



UNIVERSITI PUTRA MALAYSIA

***TREATMENT OF OILFIELD-PRODUCED WATER USING
BIOLOGICAL AND MEMBRANE PROCESSES***

ALIREZA PENDASHTEH

FK 2010 18

**TREATMENT OF OILFIELD-PRODUCED WATER USING BIOLOGICAL
AND MEMBRANE PROCESSES**

By

ALIREZA PENDASHTEH

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

December 2010

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Doctor of Philosophy

TREATMENT OF OILFIELD-PRODUCED WATER USING BIOLOGICAL AND MEMBRANE PROCESSES

By

ALIREZA PENDASHTEH

December 2010

Chairman: Professor Fakhrul-Razi Ahmadun, PhD

Faculty: Engineering

Oil and gas fields' wastewater or "produced water" is the largest waste stream generated in the extraction and process of crude oil and natural gas. It is characterized by high concentration of total dissolved solids (TDS) and dissolved and dispersed hydrocarbon compounds. Due to the increasing volume of waste all over the world in the current decade, the outcome and effect of discharging produced water on the environment has lately become a significant issue of environmental concern and the interest in reusing produced water is increasing in water-stressed regions. In order to treat and reuse produced water, removing of organic and inorganic constituents may be necessary.

The main goal of this research was to investigate the feasibility of using a sequencing batch reactor (SBR) and a membrane sequencing batch reactor (MSBR) to remove the organic matters present in produced water. In order to meet this objective, halophilic hydrocarbon degrading microorganisms were used as seed culture to the SBR. Each of the treatment systems was investigated with different feeds including synthetic and real

produced water. In order to find major foulants on the membrane surface, the characterization of fouling cake layer was studied. Different chemicals were used to find the optimum procedure for membrane cleaning.

Both the SBR and MSBR systems were capable of removing the hydrocarbons from synthetic and real produced water. For the SBR, at TDS concentration of 35,000 mg/L, hydraulic residence time (HRT) of 20 h and an organic loading rate (OLR) of 1.8 kg chemical oxygen demand (COD)/(m³d), COD and oil and grease (O&G) removal efficiencies for synthetic produced water were more than 90%. However, with increase in salt content to 250,000 mg/L, COD and O&G removal efficiencies decreased to 74% and 63%, respectively. The results of biological treatment of real produced water showed that at the same HRT, the removal rates of main pollutants of wastewater such as COD, total organic carbon (TOC) and O&G were above 81, 83, and 85%, respectively. For the MSBR, at an OLR of 1.124 kg COD/(m³d), an HRT of 20 h and TDS of 35,000 mg/L, removal efficiencies of 97.5, 97.2 and 98.9% of COD, TOC and O&G, respectively were achieved. Treating of the real produced water showed removal rates of 86.2, 90.8 and 90.0% for the same conditions. However with increasing salt content, the COD removal efficiencies of the synthetic and real produced water were reduced to 90.4 and 17.7%, respectively at the highest TDS.

The MSBR receiving synthetic hypersaline oily wastewater was modeled by artificial neural network (ANN). A feed-forward neural network trained by batch back propagation algorithm was employed to model the MSBR. A set of 193 operational data from the wastewater treatment with the MSBR was used to train the network. The training, validating and testing procedures for the effluent COD and TOC concentrations

were successful and good correlations were found between the measured and predicted concentrations (R^2 of 0.9525 and 0.9563, respectively for the two parameters mentioned).

Foulant characterization showed that membrane fouling layer is governed by the deposition of organic and inorganic substances composed of extracellular polymeric substances (EPS), hydrocarbon components and inorganic matters. Membrane cleaning tests showed that one stage cleaning of different cleaning agent can not recover flux effectively; however the two stages NaOCl followed by acid provided effective flux recovery.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**RAWATAN AIR HASILAN DARI PERLOMBONGAN MINYAK DENGAN
KAEDAH BIOLOGI DAN PROSES PENAPISAN**

Oleh

ALIREZA PENDASHTEH

Disember 2010

Pengerusi : Profesor Fakhrol-Razi Ahmadun, PhD

Fakulti : Kejuruteraan

Air buangan industri minyak dan gas atau "air hasilan " adalah aliran sisa terbesar yang dihasilkan dalam proses ekstraksi dan minyak mentah dan gas tulen. Ia dicirikan dengan kandungan keseluruhan pepejal terlarut (KPT) yang tinggi, serta komponen hidrokarbon yang terlarut and tersebar. Disebabkan peningkatan jumlah sisa di seluruh dunia pada dekat kini, keputusan dan pengaruh pembuangan air hasilan terhadap alam sekitar merupakan isu penting baru-baru ini serta minat penggunaan semula air hasilan telah meningkat di kawasan kekurangan air. Untuk merawat dan penggunaan semula air hasilan ini, penyingkiran bahan organik and bukan organik mungkin diperlukan.

