UNIVERSITI PUTRA MALAYSIA

TREATMENT OF OILFIELD-PRODUCED WATER USING BIOLOGICAL AND MEMBRANE PROCESSES

ALIREZA PENDASHTEH

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

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TREATMENT OF OILFIELD-PRODUCED WATER USING BIOLOGICAL AND MEMBRANE PROCESSES

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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)/(m^3d), 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/(m^3d), 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 Fakhrul-Razi Ahmadun, PhD

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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 menynigkirkan bahan organik yang berada dalam air hasilan. Untuk mencapai tujuan ini, mikroorgannisma halofili pengurai hidrokarbon telah digunakan sebagai benih

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

Kedua-dua RKT dan RKTM 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)/ (m^3d), kecekapan penyingkiran KOK dan minyak dan gris (M&G) untuk air hasilan tiruan adalan lebih daripada 90 %. Tetapi, dengan penembahan 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 pencermaran utama air sisa, seperti KOK, jumlah karbon organic (JKO) dan M&G masing-masing lebih daripada 81, 83 dan 85 %. Bagi RKTM, pada KPO 1.124 kg KOK / (m^3d), 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 menunjunkkan 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 degan 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.

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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.

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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:

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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

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