

**UNIVERSITI TEKNOLOGI MARA**

**SYNTHESIS AND  
CHARACTERIZATION OF  
POLYANILINE-CHITOSAN  
COMPOSITE AND ITS  
APPLICATION AS  
ELECTROCHEMICAL SENSOR FOR  
PERFLUOROCTANOIC ACID**

**NUR FARAHIN BINTI SUHAIMI**

Thesis submitted in fulfillment  
of the requirements for the degree of  
**Master of Science**  
**(Chemistry)**

**Faculty of Applied Sciences**

**June 2023**

## ABSTRACT

The overwhelming utilisation of perfluorooctanoic acid (PFOA) for household and industrial applications has posed a severe risk to human health and environmental pollution. PFOA is an anthropogenic contaminant under the Per- or polyfluoroalkyl substances (PFASs) family and is classified as a Persistent Organic Pollutant (POP) due to its long half-life degradation in the environment and toxic properties. In view of this, conducting polymers (CPs) and natural biopolymer have been often used in the development of electrochemical sensors. In this study, the pure Chitosan was extracted from crab shells using three simple steps which is deproteinization, demineralization and deacetylation. For polyaniline (PANI) and polyaniline-Chitosan (PANI-Chitosan) composite were synthesized using in-situ chemical oxidative polymerization technique by using ammonium persulfate as initiator. Therefore, PANI-Chitosan composite were synthesized with three different weight ratios of Chitosan such as PANI-Chitosan 1:0.5, PANI-Chitosan 1:1, and PANI-Chitosan 1:2. The physicochemical properties of Chitosan, PANI, and PANI-Chitosan composites were characterised using Attenuated Total Reflection-Fourier Transformed Infrared (ATR-FTIR) spectroscopy, Ultraviolet-Visible (UV-vis) spectrophotometry, Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray (EDX) spectroscopy, X-Ray Diffractometer (XRD), Thermal Gravimetric Analysis (TGA), and conductivity analysis. The development of an electrochemical sensor for the detection of PFOA in this study involved modifying a screen-printed carbon electrodes (SPCEs) with a Chitosan, PANI and PANI-Chitosan composites using the drop-casting methods. The samples that were successfully synthesised and characterized its properties was further used in electrochemical behaviour study. The resulting PANI-Chitosan composite was characterised using cyclic voltammetry (CV) and compared to the unmodified SPCE in term of their electroactive surface area (EASA). The results showed that the PANI-Chitosan 1:1 exhibited much better performance compared to the unmodified SPCE with significantly higher EASA of  $0.221 \text{ cm}^2$ . Based on this result, The PANI-Chitosan 1:1 modified SPCE was selected for further optimization studies via differential pulse voltammetric (DPV) where PANI-Chitosan 1:1 showed a linear correlation coefficient with high sensitivity of  $8 \times 10^{-7}$  to PFOA detection, with a linear range of 5-150 ppb and a limit of detection (LOD) of 1.08 ppb. The sensor's analytical performance was evaluated by measuring the current response to the reproducibility, long-term stability and presence of other interferents, and the sensor demonstrated good reproducibility with 1.25% RSD value. Additionally, PANI-Chitosan 1:1 recorded an outstanding stability for 12 days for detection of PFOA with 0.28% RSD and demonstrated good selectivity in the presence of other interferences. Overall, the developed sensor exhibited great sensitivity, excellent reproducibility, and good stability for the detection of PFOA.

## **ACKNOWLEDGEMENT**

In the name of ALLAH SWT, the Almighty God and Most Merciful. All praise to Allah and His blessing on the completion of my Master's research project. I am grateful for all of the opportunities, trials, and strength that have been provided to me in order to complete the thesis. First and foremost, I would like to thank my supervisor, Dr. Kavirajaa Pandian A/L Sambasevam, for his guidance, cooperation, encouragement, and useful ideas in completing my thesis successfully. Also, my heartfelt gratitude goes to my co-supervisors, Dr. Siti Nor Atika Baharin and Madam Nurul' Ain Jamion, as well as other lecturers at UiTM Kuala Pilah who are willing to spend their time, patience, guidance, and valuable comments to assist me in writing the paper.

