OCTADECYLSILANE AND MULTIWALL CARBON NANOTUBES BASED CELLULOSE TRIACETATE MIXED MATRIX MEMBRANE FOR NEW MICROEXTRACTION APPROACHES

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DEDICATION

This thesis is dedicated specifically to my mom for her endless support and encouragement to complete my master.

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ABSTRACT

Widespread use of pharmaceuticals and herbicides leads to accumulation of their residues in surface water with detrimental effects and they have been recognized as emerging environmental pollutants. Therefore, it is important to develop a suitable sample pre-treatment method for the determination of these compounds in water. In this study, the fabrication of a mixed matrix membrane (MMM) using carbonaceous material immobilized in cellulose triacetate polymer matrix for microextraction is reported. The applicability and reliability of utilizing carbonaceous-based MMM in two different miniaturised microextraction designs, namely dynamic MMM tip extraction and automated flow-through MMM microextraction, are comprehensively demonstrated. To evaluate the performance of dynamic MMM tip extraction, the developed approach was applied for determination of five selected nonsteroidal anti-inflammatory drugs (NSAIDs) namely indoprofen, sulindac, naproxen, diclofenac, and ibuprofen in sewage water samples prior to ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) analysis. The established method showed good linear responses in the concentration range of 0.25–500 pg/mL with correlation coefficients (r) from 0.9988 to 0.9992. The limits of detections (LODs) were 0.08–0.40 pg/mL. The relative recoveries of NSAIDs from spiked water samples were in the range of 92–99% and exhibited excellent precision (relative standard deviations, RSDs ≤ 4.9%). The proposed analytical methodology allowed pre-concentration factors up to 250. Automated flow-through MMM microextraction approach was developed for the analysis of six chlorophenoxy acid herbicides, namely 2-(4-chlorophenoxy)acetic acid, 2-(3,4-dichlorophenoxy)acetic acid, 2-(2,4-dichlorophenoxy)acetic acid, 2-(4-chloro-2-methylphenoxy)acetic acid, 2-(2,4,5-trichlorophenoxy)acetic acid, and 4-(2,4-dichlorophenoxy)butanoic acid in the spiked sewage water sample prior to high performance liquid chromatography-ultraviolet detection (HPLC-UV) analysis. Under optimum conditions, the linearity of this method ranged from 50 - 1000 ng/mL with correlation coefficients (r) ≥ 0.9939, while LODs ranged from 15 - 20 ng/mL. The recoveries of the compounds in spiked sewage water samples were from 95% to 99% with RSDs ≤7.5% and enrichment factors of 19 to 55. The developed analytical methodology has the advantage of requiring less adsorbent (only 62.5 µg) and less organic reagent (60 µL of desorption solvent).

