



Evaluation of membrane bioreactor for hypersaline oily wastewater treatment

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A B S T R A C T

Produced water is a significant waste stream generated in association with oil and gas production. It contains high concentrations of hydrocarbon constituents and different salts. In this study, a membrane sequencing batch reactor (MSBR) was used to treat synthetic and real produced water. The MSBR was evaluated in terms of biodegradation of hydrocarbons in the synthetic produced water with various organic loading rates (OLR) (0.281, 0.563, 1.124, 2.248, and 3.372 kg COD/(m³ day)), cycle time (12, 24, and 48 h), and membrane performance. The effects of salt concentrations at different total dissolved solids (TDS) (35,000, 50,000, 100,000, 150,000, 200,000, and 250,000 mg/L) on biological treatment of the pollutants in the synthetic and real wastewater were studied. At an OLR of 1.124 kg COD/(m³ day), an HRT of 48 h and TDS of 35,000 mg/L, removal efficiencies of 97.5%, 97.2%, and 98.9% of COD, total organic carbon (TOC), and oil and grease (O&G), respectively were achieved. For the real produced water, removal rates of 86.2%, 90.8%, and 90% were obtained 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.

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1. Introduction

Oil and gas filed wastewater or produced water is the highest waste volume generated from oil and gas extraction process. In some sites, for every barrel of oil, ten barrels of produced water are generated (Campos et al., 2002). The components of produced water generally include dissolved and suspended oil compounds, dissolved formation minerals, heavy metals, production chemical compounds, production solids, and dissolved gases (Hansen and Davies, 1994). The salt concentration of produced water varies from a few parts per thousand to that of a saturated brine (300,000 mg/L) (Neff, 2002) and O&G and TOC concentration reaches up to 565 and 1500 mg/L, respectively (Tibbetts et al., 1992). Currently, in the United States, produced water is not allowed for coastal discharge from shoreside oil and gas facilities. The current limits for O&G in treated produced water for ocean disposal in the United States

is maximum 42 mg/L on a daily basis and 29 mg/L average on a monthly basis (Neff, 2002), while, the monthly average limits of O&G discharge and COD prescribed by the Peoples Republic of China are 10 mg/L and 100 mg/L, respectively (Tellez et al., 2002). On the other hand, due to the increasing volume of the wastewater generated all over the world, it is a potential to reuse produced water as a supplement to limited fresh water resources in water-stress regions (Fakhru'l-Razi et al., 2009).

To reduce hydrocarbon pollutants from produced water, physical and chemical methods have been reviewed including photo-electrocatalytic decontamination, hydrocyclones, coagulation, and flocculation (Fakhru'l-Razi et al., 2009). Most of these treatment technologies are only suitable for primary treatment. However, a more efficient treatment technology should be employed before reuse and/or discharge to the environment (Campos et al., 2002).

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Biological treatment of wastewater is a cost competitive and environmental friendly alternative method to decompose organic compounds in wastewater, but salinity in produced water can affect the metabolism of microorganisms in activated sludge systems due to plasmolysis. However, in high concentration of salt, halophilic microorganisms can survive (Woolard and Irvine, 1995). Halophilic bacteria have been used in biological systems for treating low COD-produced water effectively (Tellez et al., 2002; Zhao et al., 2006). But in the oil fields industries, biological treatment of wastewaters that contain high concentration of hydrocarbon constituents and salts is particularly challenging due to the inhibition and/or toxicity of these compounds. Sequencing batch reactor (SBR) is a promising biological treatment, which includes a robust system, simple running, and high operation flexibility (Venkata Mohan et al., 2005). But salt concentration increases turbidity of biologically treated produced water (Pendashteh et al., 2010).

Combination of activated sludge systems and membrane filtration has many advantages including high effluent quality, retention of biomass and operating the system at high mixed liquor suspended solids (MLSS) concentration, small footprint (space), good disinfection capability, and higher volumetric loading (Le-Clech et al., 2006). Scholz and Fuchs (2000) investigated biodegradation of oily wastewater comprising fuel-oil, surfactant, and reverse osmoses (RO) water in a membrane bioreactor. The results showed that oily wastewater was treated with high efficiency, and complete retention of oil-degrading microorganisms was possible. However, till now there have not been enough investigations for treating high organic concentration of hypersaline oily wastewater by membrane bioreactor. The main objective of this study was to investigate the performance of a cross-flow membrane-coupled SBR for treating produced water with high concentration of COD and TDS 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.

