

**UTILIZATION OF ZELIAC AS AN ALTERNATIVE ADSORBENT TO
REMOVE LOW LEVEL CONCENTRATION OF NOM IN RIVERBANK
FILTRATION**

by

NURAZIM BINTI IBRAHIM

**Thesis submitted in fulfillment of the
requirements for the degree of
Doctor of Philosophy**

January 2018

ACKNOWLEDGEMENTS

Alhamdulillah, thanks to Allah (SWT) who has given me life, good health and strength which makes it possible for me to finish this research.

First and foremost, I would like to express a special gratitude to my supervisor and co-supervisor (Prof. Dr. Hamidi Abdul Aziz and Prof. Dr. Mohd Suffian Yusoff) for giving me their valuable guidance and support throughout my master and PhD study.

Very special thanks to the Environmental and Structure Laboratory technicians, Mrs. Shamsiah Mohd Ali, Mr. Mohammed Nizam Mohd Kamal, Mr Muhammad Zaini Mohd Zuki, Mr. Muhamad Nabil Semail, and Allahyarham Mr. Shahril Izham Md. Nor, who are helping and supporting me in the laboratory works. Their assistance was important in completing this research.

My gratitude also goes to the Ministry of Higher Education Malaysia for providing LRGS Grant No. 203/PKT/6726001 – River bank/bed Filtration for Drinking Water Source, Abstraction and the MyBrain15 Scholarship for providing financial assistant and make it possible for me to complete my research. Sincere thanks to my best friends; Norrimi Rosaida and LRGS teammates as well as my other colleague in PPKA who are encourage me to finish this study.

Finally, my deep gratitude is extended to my parent, Ibrahim Ayob and Noraini Daud, and my siblings (Mohd Izzad, Nurasmilla, Mohd Amirul Amin and Siti Naqiyyah) who are giving me courage and keeps supporting me throughout my studies. Their love and understanding has helped me to move forward and finished my study.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	ix
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xvi
LIST OF APPENDICES	xviii
ABSTRAK	xx
ABSTRACT	xxii
CHAPTER ONE: INTRODUCTION	
1.0 Background	1
1.1 Problem Statements	4
1.2 Objectives	7
1.3 Scope of Study	7
1.6 Thesis Organization	8
CHAPTER TWO: LITERATURE REVIEW	
2.0 Introduction	10
2.1 Drinking Water Sources in Malaysia	13
2.1.1 Water Source Quality	13
2.1.1(a) An Overview of Drinking Water Sources Pollution in Malaysia	16
2.1.1(b) Natural Organic Matter	18
2.1.1(c) Bio-colloids/Microorganism	28
2.1.1(d) In-organic chemicals	31
2.1.2 Current Treatment Process and Available Technologies	35
2.1.2 (a) Method of Treatment for NOM Removal	38
2.1.2 (b) Colloids Constituents Removal	41

2.1.2 (c) In-organic Constituents Removal	44
2.1.3 River Bank Filtration	45
2.1.3 (a) Pollutants Attenuation Process by RBF	48
2.1.3 (b) Drawback of RBF Treatment	50
2.1.4 Water Quality Characteristics Study using Explanatory Statistic	52
2.1.4 (a) Descriptive Analysis	52
2.1.4 (b) Box-Whisker Plot	53
2.1.5 Correlation between Water Quality Parameters	54
2.1.5 (a) Pearson's Correlation Coefficient	55
2.1.5 (b) Spearman's Correlation coefficient	55
2.1.5 (c) Statistical Significance of 'r'	56
2.1.5 (d) Linear Regression	57
2.2 Adsorbent	57
2.2.1 Adsorbent Classification	58
2.2.1 (a) Natural and Low Cost-Adsorbents	59
2.2.1 (b) Engineered Adsorbents	61
2.2.1 (c) Composite Adsorbent	63
2.2.2 Adsorbent properties	67
2.2.2 (a) Microscopic Description	67
2.2.2 (b) Surface Area, Pore Volume and Pore Size Distribution	69
2.2.2 (c) Chemical Functional Groups and Ions	72
2.3 Adsorption Process	74
2.3.1 Adsorption Mechanism	75
2.3.1 (a) Physical Adsorption	75
2.3.1 (b) Chemical Adsorption	76
2.3.2 Adsorption Equilibrium Isotherms	78
2.3.2 (a) Langmuir Isotherm	78
2.3.2 (b) Freundlich Isotherm	79
2.3.2 (c) Dubinin-Radushkevich (DR) Isotherm	80
2.3.2 (d) Temkin Isotherm	80

