng *et al.*, 2008, Deng *et al.*, 2009). Because of the poor degradability (Hyung *et al.*, 2007) and toxicity of MWCNTs they should be removed from drinking water as much as possible. While it is difficult to remove MWCNTs from water using conventional separation methods due to their micro-sized structures, this limitation may be the bottleneck to obstruct MWCNTs to be widely used as adsorbents in environmental protection in the future.

One effective method to resolve the second pollution caused by MWCNTs is to search for suitable supporters to immobilize MWCNTs for preparing macroscopic CNTs composites in order to make full use of the current micro-sized MWCNTs and its supporting the alginate is a potential candidate for MWCNTs. Alginate, the salt of alginic acid, has hydrophilicity, biocompatibility, nontoxicity, exceptional formability and is a linear chain structure of (1- 4) linked β-D-Mannuronic acid (M) and α-L-Guluronic acid (G) residues arranged in a block wise fashion (Bhat and Aminabhavi, 2006). Therefore, alginate has the excellent formability to support and fix MWCNTs. The composites not only make full use of the good PAHs adsorption

properties of MWCNTs and alginate, but also prevent micro-sized MWCNTs from breaking off the composites to cause second micro-pollution to water.

In this study, a novel application dispersive micro solid-phase extraction (D-µ-SPE) based on alginate multiwalled carbon nanotube beads (Ca-Alg-MWCNTs) as active adsorbent is presented. The dispersion of the beads has been deeply studied in order to maximize the efficiency of the extraction. Moreover, the whole procedures were optimized in order to achieve the highest recoveries. PAHs were selected as model compounds taking into account their applications to the analysis of water samples.

1.2 Statement of Problem

Conventional extraction methods for instance liquid-liquid extraction (LLE) and solid-phase extraction (SPE) involve large volumes of organic solvents and are time-consuming. To address these drawbacks, solid-phase microextraction (SPME) has been developed (Arthur and Pawliszyn, 1990). SPME uses no extraction solvent, but the lifetime of the fiber is limited and it is fragile. Recently, liquid phase micro extraction (LPME) has been introduced for sample preparation. It has been developed as many variants, such as single-drop microextraction (SDME) (Jeannot and Cantwell, 1996), hollow-fiber-protected liquid-phase micro extraction (HF-LPME) (Sanagi *et al.*, 2013), and stir bar micro extraction (SBME) (Kawaguchi *et al.*, 2006). All of these techniques use less organic solvents and have good sensitivity. However, they have long extraction times. To overcome these problems the D-µ-SPE based on Ca-Alg-WMCNTs was developed for analyse three of PAHs (fluorene, phenanthrene and fluoranthrene). The advantages of D-µ-SPE over conventional method are that D-µ-SPE allows the direct contact between the analytes/interferes with the adsorbent thank to the homogeneous dispersion of the solid in the liquid matrix sample. Although it was initially proposed to increase the method selectivity, it can also be used to increase the sensitivity by retaining the target analytes on the appropriate adsorbent material (Alcudia-León *et al.*, 2008), uses smaller quantities of adsorbents and solvents. Furthermore, is simple and use

inexpensive equipment. The advantages of using Ca-Alg-WMCNTs beads are their ease of handling and storage, greater precision during weighing and greater stiffness. Therefore, this technique is beneficial for many laboratories.

1.3 Objectives of the Study

This study was undertaken to investigate the efficiencies of Ca-Alg-MWCNTS composite beads, as D-µ-SPE Adsorbent for the extraction of polycyclic aromatic hydrocarbons from water samples the specific objectives of the study were undertaken:

- To synthesize of Ca-Alg-MWCNTs composite beads as PAHs adsorbent.
- To characterize synthesize alginate MWCNTs beads using FTIR, TGA, SEM.
- To develop and optimize effective parameters on dispersive micro solid-phase extraction (D-µ-SPE) method.
- To apply D-µ-SPE base on Ca-Alg-MWCNTs extraction method for real sample analysis prior to gas chromatography–flame ionization detector (GC-FID).

1.4 Scope of Study

For PAHs analysis, Ca-Alg-WMCNTs beads were synthesized using MWCNTs and sodium alginate. The amount of material was optimized according to their PAHs extraction efficiency. The optimized nanocomposite was characterized using FTIR, TGA and SEM. Effective parameters on extraction method (i.e. desorption solvent, extraction time, solvent volume, desorption time, the mass of adsorbent and sample volume) were optimized. The synthesized adsorbent was used as D-µ-SPE adsorbent for the monitoring of PAHs monitoring of environmental water samples. The extracted analytes were determined by GC-FID.

1.5 Outline of the Dissertation

This outline provides a brief description of the contents of each section of the dissertation. Chapter 2 presents the reader with a review of the literature relevant to the study undertaken. In Chapter 3 the methodology and experimental procedures of the study undertaken are detailed. Chapter 4 presents the results of experimental work carried out the analysis of the sample and discussion of the results. Finally, Chapter 5 covers the overall conclusions and future directions for further studies. This chapter compiles the overall results obtained, including the optimized conditions and the analytical performances of the developed methods. Future directions are presented and discussed for possible further study.

1.6 Significant of Study

The main concern associated with PAH is their capacity to react with environmentally available chemicals and as a consequence, the products of such reactions being inherently toxic to animals, plants and humans even at very low levels (Walgraeve *et al.*, 2010). On other hand, the structures of the PAHs are planar compounds, which can form both hydrophobic interaction and strong π–π bonding interaction with MWCNTs, the π–π bonding interaction is still strong enough to keep the analytes adsorbed onto MWCNTs (Ding *et al.*, 2011).

The toxicity and ubiquitousness of PAHs and CNTs within different terrestrial environments has been an increasing cause for concern amongst environmental scientists in the last decades, in particular regarding their transport within the water (Davoren *et al.*, 2007, Guiavarc'h *et al.*, 2010). In order to monitor PAHs in environmental water by using MWCNTs as adsorbent and prevent leaking MWCNTs into the water, D-μ-SPE was developed for the determination of trace level of three PAHs in water samples. Ca-Alg-MWCNTs were employed as D-μ-SPE adsorbent. The large surface area afforded by the MWCNTs and their π-π electrostatic interactions with the aromatic rings of the analytes facilitated strong adsorption between the two species. After extraction, analyte desorption was carried

out with a suitable organic solvent under ultrasonication. Due to the protection provided by the porous alginate cage (beads) in D-μ-SPE, no additional clean-up step was required. The results showed that the method could provide high extraction efficiency for the analysis of PAHs in water.

Due to the strong affinity between the adsorbent and PAHs and the large volume of sample possible, high enrichment factor, good LOD and satisfactory extraction efficiency are achieved. Thus, the proposed extraction method based on Ca-Alg-MWCNTs is a preferable candidate for alternative methods toward PAHs isolation.

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