

**FABRICATION OF THREE-DIMENSIONAL PRINTED FLOW CELL FOR
ELECTROMEMBRANE EXTRACTION OF PARAQUAT AND DIQUAT**

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ELECTROMEMBRANE EXTRACTION OF PARAQUAT AND DIQUAT

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To my beloved family & friends

*To my beloved family especially my parents and siblings and also my friends that
always give support. I would like to share this happiness with all of you and
I just want you to know that every one of you will be remembered
for the rest of my life.*

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ABSTRACT

In this study, electro-membrane extraction (EME) across a hollow polymer inclusion membrane (HPIM) was performed using a new three-dimensional printed flow-cell equipped with a bubbleless electrode. The sample solutions were introduced continuously into the flow cell during extraction, while the acceptor solution remained stagnant. The HPIM consisted of cellulose acetate (CTA) as the base polymer, tri-(2-ethylhexyl)-phosphate (TEHP) acting as the plasticiser and di-(2-ethylhexyl)-phosphoric acid (D2EHPA) as the carrier. The use of a proposed bubbleless electrode in the experimental setup allowed the use of ultra-high voltage in EME (up to 3000 V) without any interruption due to bubble formation; this cannot be performed with a conventional EME setup. Operation parameters, such as the sample flow rate and sample volume, were comprehensively investigated. Two cationic herbicides were selected as model analytes: paraquat and diquat. These analytes were extracted selectively from the flowing sample stream across the HPIM, and then enriched in 20 μL of the acceptor solution inside the lumen of the hollow membrane. The extracted solutions were then collected using a micro-syringe and subsequently injected into a capillary electrophoresis coupled with UV spectrophotometric detector (CE-UV) for separation and quantification. Under the optimised conditions, the recovery of both paraquat and diquat was in the range of 96.31–104.96% when spiked into the river water sample. The limits of detection of the method for both herbicides were in the range of 0.2–0.3 $\mu\text{g/L}$ with relative standards deviation below 8.3%. The proposed approach was successfully applied to monitor the herbicide content present in the river water sample at sub-ppb level.

ABSTRAK

Dalam kajian ini, pengekstrakan elektro-membran (EME) merentasi rongga kemasukan membran polimer (HPIM) telah dilakukan dengan menggunakan sel aliran yang telah dicetak secara tiga-dimensi yang dilengkapi dengan elektrod tanpa buih. Semasa pengekstrakan, larutan sampel telah diperkenalkan secara berterusan ke dalam sel aliran, manakala larutan penerima kekal bertakung. HPIM terdiri daripada selulosa asetat (CTA) sebagai asas polimer, Tri-(2-ethylhexyl)-phosphate (TEHP) yang bertindak sebagai pemplastik dan di-(2-ethylhexyl) phosphoric acid (D2EHPA) sebagai pengangkut. Penggunaan elektrod tanpa buih dalam proses eksperimen membenarkan penggunaan voltan yang tinggi dalam EME (sehingga 3000 V) tanpa apa-apa gangguan disebabkan oleh pembentukan buih; ini tidak boleh dilakukan dalam proses EME konvensional. Parameter operasi, seperti kadar aliran sampel dan isipadu sampel, telah disiasat secara komprehensif. Dua racun herba kationik telah dipilih sebagai analite contoh iaitu: paraquat dan diquat. Kedua-dua analite ini diekstrak daripada aliran sampel yang mengalir di seluruh HPIM, dan kemudian dikumpulkan di dalam larutan penerima 20 μ L yang berada di dalam lumen membran berongga. Larutan yang telah diekstrak kemudiannya, diambil menggunakan jarum mikro dan dimasukkan didalam vial untuk dianalisis ke dalam kapilari elektroforesis ditambah dengan pengesanan spektrofotometri UV (CE-UV) untuk pemisahan dan kuantifikasi. Dengan menggunakan nilai yang telah dioptimumkan, kadar pemulihan kedua-dua paraquat dan diquat adalah di dalam lingkungan 96.31-104.96% apabila menggunakan sampel air sungai yang telah ditambah kedua-dua analite. Had pengesanan bagi kaedah ini untuk kedua-dua racun herba adalah dalam lingkungan 0.2-0.3 μ g/L dengan standard relatif sisihan bawah (RSD) 8.3%. Pendekatan yang disyorkan telah berjaya digunakan untuk memantau kandungan racun herba yang terdapat di dalam sampel air sungai di peringkat sub-ppb.

