PREPARATION OF SAFRANINE O IMMOBILIZED ACRYLIC MICROSPHERES AND COBALT(II) ION IMMOBILIZED MICROSILICA FOR OPTICAL DETECTION OF NITROGEN COMPOUND

NUR SYARMIM BINTI MOHAMED NOOR

MASTER OF SCIENCE (INDUSTRIAL CHEMISTRY) UNIVERSITI MALAYSIA PAHANG

PREPARATION OF SAFRANINE O IMMOBILIZED ACRYLIC MICROSPHERES AND COBALT(II) ION IMMOBILIZED MICROSILICA FOR OPTICAL DETECTION OF NITROGEN COMPOUND

NUR SYARMIM BINTI MOHAMED NOOR

Thesis submitted in fulfilment of the requirements for the award of the degree of Master of Science in Industrial Chemistry

Faculty of Industrial Sciences and Technology UNIVERSITI MALAYSIA PAHANG

MARCH 2016

UNIVERSITI MALAYSIA PAHANG

DECLARATION OF THESIS AND COPYRIGHT			
Author's full name : NUR SYAR	MIM BINTI MOHAMED NOOR		
Date of birth : 18 AUGUST	Г 1989		
Title : PREPARAT MICROSPH MICROSILI COMPOUN	Title: PREPARATION OF SAFRANINE O IMMOBILIZED ACRYLIC MICROSPHERES AND COBALT(II) ION IMMOBILIZED ON MICROSILICA FOR OPTICAL DETECTION OF NITROGEN COMPOUND		
Academic Session : SEMESTER	2 2015/2016		
I declare that this thesis is classifie	ed as:		
CONFIDENTIAL	CONFIDENTIAL (Contains confidential information under the Official Secret Act 1972)		
RESTRICTED	(Contains restricted information as specified by the organization where research was done)		
OPEN ACCESS	I agree that my thesis to be published as online open access (Full text)		
 I acknowledge that Universiti Malaysia Pahang reserve the right as follows: The Thesis is the Property of Universiti Malaysia Pahang The Library of Universiti Malaysia Pahang has the right to make copies for the purpose of research only. The Library has the right to make copies of the thesis for academic exchange. 			
Certified By:			
(Student's Signature)	(Supervisor's Signature) Dr. Chong Kwok Feng		
Date:	Date:		

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science in Industrial Chemistry.

Signature: Name of Supervisor: DR CHONG KWOK FENG Position: SENIOR LECTURER Date:

Signature:

Name of Co-supervisor: DR TAN LING LING@CHONG LING LING Position: SENIOR LECTURER Date:

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature:

Name: NUR SYARMIM BINTI MOHAMED NOOR ID Number: MKD12003 Date:

TABLE OF CONTENTS

	Page
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
DEDICATION	iv
ACKNOWLEDGEMENTS	V
ABSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	viii
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF SYMBOLS	XV
LIST OF ABBREVIATIONS	xvi

CHAPTER 1 INTRODUCTION

1.1	Nitrite Ion and Ammonia	1
1.2	Problem Statements	2
1.3	Research Objectives	4
1.4	Scope of Study	4
1.5	Thesis Overview	7

CHAPTER 2 LITERATURE REVIEW

2.1	Optical Chemical Sensor	8
2.2	Principle of Fibre Optic Reflectance Spectrophotometer	9
2.3	Poly(n-butyl acrylate) micropsheres	10
2.4	Safranine O	12
2.5	Sol-Gel	13
2.6	Methylcellulose	14
2.7	Short Review on Current Works	16