I'd also like to thank my parents for their generous support, motivation, cooperation, and encouragement in completing my research project. In addition, I'd like to express my gratitude to all laboratory assistants who assist me when I need chemicals or instruments. Last but not least, a special thanks to my colleagues, friends, and anyone else who has helped me with this project, whether directly or indirectly. Alhamdulillah, and thank you again for always being there for me on my Master's journey from 2020 to 2023.

May ALLAH S.W.T reward you all with goodness.

# TABLE OF CONTENTS

	<b>Page</b>
<b>CONFIRMATION BY PANEL OF EXAMINERS</b>	<b>ii</b>
<b>AUTHOR'S DECLARATION</b>	<b>iii</b>
<b>ABSTRACT</b>	<b>iv</b>
<b>ACKNOWLEDGEMENT</b>	<b>v</b>
<b>TABLE OF CONTENTS</b>	<b>vi</b>
<b>LIST OF TABLES</b>	<b>ix</b>
<b>LIST OF FIGURES</b>	<b>x</b>
<b>LIST OF SYMBOLS</b>	<b>xiii</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xvi</b>
<b>CHAPTER ONE INTRODUCTION</b>	<b>1</b>
1.1 Research Background	1
1.2 Problem Statement	5
1.3 Objectives	7
1.4 Significance of Study	7
1.5 Scope and Limitation	9
<b>CHAPTER TWO LITERATURE REVIEW</b>	<b>11</b>
2.1 Polyaniline as Intrinsic Conducting Polymers (ICPs)	11
2.1.1 General Synthesis Methods of PANI	13
2.2 PANI Composites	14
2.2.1 PANI/bio-filler Composites (cellulose, chitosan)	14
2.3 Introduction of Chitin and Chitosan	16
2.3.1 Extraction Techniques of Chitin and Chitosan	17
2.3.2 Chitin and Chitosan Sources, Properties and Applications	21
2.3.3 Physicochemical Properties of Chitin and Chitosan	25
2.4 PANI-Chitosan Composite	28
2.5 PFAS as Emerging Contaminants	30
2.5.1 Physicochemical Properties and Application of PFOA and PFOS in	

Industry	32
2.5.2 Human Exposure and Occurrences in the Environment	33
2.6 Remediation Efforts to Curb PFOA and PFOS Pollution	34
2.6.1 Determination of PFOA and its Derivative using Conventional Technique	36
<b>CHAPTER THREE RESEARCH METHODOLOGY</b>	<b>38</b>
3.1 Chemical and Reagents	38
3.2 Extraction of Chitosan from Crab Shells (CS)	38
3.3 Synthesis of PANI <i>via</i> Chemical Oxidative Polymerization Technique	40
3.4 In-situ Synthesis of PANI-Chitosan Composite <i>via</i> Chemical Oxidative Polymerization Technique	40
3.5 Modification of SPCEs with PANI-Chitosan Composite	41
3.6 Characterizations of PANI-Chitosan Composite	42
3.7 Electrochemical Characterization	44
3.8 Voltammetric Measurements	44
3.8.1 Optimization of the Electrochemical Detection of PFOA on PANI- Chitosan 1:1 SPCE	45
3.8.2 Linear range and Detection Limit	46
3.9 Electrochemical Performance of PANI-Chitosan 1:1 SPCE	46
3.10 Detection of PFOA in water samples by DPV	47
<b>CHAPTER FOUR RESULTS AND DISCUSSION</b>	<b>48</b>
4.1 Characterization of PANI, Chitosan and PANI-Chitosan composites	48
4.1.1 Degree of Deacetylation (DDA) of Extracted Chitosan	48
4.1.2 ATR-FTIR Spectra	49
4.1.3 UV-Visible Spectra	50
4.1.4 XRD Analysis	51
4.1.5 SEM-EDX Study	54
4.1.6 TGA/DTG Analysis	58
4.1.7 Conductivity Study	62
4.2 Electrochemical characterization	63
4.2.1 Electroactive Surface Area (EASA) of the Developed Sensor	63