2.3.2 (e) Error Function Analysis for Equilibrium Isotherm	81
2.3.3 Adsorption Kinetic	81
2.3.3 (a) Pseudo first order model	82
2.3.3 (b) Pseudo-second order model	83
2.3.3 (c) Intra-particle diffusion model	83
2.3.3 (d) Bangham's model	84
2.3.3 (e) Elovich model	84
2.4 Application of Adsorbent as Filter Media	85
2.4.1 Fixed-bed Column Study	87
2.4.2 Qualitative and Quantitative Interpretation of Breakthrough Curve	87
2.4.3 Breakthrough Mathematical Model	90
2.5 Summary	91

CHAPTER THREE: MATERIALS AND METHODS

3.0 Introduction	92
3.1 Chemicals and Materials	92
3.2 Water Sampling, Monitoring and Characterization	94
3.2.1 Site Description	95
3.2.1 (a) Kerian River	95
3.2.1 (b) Tube well/Groundwater	97
3.2.1 (c) Treated Water	98
3.2.2 Water Sampling	99
3.2.2 (a) Sampling Process of River Water	99
3.2.2 (b) Sampling Process of Tube well/Groundwater	100
3.2.2 (c) Sampling Process of Treated Water	101
3.2.3 Preservation and Preparation of Samples	102
3.2.4 Water Quality Measurement and Testing	103
3.2.4 (a) In-situ Measurement	103
3.2.4 (b) Analytical Testing in Laboratory	104

3.2.5 Explanatory Statistic	109
3.2.6 Correlation Analysis	109
3.3 Adsorbent Characterization	109
3.3.1 <i>Zeliac</i> Preparation	109
3.3.2 Physical Characterization of <i>Zeliac</i> and Raw Materials	110
3.3.2 (a) Scanning Electron Microscopy (SEM)	110
3.3.2 (b) Brunauer-Emmet-Teller (BET) Surface Area, Pore size and Volume Analysis.	111
3.3.3 Chemical Characterization of <i>Zeliac</i> and Raw Materials	112
3.3.3 (a) X-Ray Fluorescence (XRF)	112
3.3.3 (b) X-ray Diffraction (XRD)	113
3.3.3 (c) Fourier transform infrared (FTIR) spectroscopy	113
3.4 Batch Experiment	114
3.4.1 Adsorbent Dosage	115
3.4.2 Contact Time	115
3.4.3 Shaking Speed	116
3.4.4 Leaching test	116
3.4.5 Equilibrium Isotherm Modelling	117
3.4.5 (a) Langmuir Isotherm Model	118
3.4.5 (b) Freundlich Isotherm Model	118
3.4.5 (c) Dubinin-Radushkevich (DR)	119
3.4.5 (d) Temkin Model	119
3.4.6 Error Analysis	120
3.4.6 (a) Sum of the Squares of the Errors (SSE)	120
3.4.6 (b) Hybrid Fractional Error Function (HYBRID)	121
3.4.6 (c) ARE Deviation (ARED)	121
3.4.6 (d) Marquadt's Percent Standard Deviation (MPSED)	121
3.3.6(e) Chi-Square test (X^2)	122

3.4.7 Adsorption Kinetic Modelling	122
3.4.7 (a) Pseudo-first order	123
3.4.7 (b) Pseudo-second order	123
3.4.7 (c) Intra-Particle Diffusion	123
3.4.7 (d) Bangham's	123
3.4.7 (e) Elovich	125
3.5 Continuous Fixed-bed Column Study	125
3.5.1 Column Set-up and Experiment	125
3.5.2 Fixed-bed Column Parameters	127
3.5.3 Breakthrough	128
3.5.4 Column Adsorption Modelling	130
3.4.4 (a) Thomas model	131
3.4.4 (b) Yoon-Nelson model	131

