APPLICATION OF RESPONSE SURFACE METHODOLOGY FOR THE OPTIMIZATION OF A MEMBRANE BIOREACTOR FOR OILFIELD PRODUCED WATER TREATMENT

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ABSTRACT

Oil and gas fields wastewater or produced water is the largest waste stream generated in exploration and extraction of oil and gas industries. It is a mixture of different organic and inorganic compounds. The discharge of produced water has caused many environmental pollution problems. In this study, a sequencing batch reactor coupled with a membrane separation process (MSBR) was employed to treat synthetic produced water. The SBR was inoculated with isolated tropical halophilic microorganism consortium capable of degrading crude oil. An experimental design based on the response surface methodology (RSM) was applied to study the effects of influencing factors such as chemical oxygen demand (COD), total dissolved solids (TDS) and hydraulic resistance time (HRT) on COD removal efficiency, total organic carbon (TOC) and oil and grease (O&G) removal efficiency and optimizing the operating conditions of the treatment process. The results of the study showed that the COD, TOC and O&G removal was affected by all the factors. Under optimized conditions the isolated microorganisms were able to reduce COD, TOC and O&G (>90%) within 12 h. Also it has been seen that RSM was an appropriate method to predict proper conditions of the effluent suitable for discharge and/or reuse.

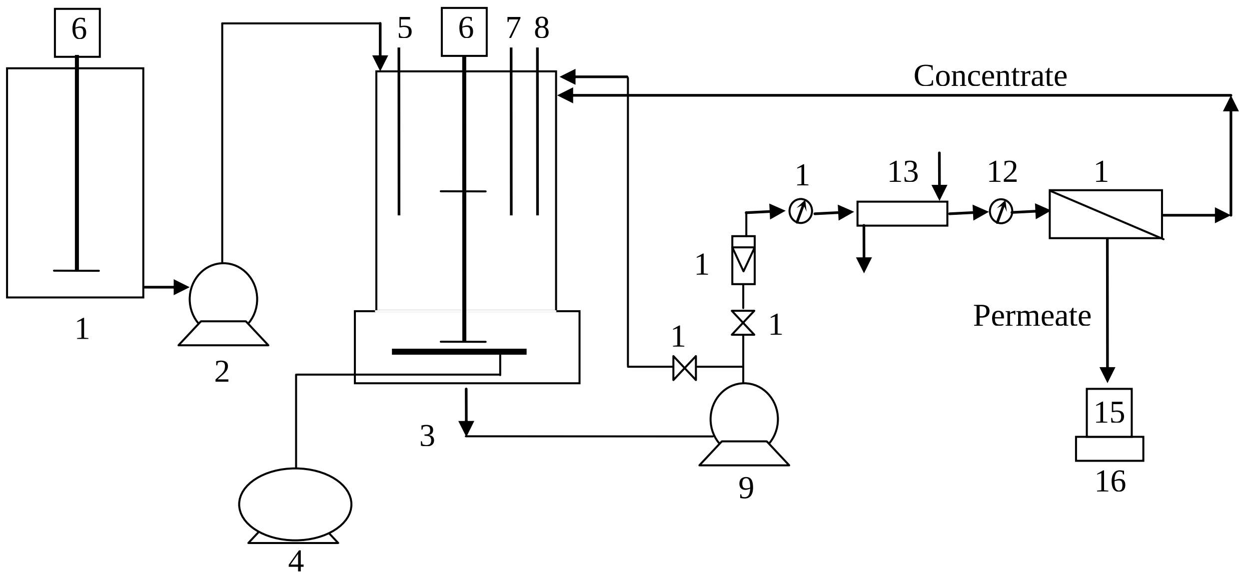
Keywords: *Produced water, Oil and gas fields, Wastewater, Treatment, Membrane bioreactor, Optimization, Response surface methodology*