Tujuan utama kajian ini adalah untuk menyelidik kemungkinan penggunaan reactor kelompok turutan (RKT) dan reaktor kelompok turutan membran (RKTM) untuk menyinkirkan bahan organik yang berada dalam air hasilan. Untuk mencapai tujuan ini, mikroorganisma halofili pengurai hidrokarbon telah digunakan sebagai benih

kultur bagi RKT. Setiap sistem rawatan diselidik dengan pelbagai suapan termasuk air hasilan tiruan dan sebenar. Lapisan kekotoran dikaji untuk mencari pengotor utama di permukaan membran. Pelbagai bahan kimia juga digunakan untuk mencari kaedah optimum bagi pembersihan membran.

Kedua-dua RKT dan RKTМ dapat menyingkirkan hidrokarbon dari air hasilan tiruan dan sebenar. Bagi RKT, pada kepekatan KPT 35,000 mg/L, pada tempoh tahanan (TT) 20 jam dan pada kadar pemuatan organik (KPO) 1.8 kg keperluan oksigen kimia (KOK)/ (m³d), kecekapan penyingkiran KOK dan minyak dan gris (M&G) untuk air hasilan tiruan adalah lebih daripada 90 %. Tetapi, dengan penambahan kepekatan garam kepada 250,000 mg/L, kecekapan penyingkiran KOK dan M&G masing-masing berkurangan kepada 74 dan 63 %. Keputusan rawatan air hasilan sebenar secara biologi menunjukkan bahawa, pada TT yang sama, kadar penyingkiran bahan pencemaran utama air sisa, seperti KOK, jumlah karbon organik (JKO) dan M&G masing-masing lebih daripada 81, 83 dan 85 %. Bagi RKTМ, pada KPO 1.124 kg KOK / (m³d), 20 hari TT dan 35,000 mg/L KPT, kecekapan penyingkiran adalah 97.5, 97.2 dan 98.9% masing-masing untuk KOK, JKO dan M&G pada keadaan yang sama. Pada keadaan yang sama, rawatan air hasilan sebenar menunjukkan kadar penyingkiran 86.2, 90.8 dan 90.0%. Tetapi dengan peningkatan kandungan garam, kecekapan penyingkiran KOK bagi air hasilan tiruan dan sebenar berkurangan masing-masing kepada 90.4 dan 17.7% pada KPT paling tinggi.

Penerimaan air kumbahan hipersalin berminyak sintetik oleh MSBR dimodelkan dengan rangkaian saraf tiruan. Sebuah rangkaian saraf suapan awal terlatih dengan algoritma

rambatn balik berkelompok digunakan sebagai model MSBR. Satu set dengan 193 data operasi dari rawatan air kumbahan oleh MSBR digunakan untuk melatih rangkaian tersebut. Latihan, validasi dan ujian prosedur terhadap kepekatan efluen COD dan TOC adalah berjaya dan korelasi baik juga didapati antara kepekatan ukuran dan jangkaan (R^2 masing-masing adalah 0.9525 dan 0.9563 untuk dua parameter yang disebutkan).

Pencirian pengotor menunjukkan bahawa lapisan kotoran membran dibentuk daripada pemendakan bahan organik dan bukan organik yang terdiri daripada bahan polimer ekstraselulose (BPE), komponen hidrokarbon dan bahan bukan organik. Kajian pembersihan membran menunjukkan bahawa pembersihan satu peringkat dengan pelbagai bahan pencucian tidak dapat memulih kecekapan aliran, tetapi dengan dua peringkat bahan pencucian NaOCl diikuti dengan asid dapat memulihkan kecekapan aliran.

ACKNOWLEDGEMENTS

All praises and thanks to Almighty Allah for giving me the opportunity to complete this work.

My deepest gratitude and sincere appreciation is owed to my supervisor Prof. Dr. Fakhrul-Razi Ahmadun for his invaluable guidance, continuous support and encouragement from the beginning till the end of this study. I would like to express my appreciation to Prof. Dr. Sayed Siavash Madaeni, Assoc. Prof. Dr. Luqman Chuah Abdullah, Dr. Zurina Zainal Abidin and Dr. Dayang Radiah Awang Biak for their great concern, valuable time and precious advices during the course of this study.