ABSTRAK

Penggunaan farmaseutikal dan herbisida secara meluas membawa kepada pengumpulan residu di dalam air yang membawa kesan memudaratkan dan ia dikenali sebagai bahan pencemar alam sekitar muncul. Oleh itu, pembangunan kaedah pra-rawatan sampel yang sesuai adalah penting untuk penentuan sebatian ini di dalam air. Dalam kajian ini, fabrikasi membran matriks bercampur (MMM) menggunakan bahan berkarbon yang tidak bergerak di dalam matrik polimer selulosa triasetat untuk pengekstrakan mikro dilaporkan. Kebolehlaksanaan dan kebolehpercayaan penggunaan MMM berasaskan karbon dalam dua reka bentuk pengekstrakan miniatur yang berbeza iaitu pengekstrakan muncung MMM dinamik dan pengekstrakan mikro MMM mengalir-lalu automatik diperlihatkan secara komprehensif. Untuk menilai prestasi pengekstrakan muncung MMM dinamik, pendekatan yang dibangunkan telah digunakan bagi penentuan lima jenis ubat anti-radang bukan steroid (NSAIDs) terpilih iaitu indoprofen, sulindac, naproxen, diclofenac, dan ibuprofen di dalam sampel air kumbahan sebelum analisis kromatografi cecair berprestasi ultra-spektromertri jisim seiring (UPLC-MS/MS). Kaedah yang dibangunkan telah menunjukkan gerak balas linear yang baik dalam julat kepekatan 0.25-500 pg/mL dengan pekali korelasi (r) dari 0.9988 hingga 0.9992. Had pengesanan (LOD) adalah 0.08 -0.40 pg/mL. Perolehan semula relatif NSAIDs daripada sampel air terpaku adalah dalam julat 92-99% dan menunjukkan kepersisan yang cemerlang (sisihan piawaian relatif, RSDs $\leq$ 4.9%). Kaedah analisis yang dicadangkan membolehkan faktor pra-pemekatan sehingga 250. Pendekatan pengekstrakan mikro MMM aliran automatik telah dibangunkan untuk menganalisis enam racun rumpai asid klorofenoksi, iaitu asid 2-4(-klorofenoksi)asetik, asid 2-(3,4-diklorofenoksi)asetik, asid 2-(2,4-diklorofenoksi)asetik, asid 2-(4-kloro-2-metilfenoksi)asetik, asid 2-(2,4,5-triklorofenoksi)asetik, dan asid 4-(2,4-diklorofenoksi)butanoik di dalam sampel air kumbahan terpaku sebelum analisis kromatografi cecair berprestasi tinggi dengan pengesanan ultra ungu (HPLC-UV). Dalam keadaan optimum, kelinearan kaedah ini berjulat dari 50 - 1000 ng/mL dengan pekali kolerasi (r) $\geq$ 0.9939, sementara LODs berjulat dari 15 - 20 ng/mL. Perolehan semula sebatian daripada sampel air kumbahan terpaku ialah dari 95% hingga 99% dengan RSDs $\leq$ 7.5% dan faktor pengkayaan sebanyak 19 hingga 55. Kaedah analisis yang dibangunkan mempunyai kelebihan iaitu memerlukan kurang bahan penjerap (62.5 μg sahaja) dan kurang reagen organik (60 μL pelarut penyaherapan).

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LIST OF ABBREVIATIONS

2,4,5-T	-	2-(2,4,5-trichlorophenoxy)acetic acid
2,4-D	-	2,4-dichlorophenoxyacetic acid
2,4-DB	-	4-(2,4-dichlorophenoxy)butanoic acid
2-PrOH	-	2-propanol
3,4-DA	-	3,4-dichlorophenoxyacetic acid
4-CPA	-	(4-chlorophenoxy)acetic acid
C_{18}	-	Polymeric octadecylsilane particles
CE	-	Capillary electrophoresis
CMS	-	Carbon molecular sieves
CNTs	-	Carbon nanotubes
COF	-	Covalent organic framework
CPAHs	-	Chlorophenoxy acid herbicides
CTA	-	Cellulose triacetate
DCM	-	Dichloromethane
DI	-	Ultrapure deionized
DI-SPME	-	Direct-immersion solid phase microextraction
DLLME	-	Dispersive liquid–liquid microextraction
DS	-	Desorption solution
DSPE	-	Dispersive solid phase extraction
E2	-	Beta-estradiol
EE2	-	Alpha-ethinylestradiol
EF	-	Enrichment factor
EME	-	Electromembrane microextractions
f- Mt	-	Modified montmorillonite
GC	-	Gas chromatography
GO	-	Graphene oxide
HCl	-	Hydrochloric acid
HF-LPME	-	Hollow fibre liquid phase microextraction
HLB	-	Hydrophilic lipophilic balance
HPLC-UV	-	High performance liquid chromatography ultraviolet