CHAPTER 3 METHODOLOGY

3.1	List of Chemicals	20
3.2	List of Instruments	21
3.3	Glassware Cleaning Procedure	22
3.4	Preparation of Analyte Stock Solutions and Buffer	22
	Solutions	
3.5	Synthesis of Poly(nBA) Microspheres	23
3.6	Immobilization of SO Reagent onto Poly(nBA)	23
	Microspheres	
3.7	Preparation of Co(II) Ion-containing Sol-Gel	23
3.8	Preparation of Pellet Sensor	24
3.9	Characterization of the Reaction between SO Reagent-	24
	based Optode and NO_2^- Ion	
3.10	 3.9.1 pH Effect 3.9.2 Dynamic Linear Range 3.9.3 Response Time 3.9.4 Reagent Concentration 3.9.5 Leaching Test 3.9.6 Photostability and Shelf Life Studies 3.9.7 Reproducibility and Repeatability 3.9.8 Interference Study 3.9.9 Validation Study Characterization of the Reaction between Silica Pellet Sensor and NH₃ 	24 25 25 25 25 26 26 26 26
	 3.10.1 pH Effect 3.10.2 Dynamic Linear Range 3.10.3 Response Time 3.10.4 Photostability and Long Term Stability 3.10.5 Reproducibility and Repeatability Test 3.10.6 Interference Study 3.10.7 Validation Study 	27 27 28 28 28 28 29

CHAPTER 4 SELF-PLASTICIZED POLYACRYLATE MICROSPHERES OPTODE FOR QUANTITATION OF NITRITE IN EDIBLE BIRD'S NESTS

4.1	Introduction	30
4.2	Results and Discussion	31
	 4.2.1 Characterization of Poly(nBA) Microspheres 4.2.2 Optical Characteristic of Immobilized SO and SO-NO² Complex on the Acrylic Microspheres 	31 34
	4.2.3 pH Effect	36
	4.2.4 Leaching Test and Stability Test	37
	4.2.5 SO Loading Effect	39
	4.2.6 Response Time	40
	4.2.7 Dynamic Linear Range	41
	4.2.8 Reproducibility and Repeatability	45
	4.2.9 Interference Study	46
	4.2.10 Validation Study	48
4.3	Summary	49
CHAPTER 5	REFLECTOMETRIC OPTOSENSOR FOR	VISUAL
CHAPTER 5	REFLECTOMETRIC OPTOSENSOR FOR DETECTION OF AMMONIA BASED ON SILICA	VISUAL PELLET
CHAPTER 5	REFLECTOMETRIC OPTOSENSOR FOR DETECTION OF AMMONIA BASED ON SILICA SENSING MATERIAL	VISUAL PELLET
CHAPTER 5	REFLECTOMETRIC OPTOSENSOR FOR DETECTION OF AMMONIA BASED ON SILICA SENSING MATERIAL	VISUAL PELLET
CHAPTER 5 5.1	REFLECTOMETRIC OPTOSENSOR FOR DETECTION OF AMMONIA BASED ON SILICA SENSING MATERIAL Introduction	VISUAL PELLET
CHAPTER 55.15.2	REFLECTOMETRIC OPTOSENSOR FOR DETECTION OF AMMONIA BASED ON SILICA SENSING MATERIAL Introduction Results and Discussion	VISUAL PELLET 50 51
5.15.2	 REFLECTOMETRIC OPTOSENSOR FOR DETECTION OF AMMONIA BASED ON SILICA SENSING MATERIAL Introduction Results and Discussion 5.2.1 Characterization of NH₃ Pellet Sensor 5.2.2 pH Effect 5.2.3 Dynamic Linear Range 5.2.4 Response Time 5.2.5 Stability Test 5.2.6 Reproducibility and Repeatability 5.2.7 Interference Study 5.2.8 Validation Study 	VISUAL PELLET 50 51 51 52 54 56 57 58 59 61

63

CHAPTER 6 CONCLUSIONS AND RECCOMENDATIONS

6.1	Conclusions	64
6.2	Recommendations	66
REFERENCES		67
APPENDICES		75

LIST OF TABLES

Table No.		Page
3.1	List of chemicals	20
3.2	List of instruments	21
4.1	The comparison between the NO_2^- ion sensor and reported optical NO_2^- ion sensor	44
4.2	The result of <i>t</i> -test analysis for interference study	47
4.3	Analysis performance of the developed NO_2^- ion sensor against IC method using edible bird's nest spiked with 40 ppm of NO_2^- ion concentration	49
5.1	The pellet sensor response to various interfering agents at different concentration ratios	60
5.2	Analysis performance of the developed NH ₃ sensor against acidimetric method	62

