



Treatment of cleaning waters from seawater desalination reverse osmosis membranes for reutilization purposes. Part II: Application of photo-Fenton and photocatalysis processes



Silvia Jiménez^{a,b}, María M. Micó^a, Marina Arnaldos^a, Beatriz Corzo^a, Sandra Contreras^{b,*}

^a R & D Department, Acciona Agua S.A.U, Parc de Negocis Mas Blau II, Avda. de les Garrigues, 22, 08820 El Prat de Llobregat, Barcelona, Spain

^b Departament d' Enginyeria Química, Universitat Rovira i Virgili, Av Països Catalans 26, 43007 Tarragona, Spain

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ABSTRACT

This is the second part of the study of cleaning waters from seawater desalination reverse osmosis membranes treatment, with the aim of reclaiming them for reuse. In the first part, Fenton process was applied in these wastewaters and a TOC removal of 67% and a final BOD₅ value of 14.8 mg L⁻¹ O₂ were achieved by using 4000 mg L⁻¹ of H₂O₂ and 200 mg L⁻¹ of Fe²⁺. In this part, photo-Fenton and photocatalysis processes were explored in order to enhance mineralization degree. The highest elimination was achieved with the photo-Fenton process at pH 3, where 79% of TOC removal was obtained with 1400 mg L⁻¹ H₂O₂ and 70 mg L⁻¹ Fe²⁺ (3 times lower than in the Fenton process) under solar radiation after 60 min, and 85.6% after 157 min, with the total removal of sodium dodecyl sulfate and obtaining a suitable water for irrigation. This photo-Fenton reaction could also be performed at pH 7, as after 157 min, the same elimination is reached. The addition of P25 accelerates the photo-Fenton process, although after one hour of treatment, similar elimination was reached for both conditions. 77% of TOC removal after 180 min was obtained under solar radiation at pH 3 by adding 1200 mg L⁻¹ of H₂O₂ with 250 mg L⁻¹ of P25 instead of Fe.

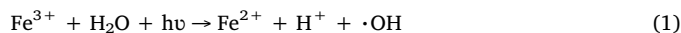
1. Introduction

This is the second part of a work focused on the treatment of reverse osmosis (RO) membranes cleaning waters for reutilization purposes. The first part was dedicated to the application of the Fenton process for the organic load removal of this type of wastewaters [1] and in the present part, photo-Fenton and photocatalysis processes are applied.

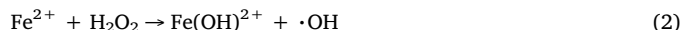
After studying the Fenton process for the treatment of simulated RO membranes cleaning waters composed of the organic matter that was adhered to the membrane, tetrasodium ethylenediaminetetraacetate (Na₄-EDTA) and sodium dodecyl sulfate (SDS), in which a maximum TOC removal of 67% was achieved with 4000 mg L⁻¹ H₂O₂ and 200 mg L⁻¹ Fe²⁺ at pH 3 [1], this study focuses on the application of photo-Fenton and photocatalysis processes, in order to choose the best treatment for the organic load removal of the RO membranes cleaning waters.

Among the Advanced Oxidation Processes (AOPs), the photo-Fenton process has been chosen due to the low cost of reagents, the ease of use of H₂O₂ and its harmless decomposition to the environment [2], and because sunlight can be used. Photo-Fenton reaction leads generally to higher velocities of degradation and mineralization, compared to the

dark Fenton, due to the creation of an extra path for hydroxyl radical formation thanks to the photoreduction of Fe³⁺ to Fe²⁺, according to Reaction (1).



In this way, ferrous cation is continuously recycled thanks to radiation, and there is always certain amount of Fe²⁺ available in the media [3]. Additionally, according to Pignatello and collaborators also the formation and photodegradation of Fe³⁺ aquocomplexes (predominant in acidic conditions) contribute to the generation of hydroxyl radicals [4] under 180–410 nm radiation.