HS-SPME	-	Headspace solid phase microextraction
KH_2PO_4	-	Potassium dihydrogen phosphate
LDH/GO	-	Hydroxide-graphene oxide
LLE	-	Liquid-liquid extraction
LOD	-	Limit of detection
LOD	-	Limit of quantification
LPME	-	Liquid-phase microextraction
MCPA	-	2-(4-chloro-2-methylphenoxy)acetic acid
MeCN	-	Acetonitrile
MeOH	-	Methanol
MMM	-	Mixed matrix membrane
MMMTE	-	Mixed matrix membrane tip extraction
MOF	-	Metal organic framework
MP	-	Membrane phase
MRM	-	Multiple reaction monitoring
MWCNTs	-	Multiwall carbon nanotubes
NaCl	-	Sodium chloride
NaOH	-	Sodium hydroxide
NSAIDs	-	Nonsteroidal anti-inflammatory drugs
PAHs	-	Polyaromatic hydrocarbons
PDMS	-	Polymer polydimethyl siloxane
PEBAX	-	Poly ether-block-amide
PEI	-	Polyetherimide
PES	-	Polyethersulfone
PFS	-	Polysulfone
PFTE	-	Polytetrafluoroethylene
PI	-	Polyimide
PMMA	-	Poly(methyl methacrylate)
SDME	-	Single-drop microextraction
SIA	-	Sequential injection analysis
SLG	-	Single layer graphene
SLM	-	Supported liquid membrane
SPE	-	Solid phase extraction

SPME	-	Solid phase microextraction
SPMTE	-	Solid phase membrane tip extraction
SS	-	Sample solution
SWCNTs	-	Single-walled carbon nanotubes
TFME	-	Thin film microextraction
UPLC-MS/MS	-	Ultra-performance liquid chromatography-tandem mass
ZIF	-	Zeolitic imidazolate framework
β-CD	-	β-cyclodextrin
μ-SPE	-	Micro Solid Phase Extraction

LIST OF SYMBOLS

g/L	-	gram per liter
I.D	-	Internal diameter
m^2/g	-	Meter square per gram
mg	-	Miligram
min	-	Minutes
mL	-	Mililiter
mL/min	-	Mililiter per minute
mm	-	Milimeter
mol/L	-	Molarity
ng/L	-	nanogram per liter
ng/mL	-	nanogram per mililiter
nm	-	nanometer
pg/mL	-	picogram per mililiter
pKa	-	Acid dissociation constant
v/v	-	volume per volume
w/v	-	Weight per volume
w/w	-	weight per weight
wt %	-	weight percentage
µg	-	Microgram
µg/L	-	Microgram per liter
µg/mL	-	Microgram per mililiter
µL	-	Microliter
µL/min	-	Microliter per minute

CHAPTER 1

INTRODUCTION

1.1 Background Study

The development of fast and sensitive determination of trace levels of contaminants in environmental complex matrices remains challenging in analytical method [1]. Sample pre-treatment is a necessary step to quantify analytes in complex matrices and enrichment of the target analytes to final acceptor phase. However, sample preparation step is regarded time-consuming step and prone to significant experimental errors in analysis.

Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are well-known classical sample pre-treatment techniques for the extraction of target compounds that are generally preferred; however, limitations often stated are time-consuming, large organic waste is produced and the need for multistep procedures with high risk of analyte loss [2]. Recent developments in sample pre-treatment have largely been aimed at the need for very small volumes of the extracting phase or the possibility to become solventless as well as the ability to incorporate several processing steps such as sampling, detection, separation, pre-concentration, and even derivatization [3].

Over the past decade, membrane technologies have grown rapidly by developing materials that offer improvements in flux and selectivity. Various techniques of membrane-based microextraction [4] have been employed in the separation and detection of organic pollutants from different environmental matrices. For instance, the use of hollow fibre liquid phase microextraction (HF-LPME) [5], solid phase membrane tip extraction (SPMTE) [6], micro–solid phase extraction (μ-SPE) [7] and thin film microextraction (TFME) [8] are proven to be simplified in experimental setup and low cost as well as reduce organic solvent consumption. In

these published techniques, membrane-based extraction techniques is based on the use of a membrane as a selective thin barrier between miscible fluids for sample pre-treatment [9].

A mixed matrix membrane (MMM) is a type of membrane formed by the incorporation of inorganic materials in polymeric membranes that has attracted much attention recently. Several inorganic nanoparticles such as zeolites [10, 11], silica [12], carbon nanotubes (CNTs) [13, 14], metal organic frameworks (MOFs) [15, 16] and graphene [17, 18] have been introduced as fillers into various polymeric matrices to enhance the performance of MMM. This combination of MMM has resulted in high efficiency in extraction of pollutants due to better flexibility, sensitivity, selectivity, mechanical, thermal, and chemical stability being achieved. The use of MMM has been reported in gas separation applications [19-24] and liquid phase separations [25-33].