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LIST OF ABBREVIATIONS

3D	-	Three Dimesional
μL	-	Microliter
μm	-	Micrometer
ABC	-	Acrylonitrile Butadiene Styrene
Am	-	Additive Manufacturing
APS	-	Ammonium Persulfate
BLM	-	Bulk Liquid Membrane
BE	-	Bubbleless Electrode
CAD	-	Computer Aided Design
CE	-	Capillary Electrophoresis
CEC	-	Capillary Electrochromatography
CGE	-	Capillary Gel Electrophoresis
CIEF	-	Capillary Isoelectric Focusing
CITP	-	Capillary Isotachophoresis
CTA	-	Cellulose Acetate
CZE	-	Capillary Zone Electrophoresis
D2EHPA	-	di-(2-ethylhexyl)phosphoric acid
DBP	-	dibutyl Phosphate
DC	-	Direct current
DCM	-	Dichloromethane
DEHA	-	Bis(2-ethylhexyl)adipate
DI	-	Deionized
DLP	-	Digital Light Processing
DMT	-	DMT Corporation
DQ	-	Diquat
EBM	-	Electronic Beam Melting
EE	-	Electroextraction
ELMs	-	Emulsion Liquid Membrane

EME	-	Electromembrane Extraction
EPA	-	Environment Protection Agency
EOF	-	Electroosmotic Flow
FDM	-	Fused Deposition Modelling
HF	-	Hollow Fibre
HIPS	-	High Impact Polystyrene
HPIM	-	Hollow Polymer Inclusion Membrane
HPLC	-	High Performance Liquid Chromatography
i.d	-	internal diameter
KCl	-	Potassium Chloride
LLE	-	Liquid-Liquid Extraction
LPME	-	Liquid Phase Microextraction
LOD	-	Limit of Detection
LOM	-	Laminated Object Manufacturing
LOQ	-	Limit of Quantification
MAPS	-	Methacryloxy propyl trimethoxysilane
mbar	-	Milibar
MEKC	-	Micellar Electrokinetic capillary Chromatography
MIT	-	Massachusetts Institutes of Technology
mL	-	miliLitre
mL/min	-	miliLitre per minute
mm	-	millimeter
mM	-	miliMolar
MRL	-	Maximum Residual Limit
NaCl	-	Sodium Chloride
NaOH	-	Sodium Hydroxide
ng/mL	-	nanogram per miliLitre
NPPE	-	2-nitrophenyl phenyl ether
NPOE	-	Nitrophenyl octylether
PC	-	Polycarbonate
PET	-	Polyethylene Terephthalate
PIM	-	Polymer Inclusion Membrane
PLA	-	Polyacetic Acid

PQ	-	Paraquat
PTFE	-	Polytetrafluoroethylene
PVA	-	Polyvinyl Alcohol
PVC	-	Poly(vinylchloride)
RSD	-	Relative Standard Deviation
SFF	-	Solid freeform technology
SLA	-	Sterelithography
SLM	-	Supported Liquid Membrane
SLS	-	Selective Laser Sintering
STL	-	Standard Tessellation Language
TEHP	-	Tris(2ethylhexyl)phosphate
TEMED	-	Trimethyl-ethylenediamine
UV	-	Ultra Violet

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The development of three-dimensional (3D) technology has become popular over the past decade, and even though the first 3D printing was actually introduced in 1983 by Charles W. Hull, this technology is still being used today (Gross *et al.*, 2014). 3D market values are expected to rise each year and reach \$16.2 billion by 2018; thus, many scientists are competing to use this technology. So nowadays, additive manufacturing technology, also known as 3D technology, has been applied in several fields including medical, manufacturing, and aerospace industries, and even food printing (Mardani *et al.*, 2016; Oskui *et al.*, 2016).

This technology claims to be simple and with a low cost, and the structure can be easily designed and reproduced. The advantage of this technology is that it allows the designer to design devices with precision, including complex geometries and dimensions. Unfortunately, in chemical research and development, only a few applications of 3D devices are reported (Mardani *et al.*, 2016) for example printed-in catalysts and components in electrochemical and spectroscopy analysis (Symes *et al.*, 2012), designing a 3D continuous-flow for organic synthesis (Dragone *et al.*, 2013) and designing 3D reactionware for chemical synthesis (Kitson *et al.*, 2016).

Electromembrane extraction (EME) based on the use of a polymer inclusion membrane (PIM) has been developed in order to overcome the limitations of supported liquid membranes (SLM), which are rather unstable upon the extraction process (Mamat & See, 2015). The membranes consist of a base polymer such as

cellulose acetate (CTA) and poly(vinyl chloride) (PVC), plasticiser, and carriers that form a thin, flexible and strong film. This results in a self-supporting membrane that can be used to separate the analyte of interest with better stability when compared to SLMs (Annane *et al.*, 2015).

Developments in EME-PIM continue to be made by various researchers. Until recently, most of the operation conditions were quite similar, using a static extraction condition; there was one paper about using a continuous flow-through of EME-PIM. The sample solution containing the analyte was continuously introduced into the system while the acceptor, which was inside the PIM, remained static. The continuous flow of EME-PIM claimed to give higher enrichment factors and save more time, as reported by See and associates in 2013. However, the setup of the experiment required many steps that were both complicated to follow and costly which need to proper handling of electrodes and also to make sure the flow of the process were in the correct order to avoid any accident happened when voltage was applied (H. H. See, Stratz, & Hauser, 2013)

EME basically uses electric forces to drive movement of the analyte ions, thus a stable voltage must be applied during the extraction process. However, the usage of voltage can cause some bubble formation when used in a high range. To overcome this problem, the bubbleless electrode invented by Gu Congying and colleagues was used. The polyacrylamide gel inside the capillary will prevent the migration of bubbles that form from the electrolysis process due to the fluidic system. Hence, the extraction system will be more stable throughout the process (Gu *et al.*, 2012).

