ARTICLE IN PRESS

Desalination xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Evaluation of integrated microfiltration and membrane distillation/crystallization processes for produced water treatment

Aamer Ali[a], Cejna Anna Quist-Jensen[b], Enrico Drioli[a,c,d,e], Francesca Macedonio[a,b,*]

[a] National Research Council, Institute on Membrane Technology (ITM– CNR), Via Pietro BUCCI, c/o University of Calabria, cubo 17C, Rende 87036, Italy
[b] Department of Chemistry and Bioscience, Section for Chemistry, Aalborg University, Fredrik Bajers vej 7H, Aalborg ø 9220, Denmark
[c] Department of Environmental and Chemical Engineering, University of Calabria, Rende 87036, Italy
[d] Hanyang University, WCU Energy Engineering Department, Seoul 133-791, South Korea
[e] Center of Excellence in Desalination Technology, King Abdulaziz University (KAU–CEDT), Jeddah 21589, Saudi Arabia

ARTICLE INFO

Keywords:
Produced water treatment
Membrane engineering
Thermodynamic analysis
Exergy
Process intensification metrics

ABSTRACT

Proper management and treatment of *produced water* has emerged as a big challenge for oil and gas industry. Increasingly stringent environmental regulations and economic constraints are compelling the use of more advanced treatment methods. Membrane operations are gaining significant interest for this application due to their broad range of separation capabilities, high efficiency and low operational cost. Commercially less-adopted membrane operations, such as membrane distillation (MD) and membrane crystallization (MCr) are gaining significant interest for produced water treatment due to their almost concentration-independent performance and less fouling potential. The current study analyzes the performance of an integrated microfiltration (MF) and direct contact membrane distillation (DCMD)/membrane crystallization (MCr) system for freshwater and minerals recovery from produced water. Based on the experimental data, thermodynamic/exergetic/quantitative analyses have been performed. Performance of the integrated processes has been compared with the conventional multi-stage flash (MSF) in terms of *process intensification metrics*.

1. Introduction

Produced water refers to the waste stream generated in oil and gas industries. It is a complex mixture of several organic and inorganic compounds. The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geologic formation, and the type of hydrocarbon product being produced. Produced water properties and volume also vary throughout the lifetime of a reservoir. The composition of produced water from different sources can vary by order of magnitude. The major compounds of produced water include [1,2]:

- dissolved and dispersed oil compounds,
- dissolved formation minerals,
- production chemical compounds,
- production solids (including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes),
- dissolved gases.

Proper treatment and management of produced water is necessary to avoid possible negative environmental impacts associated with its discharge [3]. From an economical point of view, management of produced water can become a key factor in controlling the production volume. Moreover, the treatment of produced water provides interesting opportunities to reuse it for exploration activities, irrigation, washing and miscellaneous other local needs [4].

A large number of biological, physical, chemical and physicochemical treatments have been tried for produced water treatment [2,5]. Very fewer efforts have been devoted towards exploiting the potential of minerals recovery from this stream [6,7]. Concentration of a number of minerals in produced water streams from different geographical regions is much higher than seawater. This fact adds motivation of recovering minerals from these streams, particularly in current scenario when the traditional mining industry is under extreme stress and the difference between the demand and supply of some strategic elements is increasing beyond the sustainable limit [8].

Membrane technology offers an interesting way to exploit the full potential of produced water. Membrane operations have been applied to achieve various separations in produced water treatment [9–13]. The main drive behind the use of membrane operations include less energy requirement, large range of achievable separations, small footprint, light weight, less corrosion issues and easy scaling up. The applications of membrane operations in produced water treatment range from mild treatment aiming at the removal of suspended solids to desalination.

* Corresponding author at: National Research Council, Institute on Membrane Technology (ITM– CNR), Via Pietro BUCCI, c/o University of Calabria, cubo 17C, Rende 87036, Italy.
E-mail addresses: f.macedonio@itm.cnr.it, macedonio@unical.it (F. Macedonio).

https://doi.org/10.1016/j.desal.2017.11.035
Received 22 May 2017; Received in revised form 22 November 2017; Accepted 22 November 2017

Please cite this article as: Ali, A., Desalination (2017), https://doi.org/10.1016/j.desal.2017.11.035

Effectiveness of microfiltration (MF) for the removal of suspended particles and turbidity has been well acknowledged [14–16]. MF systems have been generally integrated with a pre-treatment or post-treatment step to reduce the membrane fouling and to achieve the desired permeate quality, respectively [17,18]. MF has also been studied as pre-treatment step for the other membrane operations such as ultrafiltration (UF) and nanofiltration (NF) for the treatment of produced water [17]. Aside suspended particles and turbidity, MF has also been applied for the removal of oil from water before final discharge or subsequent treatment [19,20]. Ceramic membranes have been mostly applied for these studies due to their better mechanical properties, long lifespan and high thermal and chemical resistance.