Special thanks are due to staff of Department of Chemical and Environmental Engineering, Faculty of Engineering for their help and cooperation during my experimental work. Thanks are extended to my friends and all my lab-mates in Analytical, Biochemical and Environmental Labs.

Love and thanks to my wife for her support, understanding, care and encouragement, which always strengthen me in happiness and sorrow. To my beloved family, I would like to express my deepest affection for their never ending love and support.

Finally, thank to the Universiti Putra Malaysia (UPM) for supporting this work under research grant no 05/01/07/0158RU.

I certify that a Thesis Examination Committee has met on 30 December 2010 to conduct the final examination of Alireza Pendashteh on his thesis entitled "Treatment of Oilfield-Produced Water Using Biological and Membrane Processes" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Azni b. Idris, PhD

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Thomas Choong Shean Yaw, PhD

Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Thamer Ahmed Mohamed, PhD

Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Said Salah Eldin Hamed Elnashaie, PhD

Professor
Chemical and Biological Engineering Department
Faculty of Applied Science
University of British Columbia
Canada
(External Examiner)

BUJANG BIN KIM HUAT, PhD

Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the Degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Fakhru'l-Razi Ahmadun, PhD

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Luqman Chuah Abdullah, PhD

Associate Professor
Faculty of Engineering
University Putra Malaysia
(Member)

Zurina Zainal Abidin, PhD

Faculty of Engineering
University Putra Malaysia
(Member)

Sayed Siavash Madaeni, PhD

Professor
Department of Chemical Engineering
Razi University, Kermanshah, Iran
(Member)

HASANAH MOHD GHAZALI, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



ALIREZA PENDASHTEH

Date: 30 December 2010

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ABSTRAK	v
ACKNOWLEDGEMENTS	viii
APPROVAL	ix
DECLARATION	xi
CHAPTER	
1	
INTRODUCTION	1
1.1 Background	1
1.2 Problem Statement	2
1.3 Objectives of the Study	6
1.4 Scope of the Study	7
2	
LITERATURE REVIEW	12
2.1 Origin of Produced Water	12
2.2 Produced Water Characteristics	13
2.2.1 Dissolved and Dispersed Oil Compounds	14
2.2.2 Dissolved Formation Minerals	16
2.2.3 Production Chemical Components	17
2.2.4 Production Solids	17
2.2.5 Dissolved Gases	18
2.3 Produced Water from Oil and Gas Fields	18
2.4 Fate and Impact of Produced Water Discharge	18
2.4.1 Salinity	19
2.4.2 Dispersed and Soluble Oil	19
2.4.3 Treating Chemicals	19
2.4.4 Heavy Metals	20
2.4.5 Radionuclides	21
2.5 Produced Water Management	21
2.6 Produced Water Reuse	22
2.7 Produced Water Treatment	23
2.8 Biodegradation of Hydrocarbons	24
2.8.1 Use of Microorganisms in Biological Treatment of Oily Wastewaters	24
2.8.2 Significance of Hydrocarbons Biodegradation by Microorganisms	25
2.8.3 Composition of Petroleum	25
2.8.4 Abiotic Alteration of Characteristics of Crude Oil	26
2.8.5 Hydrocarbons Degradation Microorganisms	26
2.8.6 Factors Affecting Biodegradation of Petroleum Hydrocarbons	26