Herbicides used in the agricultural sector to kill unwanted weeds have damaged the ecosystem of agricultural fields. Herbicides eventually can increase the production of food as weed control boosts plant productivity. Herbicides can be absorbed into the environment in various ways such as washing and leaching into the surface and ground waters, which slowly accumulate and lead to a higher toxic level in the environment. From this, awareness about this has spread and has led to the development of methods to monitor the herbicides in the environment as well as to

establish a permissible limit for any individual herbicides (Chang *et al.*, 2016). For this study, paraquat and diquat have been chosen as the model analytes. Both of them have the same dangerous effects which are toxic to human, animal and also environment.

In this research, capillary electrophoresis (CE) has been chosen with its advantages of higher separation, a lower solvent used, smaller sample size, shorter analysis time and lower cost. Several other methods such as HPLC-UV and UPLC-MS/MS have also been reported but when compared with CE, they are more expensive and have a complicated procedure to follow which need steps to stabilize the systems (Pizzutti *et al.*, 2016). The purpose of using bubbleless electrodes in the EME system was to avoid the formation of bubbles during the extraction process due to the high voltage used.

Further investigations have been done regarding the parameters of the operation conditions of flow rate and volume of sample used. By the end of the study, a validation of the methods was carried out by applying optimized conditions to river water. The linearity, recovery, limit of detection and limit of quantification have also been investigated. Thus, the combination of 3D printing technology together with EME-HPIM equipped with a bubbleless electrode can be as a new approach in micro-extraction methods.

1.2 Problem Statement

An overflowing growth of weeds forces crops to compete for sunlight and nutrients and leads to significant decreases in crop production. Hence, the agricultural sector in many countries depends mostly on the application of herbicides to easily control weed growth. However, in large-scale applications in the agricultural sector, this may lead to the contamination of the atmosphere, food, soil and water systems.

Herbicide contamination may present an important risk factor as a result of the toxicity or carcinogenic nature of some of these compounds. Normally, herbicides that are present in environmental waters are at sub-ppb levels and not at a significant level for detection by a common sample preparation and analytical instrumentation. Therefore, there is a need for an effective detection method for these compounds followed by an improvement in the sensitivity for these herbicides. In conjunction with that, there is a need for a new analytical approach that can both clean up and enrich the trace amount of analytes present in the water to detectable levels and at the same time be one of the solutions.

From the previous study, the preconcentration of analytes had been successfully reported using electromembrane extraction across hollow polymer inclusion membrane. However, only limited sample volume can be treated at one time with the proposed setup and tend to unstable when high voltage was used. In addition, using continuous-flow of sample volume also had reported before to increase the usage of sample volume. Unfortunately, the setup was complicated and costly. Therefore, in the present work, the application of this 3D technology for EME using HPIM can be a new approach. Using a printed 3D flow cell can be simpler, save more time and have more cost-savings than the other approaches. The main focus is to develop a suitable 3D flow cell design for EME-PIM equipped with a bubbleless electrode to gain a better understanding of the extraction parameter and for its application to river water.

1.3 Objectives of the Study

The objectives of this study are:

- i. To design a new 3D printed flow cell equipped with bubbleless electrodes for the purpose of a continuous flow EME-HPIM approach.
- ii. To study the operation parameters of the proposed continuous flow EME-HPIM approach using paraquat and diquat as model analytes.

- iii. To apply the developed approach to monitoring the paraquat and diquat content present in river water samples at a trace level.

1.4 Scope of the Research

This study involves the development of a 3D flow cell for the determination of the herbicides paraquat and diquat through EME across HPIM incorporated with bubbleless electrodes. The use of a 3D printed flow cell in EME-HPIM is a new approach in micro-extraction methods. The process to produce the 3D printed flow cell is the stereolithography (SLA) which is one of the processes in 3D printing technology. A preliminary study has been done to the 3D design to find a suitable design to be used together with EME-HPIM methods. After obtaining a suitable design, further investigation for operation parameters flow rate of the sample and volume of sample was done. The optimum condition was then applied to river water to monitor the content of herbicides that were present. Throughout this study, CE with a UV detector was chosen as the separation analysis medium.

1.5 Significance of the Research

Herbicides, including paraquat and diquat, may dissipate from the soil through chemical degradation, microbial degradation, leaching, volatilisation, uptake by plants and decomposition. In addition, their physical and chemical decomposition, toxicity and herbicidal effects on the environment and health have been studied in detail. Therefore, an investigation into the new approach of EME-HPIM incorporated with a bubbleless electrode is required to determine and monitor the presence of these herbicides in the environment, especially in river water samples.

This study explores the combination of the modern 3D printing technology with an analytical study, which determines the paraquat and diquat in the environmental sample at sub-ppb level. Using the 3D printing approach, this study may become a new method of extraction in analytical methods. This new EME-

HPIM approach is also expected to fulfill the requirement with respect to maximum residual limit (MRL) of herbicides present in the environmental waters which at 0.1µg/L according to European Union.

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