Generally, is accepted that optimum pH for Fenton and photo-Fenton reactions is 2.8 [4]. At this pH, Fe³⁺ ion coexists with its complex Fe(OH)²⁺ in a ratio of 1:1, and both are the most photoactive species of the system. At lower pH, the concentration of Fe(OH)²⁺ decreases, favoring the generation of other complexes less photoactive. Over pH 2.8, Fe³⁺ precipitates as Fe(OH)₃.

* Corresponding author.

E-mail address: sandra.contreras@urv.cat (S. Contreras).

Photocatalysis processes based on the use of titanium dioxide (TiO₂) have emerged in the past two decades as a promising treatment option for micropollutants in wastewater effluents as in the case of photo-Fenton [5–7]. TiO₂ is an n-type semiconductor. When its surface is hit by light radiation of greater energy than that of the band gap, an electron is promoted from the valence band (VB) to the CB conduction band (CB). This creates a positive hole (h_{vb}⁺) in the VB, and an increase in one electron (e_{cb}⁻) in the CB.

If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h_{vb}⁺ may react with

surface-bound H₂O or OH⁻ to produce the hydroxyl radical (·OH), while e_{cb}⁻ is picked up by oxygen to generate superoxide radical anion (O₂^{·-}), which are the primary oxidizing species in the photocatalytic oxidation processes [8].

The main advantage of this technique, by using TiO₂ as photocatalyst, lies firstly in the fact that TiO₂ is non-toxic, stable, does not undergo photocorrosion, is chemical-resistant and economical [9]. Nevertheless, it requires high retention times and an additional step for photocatalyst recovery when suspended and even reactivation [5].

Photo-Fenton process was applied by Chitra et al. [10] for the degradation of SDS and revealed that the rate of degradation of surfactant using UV-C (15W) + Fe²⁺ + H₂O₂ was 23 times faster than if the system uses Fe²⁺ + H₂O₂ alone. Bandala et al. [11] also observed the enhancement of SDS final degradation using solar radiation on the Fenton reaction. Fenton needed higher concentrations of reagents (10 times of metal and almost 17 times of oxidant) to reach ca. 63% of surfactant removal.

Fenton and photo-Fenton experiments at pH 3 were performed by Ghiselli et al. [12] under similar conditions to study the degradation of EDTA. With Fenton process, TOC removal was very low at the end of 4 h in all the experiments, reaching a maximum of 31.9% removal in the case of 1:1 EDTA:Fe²⁺. 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 Fenton's reagent.

In relation to photocatalysis, Rekab et al. [13] studied the removal of EDTA under UV-C radiation. The degradation efficiencies of the UV/TiO₂ and UV/H₂O₂ processes seemed to be similar in terms nitrogen and carbon mineralization, although photocatalysis seemed to be a better option as in the other case H₂O₂ was needed to be added continuously during the UV/H₂O₂ experiments. Baeza et al. [14] removed EDTA at pH 3 under UV-C radiation in the presence of H₂O₂ and achieved 78% of TOC removal using 40:1 H₂O₂/EDTA (molar) after 540 min. TiO₂ addition (1 g L⁻¹) was detrimental in this case, it inhibited the oxidation reaction since TiO₂ particles produce scattering of light that hindered photocatalytic decomposition of H₂O₂.

However, no references were found regarding the oxidation of these two components coexisting in the same matrix, (as they are present on the cleaning waters of this work) nor proposing the treatment of these effluents by neither photocatalysis nor photo-Fenton processes.

2. Materials and methods

2.1. Cleaning waters

Cleaning effluents used in this article were simulated in the same way as in the previous article [1]. Table 1 shows the composition of the synthetic effluent prepared for this study.

