



## Comparative study of NF and RO membranes in the treatment of produced water—Part I: Assessing water quality

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### HIGHLIGHTS

- The new hydrophilic NF/RO membranes were used for treatment of produced water.
- The hydrophilic properties are anticipated to show a low level of membrane fouling.
- The NF treated water met standards for drinking water except for three parameters.
- The RO treated water has potential for reuse as indirect potable water.
- The NF membrane may be used as a pre-treatment for the RO.

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### ABSTRACT

This study compared the filtration of produced water using two new and highly hydrophilic nanofiltration (NF) and reverse osmosis (RO) membranes to assess removal efficiency in pre-and-post-filtration processes, and to compare the quality of water obtained against standards for reuse as indirect potable water. The results show that NF membrane successfully attains 96% of overall drinking water standards, despite its inefficiency in removing boron, molybdenum and ammonia. The study also found that the NF membrane can be used as a pre-treatment for the RO membrane to produce high quality water and reduce contaminant concentrations, thereby minimizing the potential for fouling. In contrast, the produced water treated by the RO membrane successfully met the regulatory quality standards for drinking water, with the exception of the parameters for ammonia and molybdenum. The study concluded that treated produced water has potential for reuse as indirect potable water and that both of the hydrophilic NF and RO membranes studied are suitable for treating produced water to yield a promising source of water.

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### 1. Introduction

As the world's population and the consequent demand for water supply increase, sustainable development and conservation of the precious and increasingly scarce resource of water will require maximal reuse and recycling. So far, endeavors [1–3] in produced water treatment using membrane technology have not attained optimal reuse of produced water because >99% of this water is disposed into the environment [4]. Consequently, water resource sustainability concerns suggest exploring the potential of reusing treated produced water (viz., treatment up to disposal standards) as a promising source of water.

Produced water is generated in the petroleum industry as a by-product of various processes in production and refining [5]. In the production phase, three barrels of produced water are generated

for every corresponding barrel of oil produced per day [6]. This ratio increases as oil wells mature and may reach 7–10 barrels, especially in mature oilfields [7]. Given the actual oil production in 2011 (72,560,000 bbl/d) [8], and the minimum ratio of 3 barrels of produced water against each barrel of oil produced, a minimum of 217,680,000 bbl/d of produced water was generated in 2011 alone, counting only conventional oilfields. Additional produced water generated from natural gas wells, coal-bed methane wells, shale gas wells, tight gas sands [9] and oil sands [4] would imply a total volume of produced water up to five times that of the volume of oil produced. On the contrary, in the refining phase, every barrel of crude consumes 2.5 barrels of process water [10]. As the demand for energy needs increases, the total global capacity of refineries will increase, as reflected in the rise in 2012 of more than 88 million bbl/d in 655 refineries, up from 82 million bbl/d in 2002 [8]. The total volume of process water consumed by the current global capacity of refineries is more than 220 million bbl/d of produced water generated every day, in the

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refining phase. The volume of produced water will increase as the demand for oil increases. Currently, the total volume of produced water from upstream and downstream processes in the petroleum industry exceeds 437 million barrels per day, wherein only less than 1% is recycled for the purpose of reuse [4]. By 2035 the demand for oil is anticipated to reach 110 million bbl/d [11], which implies that the volume of produced water will exceed 605 million bbl/d. Compared with the 66.4 million m<sup>3</sup> of potable water generated every day from the desalination industry [12], a similar percentage (77.3%) of such a volume of produced water (which amounts to 51.36 million m<sup>3</sup>) is generated and discharged daily from the petroleum industry. The rate of disposal of such water (which meets environmental discharge regulations) does not approach the required rate of natural water replenishment, which implies a significant depletion of water resources in the near future.

