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Treatment of cleaning waters from seawater desalination reverse osmosis membranes for reutilization purposes. Part I: Application of Fenton process

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ABSTRACT

The scope of the present work is the study of the Fenton process applied to the removal of the organic load of cleaning waters from seawater desalination reverse osmosis membranes in order to be reused for irrigation or in other stages of the process and contribute to the concept of zero discharge in a reverse osmosis desalination plant. Fenton experiments were performed at pH 3 after selecting ratios of H_2O_2/COD (wt.) between 1.9 and 20, and H_2O_2/Fe^{2+} (wt.) between 0.13 and 82.80. For the studied conditions, it was observed that the optimal reaction time was 157 min and the optimal reagents doses were above 4000 mg L^{-1} of H_2O_2 and 200 mg L^{-1} of Fe^{2+}. This combination achieved a maximum TOC removal of 67% and a final BOD_5 value of 14.8 mg L^{-1} O_2.

1. Introduction

Reverse Osmosis (RO) is the most common membrane-based desalination option in seawater desalination, dominating in the Mediterranean area [1]. RO membrane enables the separation of salts and inorganic molecules, as well as organic molecules with a molecular weight greater than approximately 100 Da through a semi-permeable membrane thanks to a pressure gradient. A typical seawater RO (SWRO) desalination process includes seawater intake, pretreatment, a RO system, and post-treatment. Before the RO process, the usual pretreatment consists on coagulation, flocculation, media filtration, and cartridge filter [2].

Despite this pretreatment, in normal operation, RO membranes can become fouled by mineral scale, biological matter, colloidal particles and insoluble organic constituents [3–8]. These deposits on the membrane surfaces cause loss in normalized permeate flow, loss of normalized salt rejection, or both [4,9].

There are several cleaning scenarios in desalination plants: basic cleanings for regular maintenance; acid cleaning against severe inorganic scaling; biocide injection for the conservation of RO modules in plant [4,10] and its posterior flushing when restarting.

Alkaline cleaning with permeate water pump cycles and soaking are commonly used against the organic fouling of the membranes. These operations generate a significant amount of wastewater [4,10] that will be treated in this work. This volume is particularly significant in those RO plants where organic fouling is especially common, for example those located where algal blooms are a typical phenomenon (corresponding to an extreme case of organic fouling). This cleaning water nowadays is finally discharged to a neutralization tank where the effluents accumulate and are neutralized, and then is resent to the sea or the public sewer system. Cleaning water contains the organic matter detached from the membrane and cleaning products, such as chelating agents (e.g. salts of ethylenediaminetetraacetate (EDTA) or citric acid), and surfactants (e. g. Sodium Lauryl Sulfate (SLS) also known as Sodium Dodecyl Sulfate (SDS), an anionic surfactant); and it has an alkaline pH [10–12]. As the cleaning solution to clean the membrane is prepared from permeate water, this effluent has low salinity; therefore, it could be reused once the pH is neutralized and the mentioned organic matter is removed, as irrigation water or in other stages of the process, contributing to the concept of a zero liquid discharge (ZLD) osmosis desalination plant.

In order to follow a strategy of aligning desalination plants operation to ZLD philosophy, in which ACCIONA Agua company is very much interested, this work is focused on exploring the feasibility of treating this kind of effluents, as a starting point for future developments.

In the framework of desalination plants, the project ZELDA focused the ZLD philosophy on the avoidance of the generation of any concentrated stream [13]. However, ACCIONA Agua is exploring the possibility of considering also the avoidance of any kind of by-product discharge as part of this philosophy, including the cleaning effluents that, as it was mentioned before, nowadays are merely neutralized and

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discharged with the brine.

Basic cleaning is usually executed for regular maintenance of the RO system and different scenarios can be determined due to the fact that depending on the position of the membrane in the whole plant, its fouling or its scaling can be more or less severe, so the resulting cleaning effluent can be more or less rich on organic matter. This work focuses in particular on the effluent resulting from regular cleaning of the organic fouling of the first module of a RO rack; this scenario implies the highest volumes of generated wastewater and its content of detached organic matter is expected to be the maximum. According ACCIONA Agua company operational practices, the resulting effluent of this cleaning contains the organic matter which was adhered to the membrane, together with the common reagents used in this process, such as tetrasodium ethylenediaminetetraacetate (Na_4-EDTA) and sodium dodecyl sulfate (SDS) as cleaning reagents, as is usually recommended by the manufacturer of the membranes [4].

Regarding its reuse, the most important parameter to control for its possible reutilization could be the SDS content, because this surfactant is an emerging contaminant [14] and is susceptible to be contemplated as target compound in the future through the implementation of the wastewater discharge legislation EU Directive 2013/39/UE [15], and regional regulations on sea discharge MAH/285/2007 [16] (which accepts a maximum level of 6 mg L^{-1} for anionic surfactants, expressed as sodium lauryl sulfate). In relation to the rest of the organic matter content, there is no European legislation framework for reuse purpose. The Spanish regulation (Royal Decree 1620/2007) [17] does not include for reuse in irrigation limits on organic matter content and it concentrates the limitations mainly on the content of salts and on biological and inorganic parameters, as is also contemplated in the World Health Organization (WHO) and the Food and Agricultural Organization (FAO) reuse guidelines [18], in which probably the countries possessing reuse regulations are based [19]. The US Environmental Protection Agency [20] recommends concentrations below 10 mg L^{-1} biochemical oxygen demand (BOD) if food crops are intended for human consumption and consumed raw, and 30 mg L^{-1} BOD for processed food crops or crops which are not consumed by humans, including fodder, fiber, and seed crops, or to irrigate pasture land, commercial nurseries, and sod farms.