LIST OF FIGURES

Figure No.		Page
1.1	The reaction between SO and NO_2^- ion	5
1.2	The color changes of the microsilica pellet when introduced with NH_3	6
2.1	Chemical structure of poly(nBA)	10
2.2	The reaction between SO and NO_2^- ion	12
2.3	Chemical structure of methylcellulose	15
4.1	FTIR spectra for (a) acrylic microspheres and (b) acrylic membrane undergoing emulsion photopolymerization	31
4.2	FESEM image of poly(nBA) microspheres	33
4.3	Size distribution of photocured acrylic microspheres	34
4.4	Reflectance intensities of immobilized SO and SO-NO ₂ ⁻ complex on the acrylic microspheres using 2 mM SO reagent and 500 ppm NO ₂ ⁻ ion at pH 1	35
4.5	The pH effect on SO-NO ₂ ⁻ complex at the wavelength 675.18 nm using 2.0 mM SO reagent and 60 ppm NO_2^- ion	36
4.6	The leaching profile of the immobilized SO on poly(nBA) microspheres in 0.2M HCl solution in pH 1 for an experimental period 60 minutes	37
4.7	The photostability graph of the immobilized SO reagent at 2 mM for 8 hours	38
4.8	The long term stability graph of the SO reagent at 2 mM for 6 months	39
4.9	The reagent concentration effect towards to formation of $SO-NO_2^-$ complex at constant 80 ppm NO_2^- ion concentration	39
4.10	The response time curve of SO-NO ₂ ⁻ complex for 6 min at 675.18 nm	40

4.11	The response curve for relative intensity for $SO-NO_2^-$ complex between NO_2^- ion concentration of 5 ppm and 2000 ppm at the wavelength of 675.18 nm and optimum pH 1	41
4.12	Linear response curve of NO_2^- ion optical sensor between 10 ppm and 100 ppm at pH1 (n=3)	42
4.13	The color scale obtained from the reaction between immobilized SO and NO_2^- ion from 5-1000 ppm at pH 1	42
4.14	Sensor reproducibility response tested with 50 ppm NO_2^- ion at pH 1 and 675.18 nm	45
5.1	Reflectance spectra of the immobilized Co^{2+} ion (a) and its complex with 50 ppm NH ₃ (b) at pH 13	51
5.2	The effect of pH on the immobilized $[Co(NH_3)_6]^{2+}$ complex at 637 nm using 50 ppm NH ₃ at pH 13	53
5.3	The response curve of the pellet sensor generated using NH_3 concentrations from 18-100 ppm at pH 13	54
5.4	The dynamic linear of NH_3 concentration range for the silica-based pellet sensing material	55
5.5	The response time of the NH ₃ optical sensor with different NH ₃ concentrations at 20, 50 and 100 ppm	56
5.6	The photostability profile of the pellet sensor for 8 hours	57
5.7	The long-term stability profile of the pellet sensor for 6 months	58
5.8	Reproducibility and repeatability analyses of the microsilica pellet sensor using 100 ppm NH_3 at pH 13 and wavelength of 637 nm	59
5.9	Calibration curve for NH_3 standard concentration by using acidimetric method (n=3)	62

LIST OF SYMBOLS

v Frequency

 λ Wavelength

LIST OF ABBREVIATIONS

$[Co(NH_3)_6]^{2+}$	Hexaamminecobalt(II) complex ion
Ca ²⁺	Calcium ion
CE	Capillary electrophoresis
Co ²⁺	Cobalt(II) ion
DMPP	Dimethoxy-2-phenylacetophenone
Fe ²⁺	Ferrous ion
Fe ³⁺	Ferric ion
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometer
HCl	Hydrochloric acid
HDDA	1,6-hexanediol diacrylate
HPLC	High performance liquid chromatography
IC	Ion chromatography
\mathbf{K}^+	Potassium ion
KCl	Potassium chloride
Mg^{2+}	Magnesium ion
Na ⁺	Sodium ion
nBA	n-butyl acrylate
NH ₃	Ammonia
$\mathrm{NH_4}^+$	Ammonium ion
NO ₂ ⁻	Nitrite Ion

NO ₃	Nitrate ion
Poly(nBA)	Poly(n-butyl acrylate)
SLS	Sodium lauryl sulfate
SO	Safranine O
SO_4^{2-}	Sulphate ion
TEOS	Tetraethyl orthosilicate