In recent times, three produced water treatment projects aimed at indirect reuse as potable water using membrane technology have helped turn produced water from a so called “pollution source” discharged from downstream and upstream processes of the petroleum industry into a new water “resource”. The first initiative has been taken by the Chennai Petroleum Company Limited (CPCL), which installed UF and RO membrane units (as post-treatment steps) in the Chennai refinery to treat and recycle produced water in the refinery and to provide a solution to the water shortage problem in the surrounding community, where 4.5 million inhabitants faced difficulties obtaining clean water [13]. In the 1980s, the refinery fed 60% of its treated produced water into the water supplies of the surrounding Chennai community. In the 1990s, the produced water treatment plant was upgraded with UF hollow fiber membranes (Koch membrane systems, Wilmington, MA) as a pretreatment to RO membranes to control fouling membrane, and in 2004 the RO plant was upgraded with 8822XR-400 RO membranes (Koch membrane system, Wilmington, MA). Simultaneously, the number of UF membrane units was increased to extend the lifetime of RO membranes, and the period of membrane replacement was thereby enhanced to 4–5 years instead of 1–1.5 years. The installation of UF membranes improved the quality of the RO feed to contain less than 0.1 NTU turbidity. The silt density index of fouling achieved a value of less than two and the performance of the membrane system exhibited 90% recovery. The resultant water production of 430,000 L of treated water per hour rendered this project one of the largest reclamation projects in India [13]. The second pioneer was the San Ardo water reclamation project in California, which represents the largest-scale application of RO membrane technology (as a post-treatment step) for produced water treatment in upstream processes in the petroleum industry today [14]. Because of the large amount of produced water (containing 7000 mg/L of total dissolved solids (TDS)) generated from the San Ardo oilfield, which reached 10 barrels/day of water for every barrel of oil produced, the adoption of water resource sustainability led to the establishment of this project. The plant produces more than 50,000 bbl/d of treated produced water for reuse to recharge the groundwater basin and supply fresh water using an Optimized Pretreatment and Unique Separation (OPUS™) technology based on RO membranes. The process includes multiple steps of pre-treatment consisting of heat exchange, degasification, chemical softening, media filtration and ion exchange softening for the RO feed. The effluent from these unit operations is then pumped through a double-pass RO system at a high pH. The permeate of an RO membrane (<76 mg/L TDS) was used for two purposes: first, to discharge treated produced water to constructed wetlands before re-injecting it into the groundwater recharge basins and, second, to use the treated produced water during the oil production process [14].

Yet another project for produced water reclamation using membrane technology is located in the oilfield in Wellington, Colorado, U.S.A. [4]. This oilfield began production in 1923 and operated until 2007, by which time its produced water exceeded 98.5% of total yield, and led to the increment of \$1 per barrel of produced water in re-injection and

disposal costs. Consequently, membrane technology was employed to remove the pollutants from the contaminated water by using both ceramic MF and RO membranes for reuse in beneficial uses. The first stage of treatment included dissolved air flotation, pre-filtration, ceramic MF membrane and activated carbon adsorption, and the treated produced water from these processes was then pumped to a groundwater aquifer to be recycled naturally before being extracted and resent to the RO plant for the final stage of treatment. The treated water from the RO membrane supplied more than 93,600 gallons of potable water per day for the people of Wellington [4].

To reiterate a key finding from these three aforementioned case studies, membrane technology reserves the highest potential in the final stages of produced water treatment (viz., as a post-treatment or in applying an effective technique for pre-treatment prior to membrane technology). The complexity of produced water content requires multiple steps of pretreatment before being fed to membranes to prevent membrane fouling. This is because the composition of produced water depends mainly on the geological and operational conditions experienced by the water [5] in its journey through different phases and processes in the petroleum industry, and is thus characterized by a multitude and diversity of complex constituents [9]. Produced water's complex composition creates several challenges for membrane technology applications, wherein the efficiency and efficacy of these applications are: (i) highly dependent on the knowledge of produced water's characteristics (prior to the actual treatment), and (ii) enhanced essentially by warding off fouling impacts and consequently extending the life of the membranes. For example, by applying low-fouling membranes such as hydrophilic membranes and choosing a suitable pretreatment technique such as a NF membrane when implementing RO membrane technology for produced water treatment. In pursuing these options, however, existing and applied traditional technologies are facing technical challenges in achieving the desired degree of reusability, which requires the removal of very small dissolved ions and organic molecules from produced water to meet the standards required for discharge or reuse [15]. In contrast, little research exists on the potential of the NF membrane as a pre-treatment step for produced water reclamation, especially when compared with those investigating this for other types of membranes such as MF or RO membranes [16,17]. Therefore, there is a dearth of information in the existing literature [18–20] regarding produced water treatment using hydrophilic NF and RO membranes, particularly a comprehensive assessment of water quality and toxicity removal for the reuse of treated produced water as indirect potable water. To that end, this study compared the filtration of produced water using two new and highly hydrophilic NF (as pre-treatment) and RO membranes, which have a low fouling tendency [21]. We assessed water quality in treating produced water in pre-and-post-filtration processes, and compared the quality of the water obtained against standards for reuse as indirect potable water. These membranes (NF1 and RO-BW30) were characterized in other work, using different techniques, namely: contact angle, attenuated total reflectance-Fourier transform infrared spectroscopy, field emission scanning electron microscopy, X-ray photoelectron scattering and membrane permeation. The findings of previous work revealed that the selected membranes are super hydrophilic and thus competitive when compared with other commercial membranes, and showed potential for produced water treatment.

## 2. Methods and materials

Two new hydrophilic commercial membranes were used in produced water filtration processes, namely RO-BW30 and NF1 membranes, and their properties and techniques used for characterization are described in Table 1. Both membranes were manufactured from polyethersulfone and supplied by AMFOR INC®, China and were found to be super hydrophilic compared with other commercial membranes, as shown in Table 8. All chemicals, solvents and reagents used in the course of experiments were of analytical grade with high purity.

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