2.2. Photo-Fenton experiments

Photo-Fenton reactions were carried out at pH 3 and the reagents used were hydrogen peroxide solution (30% w/w in H₂O, with stabilizer) (Sigma-Aldrich, USA), iron(II) sulfate heptahydrate (FeSO₄·7H₂O) (Sigma-Aldrich, USA) and hydrochloric acid (HCl) (37%, Panreac, Spain) to acidify. For each photo-Fenton experiment, 0.5 L of sample

Table 1

Composition of cleaning water including initial chemical oxygen demand (COD), total organic carbon (TOC) and biological oxygen demand (BOD₅).

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 35,704) (mg L ⁻¹)	7.4 (1.65 mg C L ⁻¹)
pH	10.3
COD (mg L ⁻¹)	414.0
TOC (mg L ⁻¹)	134.5
BOD ₅ (mg L ⁻¹)	3.1

was used and carried out in a 1L container made of borosilicate glass of 86 mm high and 157 mm diameter (Duran, Germany) and with magnetic stirring.

The reaction took place inside a solar simulator (Solarbox 3000e, Cofomegra, Italy) (SB) equipped at the top with a 2500 W Xenon lamp (Neurtek, Spain) and an outdoor light filter, which allows 290–800 nm wavelength to pass through. Irradiance was set to 250 W m⁻². The intensity of the radiation from the Xe lamp used in the SB reaching the solution was determined by actinometry, using the Parker method [15], based on the photochemical reduction of the ferrioxalate complex [Fe(C₂O₄)₃]³⁻ to Fe (II) in acid medium. The reduction takes place with a quantum yield of 1–1.2 mol Einstein⁻¹ in the range of wavelengths between 250 and 450 nm [16]. The concentration of Fe (II) over time was followed by the o-phenanthroline method [17], based on the formation of a colored complex between Fe (II) in solution and 1,10-phenanthroline in acid medium acetic acid/acetate at pH 3–4. The absorbance was measured at 510 nm. The intensity value resulted 6.5 10⁻⁴ Einstein min⁻¹.

The optimal photo-Fenton experiment that resulted from this study was also carried out by using 4 × 15 W UVA lamps (300–400 nm) (with a maximum at 360–365 nm) (Philips TL-D BLB). The intensity of the total radiation from these UVA lamps, determined also by actinometry using the ferrioxalate method, was 1.3 10⁻⁴ Einstein min⁻¹.

TOC was analyzed at 15 min, 60 min and 157 min reaction (to compare with the Fenton process studied in a previous work but using shorter times since photo-Fenton is a faster process). Samples were previously filtered through 0.20 μm Phenex Nylon filter membranes before TOC analysis.

2.3. Photocatalytic experiments

For each experiment, 0.5 L of cleaning water was used. The experiments were carried out with the solar simulator (Solarbox 3000e, Cofomegra, Italy) (SB), 4 × 15 W UVA lamps (300–400 nm) (with a maximum at 360–365 nm) (Philips TL-D BLB) and 4 × 15 W UVC low pressure lamps (that emit mostly at 253.7 nm) (Philips G15 T8).

The intensity of the total radiation from the UV-C lamps, determined by actinometry using the ferrioxalate method, was 1.3 10⁻⁴ Einstein min⁻¹.

The experiments were carried out in closed containers; those for the solar simulator and the UVA lamps were made of borosilicate glass and for the UV-C lamps were made of quartz.

In these experiments, basic pH (free pH of 10.3) and pH 3 were tested.

The study started with adsorption experiments. Those experiments were carried out in the dark at free pH (10.3) and pH 3 using 0.25 g L⁻¹ Aeroxide[®] P25 (Acros Organics, Belgium) as a commercially available TiO₂ photocatalyst for 300 min. These experiments were also performed by adding hydrogen peroxide (H₂O₂). Aeroxide[®] P25 was analyzed by X-ray diffraction and is composed of anatase (87.6%) and rutile (12.4%). The crystallites size analysis were: anatase 16.9 nm and rutile 30 nm.

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