Herein, we demonstrated two MMM microextraction methods, namely dynamic MMM tip extraction (MMMTE) and automated flow-through MMM microextraction. Fabrication of MMM using carbonaceous material immobilized in cellulose triacetate polymer matrix for microextraction was developed. The applicability and reliability of utilizing carbonaceous-based MMM in two different miniaturised microextraction designs were comprehensively investigated, optimised and validated by determining the presence of the selected nonsteroidal anti-inflammatory drugs (NSAIDs) and chlorophenoxy acid herbicides (CPAHs) in real environmental water samples.

1.2 Problem Statement

The contamination of pharmaceuticals and herbicides in environment has now become critical issues due to their continuous release into the environment. Diclofenac, together with 17 alpha-ethinylestradiol (EE2) and 17 beta-estradiol (E2) is listed as new priority restricted substance to be scrutinized in Europe in surface water. Adding to that, several CPAHs have been included in the European list of

priority pollutants. Moreover, the U.S. Environmental Protection Agency (USEPA) has set a maximum tolerated contaminant level for drinking water of 2,4-dichlorophenoxyacetic acid (2,4-D) at 70 μg/L. These organic pollutants pose significant toxicological risk to humans and marine life. However, direct analysis of samples of these pollutants is difficult because they are in complex matrices and in very low concentrations [34]. Moreover, sample extraction and clean-up procedures greatly influence the accuracy and precision of the analysis. For all these reasons, sample preparation technique is crucial for an efficient, reliable, and accurate data analysis.

Although classical extraction methods such as liquid-liquid extraction (LLE) and solid phase extraction (SPE) are generally favoured, however these extraction techniques are time-consuming and require large amounts of toxic and expensive solvents. Nowadays, miniaturized techniques have been utilized to improve extraction selectivity, less consumption of organic solvent, low-cost, and minimize the sample pre-treatment steps. However, these existing procedures, have several disadvantages in terms of cost of analysis, lower enrichment power and possible analyte carryover effects. In this present study, new miniaturised sample preparation techniques based on MMM are demonstrated for a smaller sample size, less consumption of organic solvent and more cost-effective sample pre-treatment method.

1.3 Objectives of Study

The aim of this research is to develop miniaturised microextraction techniques using the MMM microextraction technique for the analysis of NSAIDs and CPAHs in environmental water matrices. To achieve this aim, the following objectives have been planned:

- To develop and validate the dynamic MMMTE coupled with ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) for the determination of NSAIDs in environmental water matrices.

- To develop and validate the automated flow-through MMM microextraction method coupled with high performance liquid chromatography ultraviolet detection (HPLC-UV) for the determination of CPAHs in environmental water matrices.

1.4 Scope of Study

In this study, an advanced method to fabricate MMM in a commercially available pipette tip is demonstrated. This new sample preparation method designated as dynamic MMMTE was established for the analysis of NSAIDs in water samples using polymeric octadecylsilane (C_{18}) particles. Operational parameters of MMMTE such as effect of sample pH, salting-out, dynamic extraction cycle, type of solvent and desorption time were investigated. The developed dynamic MMMTE approach was coupled with UPLC-MS/MS for trace level detection of pollutants present in the environmental water samples.

On the other hand, an automated analyte pre-concentration system was developed for the analysis of CPAHs in sewage water samples using a multiwall carbon nanotubes (MWCNTs) immobilized mixed matrix membrane. The analyte adsorption and desorption processes were performed in a fully automated mode by making use of a sequential injection analysis (SIA) manifold based on a reversible syringe pump fitted with a selection valve to perform liquid handling. Several extraction conditions were comprehensively optimized including sample pH, ionic strength, sample volume, extraction time, desorption solvent and desorption time. The enriched extracts obtained from the automated approach were subsequently analysed by the HPLC-UV technique for separation and quantification.

