

Feature Article

## Produced water treatment by membranes: A review from a colloidal perspective



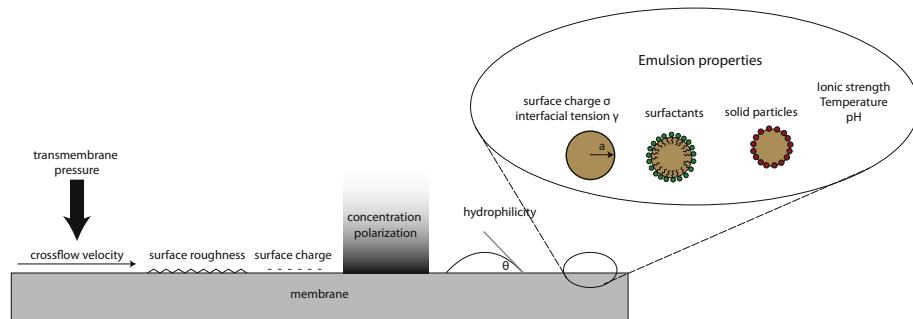
J.M. Dickhout <sup>a,c</sup>, J. Moreno <sup>a,c</sup>, P.M. Biesheuvel <sup>a</sup>, L. Boels <sup>b</sup>, R.G.H. Lammertink <sup>c</sup>, W.M. de Vos <sup>c,\*</sup>

<sup>a</sup> Wetsus European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA Leeuwarden, The Netherlands

<sup>b</sup> Shell Global Solutions International BV, Kessler Park 1, 2288 GS Rijswijk, The Netherlands

<sup>c</sup> Membrane Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

### GRAPHICAL ABSTRACT



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### ABSTRACT

While the world faces an increased scarcity in fresh water supply, it is of great importance that water from industry and waste streams can be treated for re-use. One of the largest waste streams in the oil and gas industry is produced water. After the phase separation of oil and gas, the produced water is left. This mixture contains dissolved and dispersed hydrocarbons, surfactants, clay particles and salts. Before this water can be used for re-injection, irrigation or as industrial water, it has to be treated. Conventional filtration techniques such as multi media filters and cartridge filters, are able to remove the majority of the contaminants, but the smallest, stabilized oil droplets ( $<10 \mu\text{m}$ ) remain present in the treated water. In recent years, research has focused on membranes to remove these small oil droplets, because this technology requires no frequent replacement of filters and the water quality after treatment is better. Membranes however suffer from fouling by the contaminants in produced water, leading to a lower clean water flux and increased energy costs. Current research on produced water treatment by membranes is mainly focused on improving existing processes and developing fouling-resistant membranes. Multiple investigations have determined the importance of different factors (such as emulsion properties and operating conditions) on the fouling process, but understanding the background of fouling is largely absent. In this review, we describe the interaction between the membrane and a produced water emulsion from a colloidal perspective, with the aim to create a clear framework that can lead to much more detailed understanding of membrane fouling in produced water treatment. Better understanding of the complex interactions at the produced water/membrane interface is essential to achieve more efficient applications.

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\* Corresponding author.

E-mail address: [w.m.devos@utwente.nl](mailto:w.m.devos@utwente.nl) (W.M. de Vos).

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## 1. Introduction

Produced water (PW) is the largest waste stream in the oil and gas industry, with a global estimated 3:1 volume-to-product ratio [1], adding up to an estimated volume of 21 billion barrels per year in the US and 50 billion barrels per year in the rest of the world over 2009 [2]. Therefore, regulations concerning produced water are necessary to avoid discharge of this waste water into the environment. In the North Sea Region, OSPAR regulations set the upper limit for oil content in discharged water at 30 mg/L [3]. Treating the vast amounts of PW in a cost-effective way on sometimes remote locations (such as offshore platforms) demands smart solutions, often a combination of several separation processes, so the water can be safely discharged or re-used for other purposes. Conventional treatment methods, such as hydrocyclones, gas flotation, adsorption, media filtration and macro-porous polymer extraction (MPPE) are able to remove most of the oil and other harmful components from the PW [4].

Membrane technology is an emerging technology in the field of PW treatment. Membranes can remove the smallest ( $<10\text{ }\mu\text{m}$ ) and most stable oil droplets from PW and can be tailored to the specific properties of the oil well involved. All membranes, however, suffer from fouling, in which a layer of oil, solids and other PW components forms on the membrane surface. This leads to decreased flux and thus increasing operating costs. Most membranes can be cleaned, but this often requires extra chemicals or energy, as well as downtime of the treatment installation. Reducing membrane fouling and improving membrane operation can thus lead to a decrease in operating costs and an increase in the application of membrane technology for PW treatment. In literature numerous examples can be found of optimized treatment processes, but surprisingly little articles attempt to understand the background and mechanics of membrane fouling [5–7]. In this review, we attempt to give a base of knowledge to work towards understanding membrane fouling in PW treatment with membranes. In the following sections, we will first discuss the properties of PW from a colloidal view, and the expected influence of the compounds found in PW on the emulsion stability. After that, we will discuss membranes and the surface chemistry taking place at the membrane surface, and finally we will summarize multiple examples from literature on

the separation of both simple and complex oil-in-water emulsions, including PW.

## 2. Produced water as an emulsion

PW is an oil-in-water emulsion, where the oily phase is dispersed in the aqueous phase, stabilized by surfactants. The composition of PW varies between oil fields and usually changes as the oil field ages. The main components of PW are dispersed oil, dissolved organics, suspended solids and dissolved inorganics. Additionally, process chemicals such as corrosion inhibitors, biocides and extraction enhancers can be added [8]. These molecules act as surfactants and play an important role in the emulsion stability of produced water. Typical values for produced water contents are presented in Table 1.

In order to understand PW, we will first focus on some basic principles of emulsions. Most emulsions are thermodynamically unstable. Because the interfacial area between water and oil increases when making an emulsion, the free energy in the system increases, which can be described as

$$\Delta F = \gamma \Delta A (J), \quad (1)$$

where  $\Delta F$  is the change in free energy,  $\gamma$  is the interfacial tension and  $\Delta A$  is the change in interfacial area. As can be seen from Eq. (1), making an emulsion costs energy. This necessary energy can be provided by stirring or mixing at high speeds [10,11],

**Table 1**

Ranges and mean values of the main components of produced water as found in 23 samples from offshore oil platforms in Brazil. Benzene, toluene, ethylbenzene, xylene (BTEX), polycyclic aromatic hydrocarbons (PAH), total organic carbon (TOC), total petroleum hydrocarbon (TPH), total suspended solids (TSS) and salinity. Data reproduced from [9].

Compound	Range (mg/L)	Mean (mg/L)
BTEX	1.4–20	4.9
PAH	0.44–0.61	0.53
TOC	86–971	307
TPH	86–971	10
TSS	1.9–106	11
Salinity	38,182–179,766	75,434

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