2. Materials and methods

2.1. Experimental setup

A 5-liter fermenter (Biostat-B.Braun Biotech International, Melsungen, Germany) was used as the SBR (Fig. 1). Dissolved oxygen (DO), pH, temperature, aeration, and agitation were microprocessor controlled. The agitation speed was fixed at 300 rpm (Fakhru'l-Razi et al., 2010). Aeration was provided by using an air compressor and a sparger. The DO concentration was adjusted to 3 mg/L. The wastewater was fed by a peristaltic pump (Peristaltic pump model: Watson-101U/R, Watson-Marlow, UK). Mixed liquor was pumped through two tubular crossflow ultrafiltration (UF) membrane modules (MIC-RO 240, PCI membrane systems, UK) and recycled back to the bioreactor. The microorganisms retained by the membranes were returned to the bioreactor. Permeate flux was measured gravimetrically with an electronic balance (Tanita KD-200, Tanita corporation, Tokyo, Japan). The cross-flow velocity was 2 m/s. The UF-permeate was fed to a RO unit (PCI membrane systems, UK) for further treatment and desalination. Table 1 shows the UF and RO membrane characteristics.

Table 1 – UF and RO membrane characteristics.

Membrane		
UF (FP200)	Material	Polyvinylidene difluoride (PVDF)
	Tube diameter	1.25 cm
	Length	30 cm
	Molecular cut-off weight (MWCO)	200,000 Dalton (Da)
	Membrane area	0.012 m ²
	Operating pressure	2 bar
RO (ACF 99)	Material	Polyamide film
	Tube diameter	1.25 cm
	Length	30 cm
	Membrane area	0.012 m ²
	Operating pressure	60 bar

2.2. Synthetic wastewater preparation

To determine the response of the MSBR under a controlled environment, synthetic wastewater was used. Based on halophilic medium proposed by other researchers (Peyton et al., 2002; Woolard and Irvine, 1995), produced water was simulated. The synthetic produced water constituents (TDS of almost 35,000 mg/L) in mg/L included:

NaCl : 31, 173; CaCl₂·2H₂O : 60; KCl : 2000; MgCl₂·6H₂

O : 50; NaHCO₃ : 800; NH₄Cl : 860; KH₂PO₄ : 99.

For TDS concentrations of 50,000 mg/L, 100,000 mg/L, 150,000 mg/L, 200,000 mg/L, and 250,000 mg/L, NaCl was added at 46,000 mg/L, 96,000 mg/L, 146,000 mg/L, 196,000 mg/L, and 246,000 mg/L, respectively. The composition of the wastewaters gave a C/N/P ratio of approximately 100/10/1 by adding NH₄Cl and KH₂PO₄. The pH was adjusted to 7 using NaOH. All the chemicals used in this study were of technical grade. Crude oil and real produced water were collected from Malaysia oilfields (Petronas BCOT, Sarawak). The synthetic produced water was prepared by mixing salts and crude oil in a 5-liter propylene container for 24 h (2400 min⁻¹) in a homogenizer (KIKA labortechnik, Staufen, Germany) to achieve equilibrium between the oil and water phases (Tansel et al., 1995). Biochemical oxygen demand (BOD), COD and O&G of the synthetic produced water (1 mL oil/L) were 645 mg/L, 2250 mg/L and 350 mg/L, respectively.

2.3. Real produced water

Real produced water samples were transported to the laboratory and stored at 4 °C until their utilization. All samples were thawed before feeding. The characteristics of the produced water are given in Table 2. The wastewater pH was adjusted to 7 by means of HCl before feeding to the fermenter. NH₄Cl and KH₂PO₄ were added as supplementary nutrients.

2.4. Culture selection

Hypersaline soil from Morib onshore in Malaysia served as a source of halophilic microorganisms. Isolation of microorganisms capable of degrading crude oil in the hypersaline-produced water began by placing approximately 6 g of soil into 200 mL of the synthetic produced water (1 mL oil/L and TDS of 35,000 mg/L). After 15 days 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 three steps of

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