INTRODUCTION

Membrane bioreactors (MBRs) are known as an effective method for the treatment of industrial wastewaters. MBRs offer many advantages over conventional wastewater treatment processes including: higher volumetric loading, small footprint and reactor requirements, total solids retention at all biomass concentration and less sludge production [1]. Membrane bioreactor technology has been employed for the treatment of several types of industrial wastewaters, including food industry [2], leachate [3], Pharmaceutical [4], dye [5] and oily wastewaters [6]. However, up until the present, no laboratory or bench and /or pilot scale experiments have been reported using MBR technology for treatment of high salinity oilfield produced water. Produced water is the largest waste stream in oil and gas activities. Globally produced water production is estimated at around 250 million barrels per day. It is a mixture of different organic and inorganic compounds. Salt concentration of produced water varies over a wide range (1–300,000 mg l^{-1}) and TOC concentration reaches up to 1500 mg l^{-1} [7]. The permitted oil and grease (O&G) limits for treated produced water discharge offshore in Australia are 30mg l^{-1} daily average and 50 mg l^{-1} instantaneous [8]. Based on United States Environmental Protection Agency (USEPA) regulations, the daily maximum limit for O&G is 42 mg l^{-1} and the monthly average limit is 29 mg l^{-1} [9]. As regards the significant matter of environmental concern, many countries have implemented more stringent regulatory standards for discharging produced water. The monthly average limits of O&G discharge and COD prescribed by the Peoples Republic of China are 10 and 100 mg l^{-1}, respectively [10]. Based on the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention), the annual average limit for discharge of dispersed oil for produced water into the sea is 40 mg l^{-1} [11].

In a MBR, feed characteristics, hydraulic residence time (HRT), mixed liquor suspended solids (MLSS) are important operational parameters that affect on effluent quality [12]. On the other hand, high salt concentration of wastewater, affect biodegradation rate of microorganisms. High concentration of sodium chloride causes environmental stress, microbial lysing effects, and promotes loss of biomass [13].

There have been limited investigations on studying the effect of different operational parameters on effluent of a MBR treating hypersaline oily wastewater. This paper reports on the application of RSM to predict the performance of a cross flow membrane coupled SBR for treating produced water with high concentration of COD and TDS concentration using a consortium of acclimated microorganisms seed cultures and further to evaluate whether the quality of the treated water would meet discharge limits and/or reuse requirements.



1- Raw wastewater tank
2- Peristaltic pump
3- Fermenter
4- Air compressor
5- pH probe
6- Mixer
7- Temperature probe
8-DO probe
9- Centrifugal pump
10- valve
11- Flow meter
12- Pressure gage
13- Heat exchanger
14- Membrane
15- Permeate
16- Balance

Figure 1: Schematic diagram of the MSBR

MATERIALS AND METHODS

Experimental Setup

A 5-liter fermenter (Biostat-B.Braun Biotech International) was used as the SBR (Figure 1). The fermenter was microprocessor controlled for aeration, agitation, pH and dissolved oxygen (DO). Aeration was provided by using an air compressor and a sparger. The DO concentration adjusted to 3 mg l^{-1}.The agitation speed was fixed at 300 rpm. DO and pH of the medium were monitored by the relevant probes. The mixed liquor was kept at a constant temperature through a shell and tube heat exchanger. Wastewater was fed to the bioreactor by using a peristaltic pump (Model Watson-101U/R, Marlow). A centrifugal pump moved the mixed liquor from the bioreactor to the two tubular crossflow membrane modules. Two ultrafilter membranes (FP200, PCI system) were used. The membranes had a tube diameter of 1.25 cm and 30 cm long. The effective area of the two membranes was 0.024 m^2. The crossflow velocity was 2 m/s. Permeate flux was measured gravimetrically with a Tanitak D200 electronic balance.

Synthetic wastewater preparation

Synthetic produced water was used to provide crude oil as source of carbon, required for biomass growth. Based on halophilic medium used by other researchers [14], produced water was simulated. The synthetic produced water constitution (TDS of 35,000 mg l^{-1}) in mg l^{-1} included: NaCl 31,000, $CaCl_2.2H_2O$ 60, KCl 2,000, $MgCl_2.6H_2O$ 50, and $NaHCO_3$ 800. The composition of wastewater gave a C/N/P ratio of approximately 100/10/1 by adding NH_4Cl and KH_2PO_4. The pH was adjusted to 7 using NaOH. All chemicals used in this study were of technical grade. Crude oil was prepared from Malaysia oilfields (Petronas, Sarawak). Synthetic wastewater was prepared by mixing the constituents (salts and crude oil) in a 5-liter propylene container for 24 h (2400 min^{-1}) in a homogenizer (KIKA labortechnik) to achieve equilibrium between the oil and water phases [15].

Culture selection

Hypersaline soil from Morib seaside in Malaysia served as a source of tropical halophilic microorganisms. Isolation of microorganism consortium capable of degrading crude oil in synthetic produced water began by placing approximately 6 g of soil into 200 ml of synthetic produced water (1 ml oil l^{-1} and TDS of 35,000 mg l^{-}). After 15 d of mixing on a shaker table (150 min^{-1}, 30°C), a 2 ml sample of the mixture was transferred to a fresh medium. After 3 steps of the process, the resulting mixture was free of soil [16]. Culture was transferred monthly to fresh medium for six months.