2.8.7	Metabolism of Hydrocarbons	31
2.8.8	Dispersion of Hydrocarbons	31
2.9	Isolation of Oil Degrading Microorganisms	32
2.10	Identification of Microorganisms	32
2.10.1	Biolog Microstation System	32
2.11	Biodegradation of Hydrocarbons in High Salt Concentration in a Flask Experiment	33
2.12	Biokinetic Coefficients in Batch Culture	35
2.13	Biological Treatment of Produced Water	37
2.13.1	Sequencing Batch Reactor	39
2.14	Membrane Bioreactor Technology	40
2.14.1	Overview of Membrane Bioreactors	40
2.14.2	Comparison of MBRs with Conventional Activated Sludge Systems	41
2.14.3	Types of Membrane Bioreactor Configurations	42
2.14.4	Produced Water Treatment with MBR	43
2.15	Modeling and Optimization of Wastewater Treatment	44
2.15.1	Artificial Neural Network	45
2.15.2	Applications of Artificial Neural Networks in Wastewater Treatment	50
2.16	Membrane Fouling	51
2.16.1	Factors Affecting Membrane Fouling	52
2.17	Foulant Characterization	60
2.18	Mitigation of MBR Fouling	61
2.18.1	Membrane Cleaning	61
2.18.2	Factors Affecting Chemical Cleaning Procedure	65
2.18.3	Membrane Cleaning Assessment	65
2.18.4	Limitation of Fouling	66
2.19	Summary	67
3	MATERIALS AND METHODS	69
3.1	Materials	69
3.1.1	Crude Oil	70
3.1.2	Produced Water	70
3.1.3	Oil Polluted Soil Samples	70
3.1.4	Non-Polluted Soil	71
3.2	Methods	71
3.2.1	Soil pH	71
3.2.2	Determination of Soil Organic Matters Content	71
3.2.3	Soil Salinity (Soil Water Extract Salinity)	71
3.2.4	Hydrocarbons in Soil	72
3.2.5	Synthetic Saline Water Preparation	72
3.2.6	Synthetic Produced Water Preparation	73
3.2.7	Preparation of Commercial Microorganism's (B350M) Culture	73
3.2.8	Isolation of Oil-Utilizing Microorganisms from Non-	74

	Polluted Soil	
3.2.9	Preparing Microorganisms Culture from Polluted Soil	75
3.2.10	Biodegradation Experiment	76
3.2.11	Extraction and Analysis of Petroleum Hydrocarbons in Crude Oil	76
3.2.12	Identification of Bacterial Strains	77
3.2.13	Bioreactor	79
3.2.14	Determination of Biodegradation Kinetics of Synthetic Produced Water	79
3.2.15	Synthetic Produced Water Treatment with SBR	83
3.2.16	Membrane Bioreactor Experiments	84
3.2.17	Model Development: Artificial Neural Network Analysis	91
3.2.18	Foulants Characterization	94
3.2.19	Membrane Cleaning	98
3.2.20	Analytical Methods	100
4	RESULTS AND DISCUSSION	104
4.1	Sarawak Crude Oil	104
4.2	Soil Samples	104
4.3	Biodegradation of Crude Oil by NPSC, OPSC and B350M at Different Concentrations of Sodium Chloride	105
4.4	Biodegradation of Different Fractions of Crude Oil by the Isolated Consortia	109
4.5	Biolog Identification Results	114
4.6	Evaluation of Biokinetic Coefficients	116
4.6.1	Biokinetic Studies	120
4.7	Treatment of Produced Water by Using a Sequencing Batch Reactor	122
4.7.1	Treatment of Synthetic Produced Water	122
4.7.2	Real Produced Water Treatment by Using SBR	132
4.8	Treatment of Produced Water with Membrane Sequencing Batch Reactor	134
4.8.1	Treatment of Synthetic Produced Water	134
4.8.2	Real Produced Water Treatment with Membrane Sequencing Batch Reactor	150
4.8.3	Comparison Synthetic and Real Produced Water Treatment	162
4.8.4	Water Discharge, Recycle and Reuse Options	163
4.9	Artificial Neural Network Analysis of the MBR Treating Produced Water	164
4.9.1	Effect of Parameters	169
4.9.2	Optimization of the Effluent COD for Discharging to Environment	171
4.10	Membrane Foulants Characterization	172

4.10.1	Treatment Process Performance	172
4.10.2	Membrane Fouling Behavior	173
4.10.3	Organic and Inorganic Matters in the Cake Layer	174
4.10.4	MOS of Organic Carbons of the Cake Layer and EPS in the Mixed Liquor Suspension	175
4.10.5	FTIR Analysis	176
4.10.6	TOC, Protein and Polysaccharide Concentrations in the Washed Liquid	177
4.10.7	SEM Analysis Results	178
4.10.8	AFM Analysis Results	179
4.10.9	PSD Analysis Results	181
4.10.10	EDX Analysis	183
4.11	Fouling Mitigation and Cleaning	185
4.11.1	Effect of Different Flocculant on the Performance of Membrane Filtration	185
4.11.2	Ultrasonic Control of Membrane Fouling for a Long Experiment	186
4.11.3	Chemical Cleaning	188
5	CONCLUSIONS AND RECOMMENDATIONS	204
5.1	Conclusions	205
5.2	Recommendations	209
	REFERENCES	211
	APPENDICES	239
	BIODATA OF STUDENT	256
	LIST OF PUBLICATIONS	257