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.0 Introduction	132
4.1 Water Characteristics and Quality	132
4.1.1 Explanatory Statistics	132
4.1.1(a) Descriptive Statistics of Water Quality Parameters	133
4.1.1(b) Box and Whisker Plot	158
4.1.2 Correlation between Water Quality Parameters	164
4.1.2(a) Pearson Correlation	164
4.1.2(b) Spearman's Correlation	172
4.1.2(c) Linear Regression and R^2	173
4.2 <i>Zeliac</i> Properties and Characteristics	176
4.2.1 Physical characteristics of <i>Zeliac</i>	177
4.2.1(a) Scanning Electron Microscope (SEM) and EDAX	177
4.2.1(b) Brunauer-Emmett-Teller (BET) Analysis	179
4.2.2 Chemical characteristics of <i>Zeliac</i>	180
4.2.2 (a) XRF Analysis	180

4.2.2 (b) XRD Analysis	183
4.2.2 (c) FTIR Analysis	181
4.3 Batch Experiment Study	186
4.3.1 Effect of Dosage	188
4.3.2. Effect of Time	189
4.3.3. Effect of Agitation speed	191
4.3.4. Removal of Iron and Manganese by <i>Zeliac</i>	192
4.3.5 Potential leaching of elements from <i>Zeliac</i>	193
4.4 Adsorption Mechanism	195
4.4.1 Equilibrium Isotherm Study	195
4.4.2 Error Analysis	201
4.4.3 Kinetic study	203
4.5 Continuous Fixed-bed Column Study	206
4.5.1 Breakthrough Curve	211
4.5.1 (a) Effect of Adsorbent Particle Size	217
4.5.1 (b) Modelling Breakthrough Curve	219
4.5.2 Physical or Chemical Changes after Treatment	225
Process in Fixed-bed Column Study	

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions	232
5.2 Recommendations	234

REFERENCES	235
-------------------	-----

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

		Page
Table 2.1	A summary of general water quality parameters used in qualitative analysis.	15
Table 2.2	Concentration of DOC observed in natural water at different places	25
Table 2.3	Summary of several important effects of NOM presence in raw and drinking water.	26
Table 2.4	List of several DBPs possibly produce during disinfection process	28
Table 2.5	Microorganism of concern in drinking water sources and supply	30
Table 2.6	Adverse effect of four in-organic chemicals typically found in Malaysia river water and groundwater	35
Table 2.7	Conventional treatment process and its application	37
Table 2.8	Advances and alternative treatment process and its application	38
Table 2.9	Summary of TOC/DOC and SUVA values in drinking water source and treated water collected from different places	41
Table 2.10	Summary of several proposed treatment methods suggested for NOM removal	43
Table 2.11	A new develop composite adsorbent and its removal parameters	64
Table 2.12	Physical and chemical characteristics of <i>Zeliac</i> report in the previous study	66
Table 2.13	Comparison of two XRF spectrometers techniques	74
Table 2.14	The characteristics of physical and chemical adsorption	77

Table 3.1	List of chemicals and materials for this study	94
Table 3.2	Details equipment's and preservation procedures applied in order to reduce changes to sample	102
Table 3.3	Multi-parameter probe specifications	104
Table 3.4	Ratio of raw materials required to prepare 100 kg of <i>Zeliac</i>	110
Table 3.5	Langmuir isotherm model in four linear forms	118
Table 3.6	Fixed-bed column parameters	128
Table 4.1	1 Physical characteristics of Kerian River water and groundwater from April 2014 to August 2015	134
Table 4.2	Physical characteristics of treated water at different stages of treatment processes in LBWTP (13 month, n= 21)	136
Table 4.3	Chemical Characteristics of Kerian River water and groundwater from April 2014 to August 2015	142
Table 4.4	Chemical characteristics of treated water at different stages of treatment processes in LBWTP (13 month, n= 21)	144
Table 4.5	Biological characteristics of water samples	156
Table 4.6	Correlation coefficients of 19 water quality parameters measured in Kerian River water	165
Table 4.7	Correlation coefficients of 20 water quality parameters measured in river bank tube well water	169
Table 4.8	Correlation coefficients of 17 water quality parameters measured in final treated water	171
Table 4.9	Comparison of R-values using Pearson Correlation and Spearman Correlation of Kerian River water at significant level of $p < 0.05$	173

