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2D fluorescence spectroscopy for monitoring ion-exchange membrane based technologies — Reverse electrodialysis (RED)

Sylwin Pawlowski, Claudia F. Galinha*, João G. Crespo, Svetlozar Velizarov

LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

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ABSTRACT

Reverse electrodialysis (RED) is one of the emerging, membrane-based technologies for harvesting salinity gradient energy. In RED process, fouling is an undesirable operation constraint since it leads to a decrease of the obtainable net power density due to increasing stack electric resistance and pressure drop. Therefore, early fouling detection is one of the main challenges for successful RED technology implementation. In the present study, two-dimensional (2D) fluorescence spectroscopy was used, for the first time, as a tool for fouling monitoring in RED. Fluorescence excitation-emission matrices (EEMs) of ion-exchange membrane surfaces and of natural aqueous streams were acquired during one month of a RED stack operation. Fouling evolvement on the ion-exchange membrane surfaces was successfully followed by 2D fluorescence spectroscopy and quantified using principal components analysis (PCA). Additionally, the efficiency of cleaning strategy was assessed by measuring the membrane fluorescence emission intensity before and after cleaning. The anion-exchange membrane (AEM) surface in contact with river water showed to be significantly affected due to fouling by humic compounds, which were found to cross through the membrane from the lower salinity (river water) to higher salinity (sea water) stream. The results obtained show that the combined approach of using 2D fluorescence spectroscopy and PCA has a high potential for studying fouling development and membrane cleaning efficiency in ion exchange membrane processes.

1. Introduction

During mixing of river water with sea water, energy associated to the chemical potential difference between these two water bodies is released. This energy source is completely renewable and sustainable (Ramon et al., 2011; Vermaas et al., 2013a). However, to obtain electrical energy from salinity gradients, the mixing of the solutions of different salinity must be controlled. In a reverse electrodialysis (RED) stack (Fig. 1), the diluted and concentrated saline aqueous streams flow through an array of separated compartments formed by alternately arranged cation- and anion-exchange membranes, stacked between two electrodes. The ion-exchange membranes allow for transport of the respective counter-ions, while transport of co-ions is hindered due to the Donnan exclusion effect. The counter-ions, are transported from concentrated to dilute compartments, with cations and anions migrating toward the respective electrodes, at which, in order to maintain electro-neutrality, a redox couple solution is recirculated through the two electrode compartments. Thus, the chemical salinity gradient energy is converted into electrical energy, i.e. an electron flux through an external circuit connecting the two electrodes.

However, a conjugation of selective membranes and natural waters, with a significantly variable composition, may lead to fouling formation and, consequently, to a decrease in the power obtained (Vermaas et al., 2014a). Remnants of diatoms, clay minerals and organic fouling were found on anion-exchange membrane (AEM) surfaces, while cation-exchange membranes (CEM) were more susceptible to scaling (Vermaas et al., 2013b). Since most organic substances in natural water streams are negatively charged (Tanaka et al., 2012), fouling of anion-exchange membranes by organic compounds has been identified as the most important process limitation not only in RED (Vermaas et al., 2013b) but also in traditional desalting electrodialysis (Lee et al., 2002). Negatively-charged organic foulants can shield the fixed positively-charged groups of the anion-exchange membranes, thus lowering their selectivity and increasing their electric resistance

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* Corresponding author.
E-mail address: cf.galinha@fct.unl.pt (C.F. Galinha).

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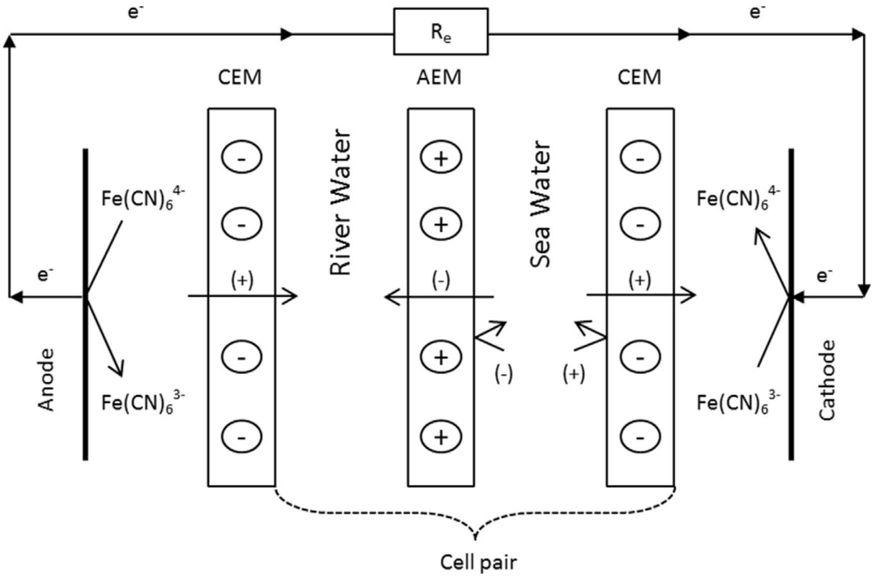