Recently, MD has gained significant attention for desalination of produced water. The main characteristics of the process, which make it interesting for this particular application, include operational performance almost independent of solution concentration, ability to use low grade heat generally available with produced water, ultra-pure product quality and less fouling and scaling potential [21]. Technical feasibility of produced water treatment by using MD has been demonstrated in recent literature. The main configurations tested include direct contact MD [22,23], air gap MD [24,25] and vacuum MD [26]. Distillate of excellent quality has been achieved in these investigations.

Potential of MD to concentrate the solutions to their saturation level, without significant decay in performance, has been well exploited as membrane crystallizer. In membrane crystallization (MCr), crystals and freshwater are extracted simultaneously from saturated solution. Membrane crystallizers have several advantages over the state-of-the-art crystallizers including homogeneous saturation throughout the solution at any time, separation of evaporation and crystallization steps, narrow crystal size distribution and easy-to-tune crystal morphology [27,28]. The process has been recently applied for salts recovery from produced water [7] and to mitigate the scaling problem in MD [29]. The process can be applied to recover valuable and strategic minerals from produced water or to concentrate the solution for subsequent use in chlor-alkali process [6].

In the present work, the potentiality of an integrated MF plus MCr membrane process for PW treatment was analysed. First of all the membrane-based process was studied from a thermodynamic point of view (for estimating the amount of salts that can be obtained from the utilized PW). The output of the thermodynamic simulation was compared with the results of the experiments. Details about experiments (flux, operating conditions, amount of recovered crystals etc.) on MCr for produced water treatment can be found in [7]. Experimental data allowed analyzing the performance of the system also in terms of *conventional Process Intensification Metrics* (in terms of amount of desalted water obtained, energy consumption of the process, amount of produced waste) and from an exergetic point of view (for the individuation of the sites of greatest losses). Afterwards, the developed simulations were utilized as general approach for the analysis of a membrane-based process treating different produced water streams. The process was quantitatively analysed via "conventional" and "innovative" process intensification metrics with the aim to compare the performance of membrane and conventional systems in produced water treatment.

Table 1
Main properties of the feed PW.

Property	Value
Cl^-, ppm	144.057
Na^+, ppm	76.646
$SO_4{}_-{}^2$, ppm	1.213
Mg^{+2}, ppm	8.361
Ca^{+2}, ppm	6.065
$PO_4{}^{-3}$, ppm	1.055
K^+, ppm	1.396
$NO_3{}^{-1}$, ppm	613
F^-, ppm	472
TDS, ppm	240.000
P, MPa	0.1
T, °C	25

2. Evaluation of an integrated MF and MCr process for produced water treatment: Theoretical and experimental study

The system considered for the analysis has been described in a previous publication [7,23] and is shown in Fig. 1. Microfiltration and activated carbon filtration were utilized as pre-treatment for oil separation, removal of suspended solids and removal of H_2S. Then, MCr was applied for desalination and salts recovery. The analysis was performed for a 200 L/h plant.

In Table 1 the main properties of the considered produced water can be found. The operative conditions, membrane and module properties for MCr are provided in Table 2 and are referred to the conditions utilized during the experiments. In particular, in the referred study [7] it was experimentally proved that high quality NaCl crystals (purity > 99.9%) can be obtained from the analysed produced water (Table 1).

2.1. Thermodynamic modeling through PHREEQC solubility software

As simulation tool for salt precipitation, the geochemical software PHREEQC (interactive-version 3) using the Pitzer specific-ion-interaction aqueous model [30] was adopted. Input parameters for PHREEQC are the concentration of the different species in the treated produced water (Table 1), along with other specifications including temperature and pH. The output of the software provides the saturation index (SI) of all possible salts. The saturation index, comparing ion activity product (IAP) with the solubility product (*Ksp*), indicates the eventual salts precipitation.

$$SI = \frac{IAP}{K_{sp}} \tag{1}$$

If *SI* is negative, the solution is unsaturated, when *SI* is positive the solution is supersaturated with respect to that salt and it precipitates as crystal. Therefore, PHREEQC can be used to predict the order in which the salts precipitate from the considered produced water. Another output of PHREEQC is "yield", i.e. the amount of salts that can be recovered per m^3 of treated water. In Fig. 2, the comparison of the results of the simulation via PHREEQC with those of the experiments is illustrated. It can be seen that precipitation of NaCl begins for both the model and experiments close to a recovery factor of 30%. Moreover, after this point, both the results of the simulation and those of the

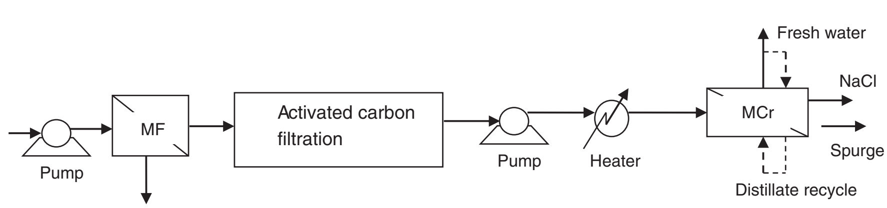

Fig. 1. Flow sheet of the analysed process.