Table 4.10	BET analysis of raw materials and composite media <i>Zeliac</i>	179
Table 4.11	Major and minor elements determined in raw materials and <i>Zeliac</i>	181
Table 4.12	Elements detected from the leaching test of composite media <i>Zeliac</i> at optimum condition from batch study.	194
Table 4.13	Constant parameters computed from isotherm models	199
Table 4.14	Error analysis for linearized isotherm models	202
Table 4.15	Summary of constant parameters value of kinetic models	210
Table 4.16	Breakthrough and ineffective point for selected parameters for this study	217
Table 4.17	Parameters of Thomas and Yoon-Nelson models	224
Table 4.18	Chemical composition of raw and used <i>Zeliac</i>	227
Table 4.19	FT-IR spectra of <i>Zeliac</i> before and after filtration	230

LIST OF FIGURES

		Page
Figure 2.1	Status of Malaysia River Water Quality	18
Figure 2.2	The illustration show mechanisms of natural filtration in RBF system	47
Figure 2.3	Box and whisker plot elements	54
Figure 2.4	(A) The development of inter-or intra-particle porosity in the micro, meso-, or macro-porous region, (B) Zeolites are the most typical micro-porous solids processing well-defined intra-particle porosity, (C) Clays are layered micro-porous solids whose interlayer space is expandable by intercalated species	70
Figure 2.5	The common isotherm shape obtained from the analysis of; a) purely micro-porous (Type I, isotherm profile), b) non-porous and macro-porous material (Type II, isotherm profile) and c) meso-porous and micro-porous material (Types IV, isotherm profile) (Source: Kuila and Prasa, 2013).	71
Figure 2.6	Size distributions of various types of environmental colloids and particles and several of the analytical techniques that are used to characterize them. Abbreviations: FFF = field-flow fractionation; FCS = fluorescence correlation spectroscopy; LIBD = laser-induced breakdown spectroscopy.	86
Figure 2.7	An example of breakthrough curves obtain from a plot of concentration against volume of effluent. Co: initial concentration, Cb: breakthrough concentration, Ce: exhaustion concentration	88
Figure 3.1	Flow of research methodologies	93
Figure 3.2	The location of Kerian River in map of Peninsular Malaysia (Sources: Isa et al., 2010); (b) Sampling location in Lubok Buntar (Source: Edited from Google earth satellite imagery date 9/1/2016); (c) Coordinate of sampling point (Source: Google earth satellite imagery date 9/1/2016)	96

Figure 3.3	(a) The picture of USM tube well; (b) Surrounding area of USM engineering campus (Source: Edited from Google earth satellite imagery date 9/1/2016); (c) Location of USM tube well (Source: Google earth satellite imagery date 9/1/2016)	98
Figure 3.4	Schematic diagram of the water treatment process in Lubok Buntar	99
Figure 3.5	Water sampling steps for water supply wells	100
Figure 3.6	Set-up for fixed-bed column study on colloid transport and pollutants absorption using <i>Zeliac</i> as porous media	127
Figure 4.1	Distribution of DOC in Kerian River water, treated water at different stages of treatment processes in LBWTP and river bank tube well water. The abbreviations used in the plotted graph are Kerian River water (KRW), final treated water (TW), tube well water (RBF), after aeration process (AW), after coagulation process (CW) and after filtration process (FW).	159
Figure 4.2	Distribution of UV ₂₅₄ in Kerian River water, treated water at different stages of treatment processes in LBWTP and river bank tube well water	161
Figure 4.3	Distribution of SUVA in Kerian River water, treated water at different stages of treatment processes in LBWTP and river bank tube well water	162
Figure 4.4	NOM surrogate parameters relationship using Kerian River water monitoring data (n = 28): a) linear graph of UV ₂₅₄ – DOC for all data collected, b) linear graph of UV ₂₅₄ –SUVA, c) linear graph of DOC – SUVA	175
Figure 4.5	Surface morphology analysis of composite media (<i>Zeliac</i>) and raw materials for the mixture (Zeolite, Limestone, AC, RHA).	178