Table 1: Synthetic produced water characteristics

ml oil l^{-1}	Hydrocarbon (mg l^{-1})	COD (mg l^{-1})	Organic Loading rate (kg COD m^{-3} $d^{-1)}$	O&G (mg l^{-1})	TOC[1] (mg l^{-1})
0.25	204.5	562	0.281	87.5	137.5
0.5	409	1125	0.563	175	275
1	818	2,250	1.124	350	550
2	1,636	4,500	2.248	700	1100
3	2,454	6,750	3.372	1050	1650

[1]*Calculated*

Start-up of the SBR

The SBR was inoculated with the culture medium. After inoculation, the reactor was operated with synthetic produced water (1 ml oil l^{-1}) to increase biomass concentration. The biomass was kept in refrigerator for next runs. The reactor operated at different operating conditions and the temperature was kept at a constant 30ºC.

Analytical methods

Since chlorine concentration was high, COD of the samples were determined according to Freire and Sant'Anna [17] method. MLSS, TDS and O&G were measured according to the standard method [18]. TOC was measured by Shimadzu TOC-VCSH.

Design of experiments and statistical analysis

A four-factor-five-level central composite design (CCD) was used in this study. The important parameters and their levels selected were as follows: TDS (35,000-250,000 mg l^{-1}), OLR (0.281-3.372 kg COD m^{-3} d^{-1}), MLSS (1560-8500 mg l^{-1}) and HRT (8-44 h). Design Expert version 8.0.1.0 (State-Ease Inc., Minneapolis, MN, USA) was used to fit the second order model to the parameters according to the following equation:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \qquad (1)$$

Where Y is the response (COD and TOC), x_i and x_j are the independent parameters and β_0, β_i, β_{ii} and β_{ij} are the regression coefficients. And analysis of variance (ANOVA) and R^2 statistic were used to determine whether the develop model was adequate to describe the data. Based on experimental design, 17 runs were performed to study the effect of different parameters and each test was performed 5 days.

RESULTS AND DISCUSSION

In order to study the combined effects of the important operational parameters, pilot plant experiments were performed at different combination of TDS, OLR, MLSS and HRT based on the proposed experimental design. The best fitting model was chosen by regression analysis. Fitting of the data to various models showed that COD and TOC concentrations were well described with quadratic polynomial models as follows (in terms of coded parameters):

$$COD= +99.28 + 63.92A-2.64B+57.99C-1.05D+10.12AC+14.79BD-4.37CD+18.51A^2+16.21C^2 \qquad (2)$$
$$TOC=25.03+11.49A-1.11B+14.13C-0.89D+3.37A^2+3.72C^2 \qquad (3)$$

where A is TDS, B is HRT, C is OLR and D is MLSS.

The very small P-values (< 0.0001) and a suitable R^2 (0.99 for COD and 0.97 for TOC prediction models) showed that the quadratic model was highly significant and suitable for describing the relationship between the responses and parameters. Fig 2 (a) and (b) show the correlation between actual COD and TOC concentrations and predicted values (using equations 2 and 3). Figure 3(a) shows the effect of TDS and OLR on effluent COD concentrations. During this study it was found that COD and TOC removal efficiencies are more dependants on OLR and TDS. It has been reported that COD loading in industrial wastewater treatment with membrane bioreactor technology was between 0.25-16 kg COD $m^{-3}d^{-1}$, and corresponding COD removal rate ranged 90 and 99.8%, respectively [12]. Scholz and Fuchs (20] studied biodegradation of a mixture of fuel oil and surfactant in distilled water in a crossflow membrane bioreactor. They achieved a 99% fuel oil removal for oil loading rate from 0.82 to 4.91 g oil $l^{-1}d^{-1}$. Although this study performed at different TDS concentrations, but COD removal efficiencies at different stages were comparable.