In this work Fenton process is studied as a plausible treatment for the organic load removal of the RO membranes cleaning waters in desalination plants. Fenton reaction consists in a combination of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}), in an acid medium, leading to the decomposition of H_2O_2 mainly into a hydroxyl ion and a hydroxyl radical that possesses a high oxidation potential to oxidize organic molecules [21]. Among the Advanced Oxidation Processes (AOPs), Fenton reaction was chosen because of the low cost of iron, the ease of use of H_2O_2 and its harmless decomposition to the environment [22].

Previous studies revealed information on the different AOPs for the degradation of SDS and other anionic-based surfactants [23,24]. Fenton process was also applied by Bandala et al. [25] and Chitra et al. [23] for the degradation of SDS, although it showed that reaction using sunlight, Fe^{2+}, and H_2O_2 (solar photo-Fenton) was faster.

On the other hand, Na_4EDTA, is a synthetic chelating agent found in the cleaning waters. Suárez et al. [26] achieved a recovery of 90% using nanofiltration when the Na_4EDTA concentration in water was nearly 0.2% w/w. There are also studies based in the degradation of EDTA by AOPs [27,28]. The results from the comparative study on the kinetics of EDTA degradation carried out by Chitra et al. [27], revealed that the reaction using UV, ultrasound, Fe^{2+} and H_2O_2 was faster than that obtained in any of the other tested processes. Ghiselli et al. [29] performed Fenton and photo-Fenton experiments at pH 3 under similar conditions to study the degradation of EDTA. With Fenton process, TOC removal was very low at the end of 4 h for all experiments, reaching a maximum of 31.9% removal in the case of 1:1 EDTA:Fe^{2+} ratio. In addition, some by-products formed in this process, in particular oxalic acid, can accumulate in the reaction media due to its refractory nature to the Fenton's reagent.

However, no references were found regarding the degradation of these two components coexisting in the same matrix, as they are present in the cleaning waters of this work, nor the possibility of treating these effluents that are generated in large volumes in the desalination plants and that could have application, e.g. for irrigation, which states the novelty of this research.

2. Materials and methods

2.1. Cleaning waters

Cleaning effluents were simulated for this work.

Based on laboratory analyses from autopsies of first position RO modules from a seawater desalination plant in Sureste (Tenerife, Spain), organic fouling was estimated. This data was obtained through the measurement by LC-OCD and resulted around 4.12 g C per module [30]. Besides, it was observed that the predominant fraction of organic matter corresponded to biopolymers (Fig. S1, Supplementary Information). According to this, an anionic modified potato starch from Cargill (C flake 35704) was chosen for simulating the organic content. Currently this product is marketed under the name Anifloc (Nova Casanova MCM S.L., Spain). As shown in Fig. S1, this starch practically only provides organic carbon from the fraction of biopolymers, considered the predominant fraction in the solid from the organic fouling of a RO module [31]. Thus, it was obtained that 100 mg L^{-1} of starch corresponded to 22.4 mg L^{-1} of dissolved organic carbon.

In an average desalination plant with 100 tubes of RO modules per rack, 250 m^3 of water is used for the basic cleaning against organic fouling. According to the manufacturer instructions, this cleaning solution contains Na_4-EDTA (0.2%), NaOH, SDS (0.1–0.2%) and HCl. Considering the cleaning of a 100-tube rack, a total of 250 m^3 will be used. After a basic cleaning, a 100 m^3 acidic displacement is always performed. Both volumes are stored in the same neutralization tank and its combination is the effluent that finally should be treated, but in this research, the focus was just on organic fouling cleaning. Table 1 shows the composition of the synthetic effluent prepared for this study based on that scenario described.

2.2. Fenton experiments

Fenton reactions were carried out at pH 3 and the reagents used were hydrogen peroxide solution (30% w/w in H_2O, with stabilizer) (Sigma-Aldrich, USA), iron(II) sulfate heptahydrate ($FeSO_4·7H_2O$) (Sigma-Aldrich, USA) and hydrochloric acid (HCl) (Panreac, Spain) to acidify. The Fenton experiments were carried out in 1L topaz bottles to avoid light influence made of borosilicate glass (Duran, Germany) and with magnetic stirring.

Stoichiometric H_2O_2 required for the oxidation of organic matter was calculated as reported by Kim and colleagues [32] who considered that the stoichiometric ratio H_2O_2/COD (w) should be 2.125. Therefore,

Table 1
Composition of cleaning water including initial chemical oxygen demand (COD), total organic carbon (TOC) and BOD_5.

Quality Parameter of the simulated cleaning water	Value
Na_4-EDTA (Sigma-Aldrich, USA) (mg L^{-1})	200.0
SDS (Sigma-Aldrich, USA) (mg L^{-1})	150.0
Anionic modified potato starch from Cargill (C flake 35704) (mg L^{-1})	7.4 (1.65 mg L^{-1}C)
pH	10.3
COD (mg L^{-1})	414.0
TOC (mg L^{-1})	134.5
BOD_5 (mg L^{-1})	3.1