Figure 4.6	Mineral composition of <i>Zeliac</i> and raw materials (Symbol: C-Clipnotilolite, Cal-Calcite, Q-Cristobalite low)	184
Figure 4.7	Functional groups present in <i>Zeliac</i> before adsorption process	187
Figure 4.8	Effect of <i>Zeliac</i> dosage on removal of UV ₂₅₄ , Colour and NH ₃ -N from Kerian River water	189
Figure 4.9	Effect of time on removal of UV ₂₅₄ , Colour and NH ₃ -N from Kerian River water	190
Figure 4.10	Effect of speed on removal of UV ₂₅₄ , Colour and NH ₃ -N from Kerian River water	192
Figure 4.11	Analysis of isotherm model for UV ₂₅₄ adsorption; a) Langmuir-2, b) Freundlich, c) Dubinin-Radushkevich, d) Temkin	196
Figure 4.12	Analysis of isotherm model for colour adsorption; a) Langmuir-2, b) Freundlich, c) Dubinin-Radushkevich, d) Temkin	197
Figure 4.13	NH ₃ -N adsorption onto <i>Zeliac</i> surface fit to Langmuir isotherm model	198
Figure 4.14	Kinetic study for UV ₂₅₄ adsorption; a) Pseudo-first-order, b) Pseudo-second-order, c) Bangham's, d) Intra-particle diffusion, e) Elovich	204
Figure 4.15	Kinetic study for NH ₃ -N adsorption; a) Pseudo-first-order, b) Pseudo-second-order, c) Bangham's, d) Intra-particle, e) Elovich	206
Figure 4.16	Colour adsorption found to only fit with Pseudo-second-order	209
Figure 4.17	Influence of particle size on selected pollutants uptake (a) Breakthrough curve of colour (b) Breakthrough curve of UV ₂₅₄ (c) Breakthrough curve of NH ₃ -N	213

Figure 4.18	Influence of particle size on selected pollutants uptake (a) Breakthrough curve of suspended solid (b) Breakthrough curve of Total coliform (c) Breakthrough curve of <i>E. coli</i>	215
Figure 4.19	Linear regression line (a and c) and comparison of the experimental and predicted breakthrough curves (b and d) of UV ₂₅₄ using Thomas model at different particle size 1.18 – 2.00 mm (Column A) and 0.425 – 0.600 mm (Column B)	220
Figure 4.20	Linear regression line (a and c) and comparison of the experimental and predicted breakthrough curves (b and d) of Colour using Thomas model at different particle size 1.18 – 2.00 mm (Column A) and 0.425 – 0.600 mm (Column B)	221
Figure 4.21	Linear regression line (a and c) and comparison of the experimental and predicted breakthrough curves (b and d) of UV ₂₅₄ using Yoon-Nelson model at different particle size 1.18 – 2.00 mm (Column A) and 0.425 – 0.600 mm (Column B)	222
Figure 4.22	Linear regression line (a and c) and comparison of the experimental and predicted breakthrough curves (b and d) of colour using Yoon-Nelson model at different particle size 1.18 – 2.00 mm (Column A) and 0.425 – 0.600 mm (Column B)	223
Figure 4.23	The changes of TDS concentration against time for Column A with particle size of 1.18 – 2.00 mm, Column B with particle size 0.425 – 0.600 mm and Influent (Kerian River water)	226
Figure 4.24	SEM micrograph image taken (a) before and (b) after completing fixed-bed column experiment	229
Figure 4.25	The changes in major peak of Zeliac before and after adsorption process	229