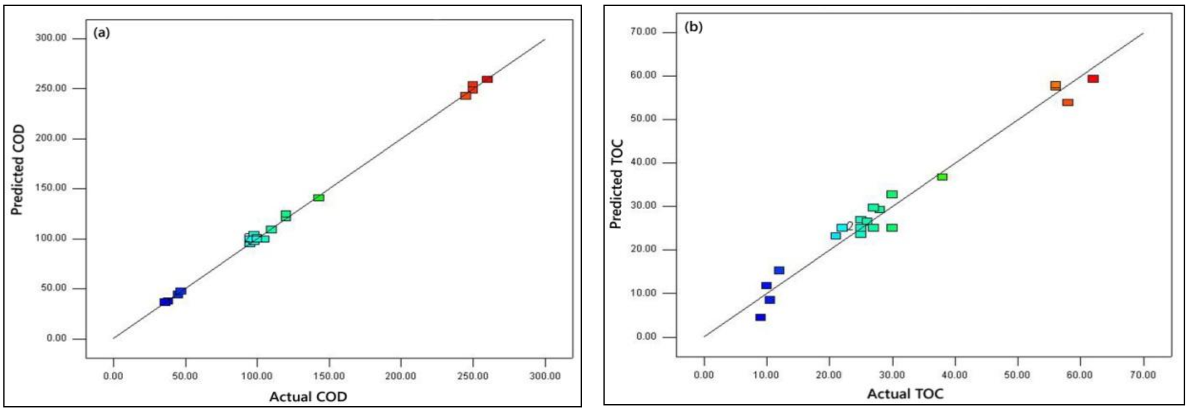


Figure 2(a): Comparison of actual and predicted COD; 2(b) Comparison of actual and predicted TOC

Table 2: Produced water reuse and discharge limits

Parameter	[1]Re-injection limits	[2]Discharge to sea limits
O&G (mg l^{-1})	42	42
SS (mg l^{-1})	<10	-
TDS (mg l^{-1})	-	-

[1][19]; [2][10]

Results showed that suspended solids concentration of permeate was less than detectable limits and O&G concentration was less than 5 mg l^{-1} during all runs. Based on Table 1 and results obtained in this study it could be concluded MSBR permeate can be reuse for re-injection to oil well to enhance oil recovery. Also it can discharge to sea because O&G concentration is less than discharge limits.

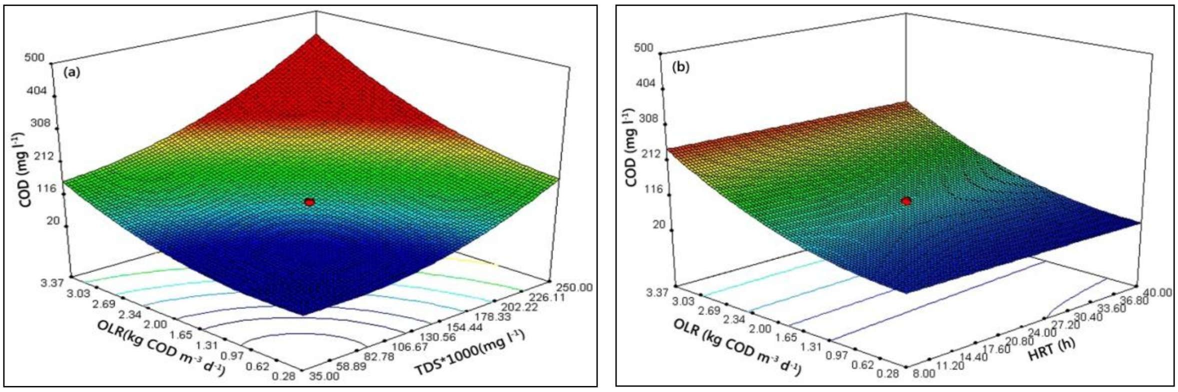


Figure 3(a): Response surface plot showing the effect of TDS and OLR on effluent COD; 3(b) Response surface plot showing the effect of HRT and OLR on effluent COD

Figure 3(b) shows effect of HRT and OLR on COD removal efficiency. It was found that there is no significant difference between COD removal efficiency from HRT of 20 h to 44 h. Similar results were obtained by Sutton et al. [21] who used MBR for treating oily wastewater. They showed that longer HRT did not improve the efficiency of oily wastewater treatment with membrane bioreactors. The HRT values ranged between 1.87 and 3.74 days and the COD removal rate remained at 90%. On the other hand, results showed that in lower TDS, effect of HRT was more than higher TDS. It may be due to effect of high salt concentration on activity of microorganisms.

CONCLUSIONS

The MSBR-system inoculated with acclimated tropical halophilic microorganisms showed an efficient, reliable and compact process for hypersaline produced water treatment without prior dilution. This study shows that response surface methodology was an appropriate method to predict proper conditions of the effluent suitable for discharge and/or reuse.

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