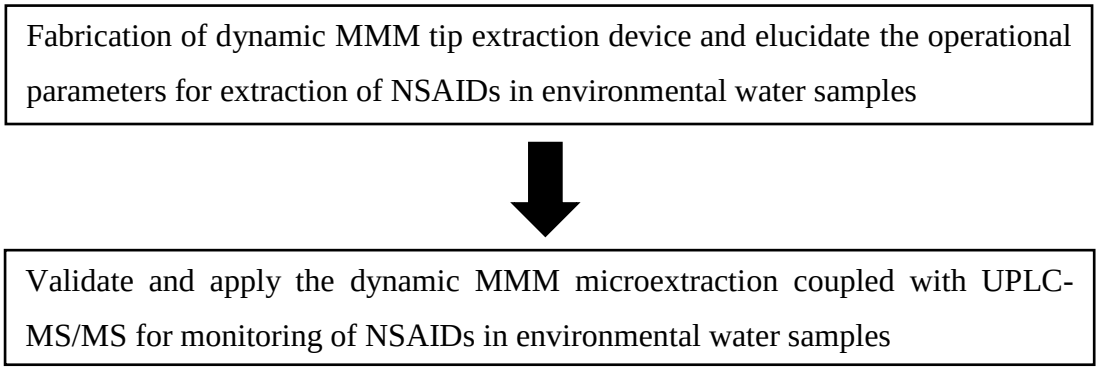
1.5 Significance of Research

This research is significant to the development of the sample pre-treatment step in the MMM microextraction technique. This procedure has been developed to speed up and simplify the microextraction method, smaller initial sample volumes is required, high sensitivity and selectivity is achieved. It also minimizes organic solvent consumption and improve the efficiency of extraction of organic pollutants. This study has focused on the wider range of nanomaterial adsorbents based on MMM application in various sizes and shapes to tailor different experimental designs and sample size requirements for the analysis of NSAIDs and CPAHs in environmental analysis. Besides that, through this work determination of various organic pollutants in complex, matrices can be regarded as green analytical chemistry method due to consumption of microliters organic solvent, simplicity of the microextraction setup and cost effectiveness.

1.6 Flowchart/Scheme of the Research

In Chapter 1, a detailed account of the research background, problem statement, objective, scope, and significance of the study. In Chapter 2 provides the literature review on conventional extraction and microextraction techniques, mixed matrix membrane and model analytes in this study.

In Chapter 3, the experimental methodology and application of the dynamic mixed matrix membrane tip extraction for the determination of five selected NSAIDs in environmental water samples.



In Chapter 4, the experimental methodology and application of automated flow through cell MMM microextraction for the determination of six selected CPAHs in environmental water samples.

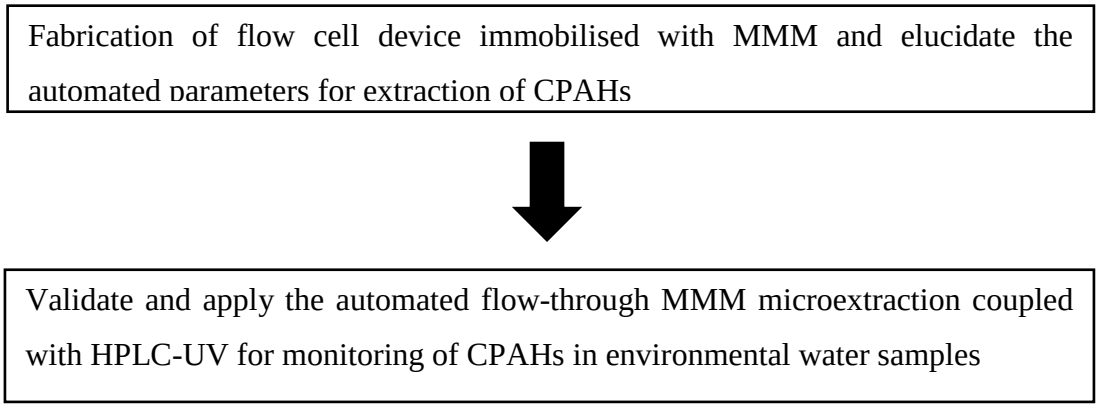


Figure 1.1 Flowchart of research work for MMM microextraction

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