LIST OF ABBREVIATIONS

Al ₂ O ₃	Aluminum oxide
BET	Brunauer-Emmet-Teller
C	Carbon
Ca	Calcium
CaO	Calcium oxide
COD	Chemical Oxygen Demand
DBPs	Disinfection by-Products
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOE	Department of Environment
EBCT	Empty Bed Column Time
Fe	Ferum/ Iron
Fe ₂ O ₃	Iron oxide
FTIR	Fourier transform infrared
H ₂ SO ₄	Sulphuric acid
HAAs	Haloacetic acids
HCl	Hydrochloric acid
HLR	Hydraulic Loading Rate
HNO ₃	Nitric acid
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
K ₂ O	Potassium oxide
LBWTP	Lubok Buntar Water Treatment Plant
Mg	Magnesium

MgO	Magnesium oxide
Mn	Manganese
MOH	Ministry of Health
Na ₂ O	Sodium oxide
NaOH	Sodium hydroxide
NH ₃ -N	Ammonia nitrogen
NOM	Natural Organic Matter
NWQS	National Water Quality Standards
POC	Particulate Organic Carbon
RBF	River Bank Filtration
SADA	Syarikat Air Darul Aman Sdn. Bhd
SEM	Scanning Electron Microscopy
SiO ₂	Silicon dioxide
SO ₃	Sulfur trioxide
SPC	Specific Conductivity
SS	Suspended Solids
SUVA	Specific UV Absorbance
TDS	Total Dissolved Solids
THMs	Trihalomethanes
TOC	Total Organic Carbon
USM	Universiti Sains Malaysia
UV ₂₅₄	UV Absorbance at Wavelength of 254 nm
WTP	Water Treatment Plant
XRD	X-ray Diffraction
XRF	X-Ray Fluorescence

LIST OF APPENDICES

Appendix A	Drinking Water Quality Standards
Appendix B	Basic Operational Procedure of Humic Substances Isolation Process
Appendix C	Classification of Physi-sorption Isotherms Recommended by IUPAC
Appendix D	Lithology and Well Design in Lubok Buntar
Appendix E	Groundwater Flow Study Lubuk Buntar Area by using Colloidal Borescope System
Appendix F	Kerian River Water Quality
Appendix G	Water Temperature According to Different Water Sources
Appendix H	Spearman Correlation Coefficient Analysis
Appendix I	EDAX Analysis
Appendix J	Chemicals Elements Content
Appendix K	Different Forms of Langmuir Linear Isotherm Models.
Appendix L	Parameter Computed from Breakthrough Curve
Appendix M	Linear Regression Line and Comparison of the Experimental and Predicted Breakthrough Curves using Thomas Model
Appendix N	Performance of <i>Zeliac</i> Compared to the Single Media Performance Conducted in Other Studies

**PENGGUNAAN ZELIAC SEBAGAI PENJERAP ALTERNATIF BAGI
PENYINGKIRAN BAHAN ORGANIK SEMULA JADI BERKOSENTRASI
RENDAH DALAM TAPISAN TEBING SUNGAI**

