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Validation of recycled membranes for treating brackish water at pilot scale

Raquel García-Pacheco[a,*], Junkal Landaburu-Aguirre[a], Patricia Terrero-Rodríguez[c], E. Campos[c], Francisco Molina-Serrano[c], Javier Rabadán[a], Domingo Zarzo[c], Eloy García-Calvo[a,b]

[a] IMDEA Water Institute, Avenida Punto Com. n°2. 28805, Alcalá de Henares, Madrid, Spain
[b] Chemical Engineering Department, University of Alcalá, Ctra. Madrid-Barcelona Km 33.600, 28871. Alcalá de Henares, Madrid, Spain
[c] Molina de Segura, 8, 30007, Murcia, Spain

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ABSTRACT

Over the 65% of the installed desalination capacity is related on reverse osmosis (RO) membrane technology. However, membranes have to be replaced when fouling effect is irreversible. In fact, it is estimated that > 840,000 end-of-life RO membranes modules are discarded annually at worldwide scale, mostly in landfills.

In this study, end-of-life RO membranes were recycled at pilot scale by using concentrated solutions of free chlorine. Chemical attack enables the removal of polyamide layer partially or totally, obtaining nanofiltration (NF) and ultrafiltration (UF) membranes, respectively. 5 diverse end-of-life models were tested. Recycled membrane performance (permeability and rejection coefficients) was identified by filtering natural brackish water (BW). Further, validation test were conducted in order to analyze the recycled membrane stability by filtering BW long-term at Cuevas del Almanzora Desalination plant. For this purpose, two real pressure vessels with the capacity of hosting 6 membranes each were adapted. Recycled membranes did not show performance decline after 4 month of filtration. Promising results have been observed. Recycled seawater membranes with properties between RO and NF were validated as potentially fusible membranes. Recycled BW membranes, with high sulphate ion selectivity, were evaluated as a potential alternative of the current NF commercial membranes.

1. Introduction

As a result of population growth, urbanization and cyclical droughts, water demands will significantly increase by 2050. The water consumption is estimated to increase around 20% (considering only agriculture sector) [1]. In this context, diverse type of fresh water sources will be most necessary to achieve this goal. Nowadays, alternatives should be focused on using a variety of sources, such as local and imported surface water, groundwater, desalinated brackish water (BW), desalinated seawater (SW) and recycled water [2]. Membrane technology can be applied to produce fresh water production from all those resources and consequently, it is expected to keep growing for the coming decades.

Desalination for agriculture by membranes is a feasible option to obtain fresh water, some of the key factors are i) there is water economy dependency, which need non fluctuation resource; ii) there is existing infrastructure for water distribution, iii) the distance between plant and the available cultivated area is close to the desalination plant (lower water pumping cost), iv) water supply governance (who owns, takes the initial investment and manages the plant) and v) environmental regulations [3,4]. In Spain, around 75% of water demands comes from agriculture and irrigation (in areas such as Almería it can be > 90%) [5], which explains the search of alternative water sources. Águilas-Guadalentín SW reverse osmosis (SWRO) plant (Murcia, 210,000 m^3 day^{-1}) and Carboneras SWRO plant (Almería, 120,000 m^3 day^{-1}), are clear examples of desalination plants for water irrigation usage in regions with cyclic droughts and water scarcity [5]. In 2015 desalinated SW production for agriculture in south east Spain (including Almería region) was 105 millions m^3, with a maximum capacity of 170 million m^3, which represents 11.2% of the overall water resources in the area [6,7].

Spiral wound TFC-polyamide (PA) membranes dominates the desalination market, holding 66.5% of the total installed capacity (86.8 Hm^3 day^{-1}) [8]. Therein this way, the membrane market is mature and high standardized. According to manufactures specification, RO membranes achieve an average of 99.6% NaCl rejection coefficient (data estimated from 89 RO membranes datasheets of Toray, Hydranautics, Dow Filmtec and Koch). Additionally, while many strategies are applied in order to prolong membrane lifespan, fouling is inevitable and membranes are replaced once do not recover their performance after cleaning procedures [9]. The average replacement rate is commonly between 10 and 20% for SW desalination and between 5

* Corresponding author.
E-mail address: raquel.pacheco@imdea.org (R. García-Pacheco).

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and 10% for BW desalination [10,11] with an associated cost between 5%–8% of the total produced water cost [5,12]. Recently, Landaburu-Aguirre et al. [9] have estimated that > 840,000 end-of-life RO membranes are discharged annually at worldwide (equivalent to > 14,000 Tn $year^{-1}$).