ABSTRAK

Peningkatan bahan organik semulajadi (NOM) dalam air permukaan adalah membimbangkan kerana ia merupakan bahan utama kepada produk sampingan disinfektan (DBP) dalam sistem olahan air minuman konvensional yang boleh membahayakan kesihatan. Manakala, tapisan tebing sungai (RBF) adalah pilihan yang baik untuk mengurangkan pencemaran air permukaan dan mengatasi masalah kekurangan air terutamanya semasa keadaan cuaca yang melampau seperti kemarau dan banjir. Oleh itu, tujuan kajian ini adalah untuk mengurangkan kemungkinan pembentukan DBP dengan mengawal tahap NOM dalam air dan pada masa yang sama merawat bio-koloid dan bahan pencemar ionik dengan menggunakan bahan penjerap komposit *Zeliac* secara RBF. Hasil pemantauan kualiti air menunjukkan bahawa NOM di Sungai Kerian mencatatkan purata 3.6 mg/L DOC dan 0.10 cm⁻¹ UV₂₅₄. Total koliform didapati melebihi standard kualiti air mentah dengan kepekatan purata 1.5x10⁴ MPN/100 mL. Nilai purata UV₂₅₄ (0.03 cm⁻¹) yang sama diperolehi bagi air dari RBF dan LBWTP. Pada masa yang sama, tahap DOC yang lebih tinggi diukur dari air terawat (1.6 mg / L) berbanding RBF (0.81 mg / L). Untuk bio-koloid, tiada *E. coli* dikesan dalam air dari RBF, namun bakteria koliform masih hadir. Kepekatan parameter lain juga telah berkurangan kecuali Fe dan Mn. Hasil kajian ini menunjukkan bahawa air yang diambil dari RBF masih memerlukan rawatan lanjut bagi memastikan air tersebut selamat dan bersih untuk kegunaan manusia. Kajian terhadap ciri *Zeliac* menunjukkan bahawa bahan penjerap ini mempunyai 40.6 m²/g luas permukaan dan 16.5 nm purata saiz liang. Kewujudan Ca, Si dan Al menjadikan

Zeliac sebagai penukar kation yang baik. Di samping itu, kumpulan hidroksil dan karboksil membuktikan bahawa *Zeliac* dapat menarik bahan pencemar ion positif dan pada masa yang sama, kumpulan karbonil dapat membantu dalam penjerapan karbon organik. Berdasarkan, kajian isoterma dan kinetik, penyingkiran bahan pencemar dikawal oleh penjerapan ke permukaan heterogen melalui perkongsian antara bahan atau pertukaran ion. Pada dos optimum 7 g per 100 mL sampel, kecekapan penyingkiran UV₂₅₄, warna dan NH₃-N masing-masing adalah 72.8% (0.129-0.035 cm⁻¹), 78.6% (42-9 PtCo) dan 77.1% (0.70-0.16 mg/L). Dalam eksperimen penjerapan turus, perbezaan saiz butiran *Zeliac* didapati tidak memberikan kesan yang signifikan terhadap prestasi penyingkiran. Titik bolos untuk UV₂₅₄ dan bio-koloid masing-masing berlaku pada 103 dan 31 jam pada kadar beban hidraulik 1 cm/min. Hasil ini menunjukkan prestasi *Zeliac* yang baik dalam menyingkirkan sebatian organik dan ionik dalam sumber air minuman serta keupayaannya sebagai media penapis alternatif dalam RBF.

UTILIZATION OF ZELIAC AS AN ALTERNATIVE ADSORBENT TO REMOVE LOW LEVEL CONCENTRATION OF NOM IN RIVERBANK FILTRATION

ABSTRACT

An increase of NOM in river water is a concern as it is the main precursor to health hazard disinfection by-products (DBPs) in conventional drinking water treatment system. River bank filtration (RBF) is a good option to reduce surface water pollution and overcome water shortage problem especially during extreme weather events such as droughts and floods. Therefore, this study aims to reduce the possibility of DBPs formation by controlling the level of NOM and treating it together with bio-colloids and ionic pollutant by composite adsorbent *Zeliac* in RBF. Water quality monitoring study shows that NOM in Kerian River recorded an average of 3.6 mg/L DOC and 0.10 cm⁻¹ UV₂₅₄. Total coliform exceeded the raw water quality standard with an average concentration of 1.5x10⁴ MPN/100 mL. The same mean level of UV₂₅₄ (0.03 cm⁻¹) was determined in the water from RBF and LBWTP. Meanwhile, higher level of DOC measured from final treated water (1.6 mg/L) than RBF (0.81 mg/L). For bio-colloids in RBF, no *E. coli* was present but total coliform was still detected in the water. Other determined parameters were also reduced except for Fe and Mn. This finding signifies the water abstracted from RBF well still requires further treatment to ensure the water is safe and clean for human consumption. The characteristics study of *Zeliac* shows that the adsorbent has a surface area of 40.6 m²/g and average pore size of 16.5 nm. The existence of Ca, Si and Al makes *Zeliac* a good cations exchanger. In addition, hydroxyl and carboxyl groups proved that *Zeliac* can attract positive ions or anionic organic pollutants depending on the water sample acidity. According to the

equilibrium and kinetic study, the removal of pollutants was controlled by multilayer adsorption onto heterogeneous surface of *Zeliac*. At optimum dosage of 7 g per 100 mL sample, the removal efficiency of UV₂₅₄, colour and NH₃-N were 72.8% (0.129 – 0.035 cm⁻¹), 78.6% (42 - 9 PtCo) and 77.1% (0.70 – 0.16 mg/L), respectively. In column adsorption experiments, it was found that granular size of *Zeliac* gave no significant effect to the removal performance. The break point for UV₂₅₄ and bio-colloids occurred at 103 and 31 hours of experiment respectively at hydraulic loading rate of 1 cm/min. These results show a good performance of *Zeliac* in removing both organic and ionic compounds in drinking water source as well as its capability as an alternative filter media in the RBF.

CHAPTER ONE

INTRODUCTION

1.1 Background

Surface water in Malaysia are exposed to organic, inorganic and pathogenic microorganism pollutions as a result of poor management of septic tank, wastewater, agriculture products runoff and earthwork (DOE, 2015). According to the annual report by Department of Environment (DOE) Malaysia, 48% from 473 rivers monitored in 2014 were polluted by these sources. The high percentage reflected the situation where water resources in Malaysia has been deteriorated and the condition may continue to worsen. Among all pollutants load entering surface water, bio-colloids and natural organic matter (NOM) are the two major pollutants attributed by wastewater discharge and surface runoff.

NOM is a complex mixture between organic compounds generated by biological degradation processes in the water body (autochthonous materials) with organic compounds that enter the water from human activities (allochthonous materials) (Croue et al., 1999; Matilainen et al., 2011). Generally, NOM is determined in terms of dissolved organic carbon (DOC) and UV absorbance at 254 nm (UV₂₅₄). Meanwhile, bio-colloids usually refer to microorganism in water such as bacteria and protozoa (Crittenden et al., 2012). Elevation of NOM and bio-colloids concentration in surface water raises concern in safety of drinking water. The main concern is related to the potential formation of carcinogenic/mutagenic disinfectant by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) from the reaction of NOM with disinfectant (Sharp et al., 2006; Fan et al. 2014; Richardson and Postigo.

2015). According to Krasner et al, (2006) and Richardson et al, (2007), continuous consumption of DBPs can lead to cancers, miscarriages and nervous system complications. As a results, a very low concentration of DBPs was regulated for drinking water supply (Richardson, 2009). On the other hand, the increase of bio-colloids typically increases the possibility of microbial contamination (WHO, 2012). Approximately 842, 000 death cases involving diarrheal illness were reported as a result of drinking water contamination (WHO, 2016).

The situation may worsen during extreme weather events such as El Nino (drought) and El Nina (floods) which give a large impact in water resource quality and quantity (Delpla et al., 2009; Chan, 2015). According to previous studies, significant increase of NOM and bio-colloids in surface water were observed during these events (Prathumratana and Kim, 2008; Delpla et al., 2009; Hrdinka et al., 2015). This situation poses bigger challenges to the authorities in providing and delivering safe drinking water using conventional treatment system because of high pollutant loads and low surface water level (Hrdinka et al., 2012; Ching et al., 2015). Normally, optimized coagulation used for NOM removal in conventional treatment system is only capable of removing approximately 50% of NOM present in the water (Tubić et al., 2013). Therefore, an alternative method for water management is necessary to ensure safe and stable drinking water supply especially during extreme weather.

River bank filtration (RBF) is one attractive option that can be applied. RBF is a cost-effective water treatment process that is less vulnerable to climate changes or variations and is capable to remove physical, chemical and biological pollutants from surface water through natural filtration in aquifer sediments at the riverbank (Doussan et al., 1997; Grischek et al., 2003; Ahmed and Marhaba, 2016). This technique requires a well to be drilled adjacent to a river for water abstraction. Abstracting water