Alternative managements to end-of-life membrane disposal such us direct reuse, direct recycling, indirect recycling or energy recovery have been summarized in literature [9,13,14]. Among all of them, the most studied process is direct recycling. In this case, chlorine is the most used agent to alter membrane performance since it is globally accepted that PA membrane has a chlorine tolerance level below 1000 ppm h [15]. In fact, most of the studies have been focus on ultrafiltration (UF) transformation since the beginning [16,17] and even more, there is a pilot scale study which showed promising results of reusing UF recycled membranes to treat wastewater [18]. In addition, Ettori et al. [19] investigated at pilot scale (4″ spiral wound modules with 7.9 m^2 membrane area) the degradation of RO membrane due to the presence of free chlorine in the filtering water. However, since the accumulated free chlorine dose was up to 4000 ppm h, only nanofiltration (NF)-like properties could be observed. More integral approach has been reached by other authors conducting recycling experiments at laboratory scale until reaching NF and UF performance [20–22]. Indeed, García-Pacheco et al. [21] showed a high selective separation coefficients of all recycled membranes transformed to NF performance, especially for sulfate anions. Molina et al. [22] conducted an exhaustive membrane surface characterization of NF and UF recycled membrane (contact angle, ATR-FTIR, SEM, MWCO and Feret Diameter). Moreover potential markets associated to membrane direct recycling and reuse have been discussed in García-Pacheco et al. [14]. In this publication it is shown the potential clients of recycled membranes, investors and social barriers. Nevertheless, even though there is a recognized potentiality of the recycled membranes, to the knowledge of the authors no reusing NF recycled membranes experiences at pilot or real scale have been found.

In this way, the goal of this work is to investigate at pilot scale the direct recycling process and to validate recycled membranes for BW treatment. Recycled membranes were operating for the first time in a real desalination facility during 4 months and results are compared with commercial NF membranes.

2. Materials and methods

2.1. Membrane and chemical reagents

All transformation assays were performed on several spiral wound end-of-life PA RO membrane (8″ diameter modules). During membrane lifespan, membranes were used to treat BW and SW. Membranes are classified with the following nomenclature: i) SW or BW, ii) number, which is related to the desalination plant where they came from and iii) letter, which deals with the membrane model. Totally, 5 membrane models were employed from 7 different desalination plants. Pristine commercial NF membranes were also used to compare their performance with the recycled membranes and are called NF-1 and NF-2. All membranes were conserved in sodium bisulphite (500–1000 ppm) solution prior to be analyzed. Membrane fouling was identified by autopsy, which required dismantling the spiral wound (Fig. 1). Fouling characterization results are shown elsewhere [22,23]. Table 1 summarizes information of the end-of-life RO membranes such as the desalination plant where membranes were installed, end-of-life membrane weight, initial permeability, initial salt rejection coefficients and fouling type.

Sodium hypochlorite (NaOCl, 14%) was used for membrane recycling and was purchased from Lejías Navarro (Murcia, Spain).

2.2. Membrane transformation protocol

The conceptual scheme employed to conduct the recycling process

Fig. 1. End-of-life RO membrane autopsy: a) dissection of membrane module; b) extraction of membranes coupons and c) membrane storage.

is shown in Fig. 2. NaClO, was used to carry out controlled degradation of the selective PA layer of the end-of-life membranes. In this way, end-of-life RO membranes were converted into NF or UF membranes, depending on the degree of exposure of the membrane to free chlorine.

The pilot recycling system (Fig. 3) consists of the following parts: i) passive recycling reactor, which at the same time has a structure that can contain vertically 6 spiral wound membranes. The structure is hold by a cylindrical PP container that is filled with the solutions; ii) low pressure pumps, iii) valve circuits, iv) 1 m^3 containers that storage the NaClO and $NaHSO_3$ solutions and v) 5 m^3 container used to carry out the neutralization of free chlorine with sodium bisulphite.

The direct protocol used is outline below:

NaClO was prepared by diluting the commercial product in water (permeate of RO desalination plant with around 365 µS/cm conductivity) until achieving the free chlorine concentration set for the experiments (ranged between 6000 and 16,000 ppm). This solution was reused for all the transformation experiments and its free chlorine concentration was regulated according to the in situ determination of pH, conductivity and redox. Therefore, commercial NaClO was added when necessary in order to guarantee a constant concentration in each assay. Moreover, sodium bisulphite ($NaHSO_3$) solution was prepared by diluting the commercial reagent (around 3 mg of $NaHSO_3$ per 1 mg free chlorine) with water and it was stored in other chemical storage container.

Six end-of-life membranes were placed in the structure (using a hoist when necessary). Then, NaClO solution was transferred to the membrane container. When the reactor was fulfilled ¾ parts of its volume, transversal circulation was applied in order to homogenize the