Fig. 1. Schematic representation of RED principle (CEM – cation-exchange membrane, AEM – anion-exchange membrane, R_e – external load resistance).

(Vermaas et al., 2013b).

Fouling formation and, especially, preferential channeling due to clogging, can be detected *in situ* by monitoring the pressure drop (Vermaas et al., 2014a). However, the pressure drop is also affected by the solutions flow rate, the number of the compartments in the RED stack and a possible non-uniform fluid distribution caused by the design of the distribution channels (Gurreri et al., 2012; Pawlowski et al., 2014a). Moreover, the pressure drop increases significantly only if a large channel volume is inaccessible for the flow (Vermaas et al., 2014a), while the obtainable power density may been significantly decreased (Vermaas et al., 2013b). This power density decrease is mainly associated to an increase of the non-ohmic resistance, which can be followed on-line by chronopotentiometric measurements (Vermaas et al., 2014a). However, as the non-ohmic resistance, or its equivalent in terms of the diffusion boundary layer thickness, depends also on the position in the stack and in the channel (Gurreri et al., 2014; Pawlowski et al., 2014b), the quantification of fouling by non-ohmic resistance can be affected by the liquid diffusion boundary layer thickness. Moreover, the very fouling formation could be non-uniform along the channel length.

Therefore, more accurate analytical tools for fouling monitoring are needed. As the decrease in the obtained power density is, most likely, caused by organic fouling (Vermaas et al., 2013b), which contains natural fluorophores, fluorescence spectroscopy can be used for its detection (Galinha et al., 2011a). Fluorescence spectroscopy explores the natural fluorescence of a large variety of compounds for their detection. A fluorophore compound, when excited, emits light, which can be recorded by fluorescence spectroscopy. In complex media, since many different fluorophore compounds can be present, to access them all, simultaneous scanning of excitation and emission light, within an adequate wavelength range, is needed (2D fluorescence spectroscopy) (Galinha et al., 2011a). 2D fluorescence spectroscopy results in an excitation-emission matrix (EEM), which can provide fast information about the composition of complex biological media. The complex information contained in EEMs, resulting from the presence of several fluorophores and light interferences, can be deconvoluted by mathematical tools in order to extract useful information from fluorescence spectra. So far, 2D fluorescence spectroscopy, combined with mathematical tools, has been applied for characterization and monitoring of biomedia (Galinha et al., 2011b, 2012; Pons et al., 2004; Surribas et al., 2006), natural aquatic environments (Stedmon et al., 2003) and food industry derivates (Lenhardt et al., 2015).

In the present study, we explored for the first time a possible utilization of 2D fluorescence spectroscopy as a fouling monitoring tool in ion-exchange membrane-based processes, particularly, in RED. Two tests, with a RED stack fed with natural sea and river waters as concentrated and diluted saline streams, respectively, were performed, each within one month time period. A third, one day test, with a synthetic humic acids solution, was performed to investigate their transport in the RED stack. Fluorescence EEMs of the ion-exchange membrane surfaces were acquired along the period of their utilization and after their cleaning. Fouling formation and evolution, as well as the membrane cleaning efficiency were then evaluated through principal component analysis (PCA) of the EEMs obtained. The same strategy was applied to assess samples of the two aqueous streams collected along the working periods, in order to identify possible time variable changes in their compositions.

2. Materials and methods

2.1. Reverse electrodialysis

For the three tests performed in this study, RED stacks composed of 3-cell pairs electrodialysis EDR-Z-Mini unit (MEGA a.s., Czech Republic), equipped with heterogeneous ion exchange membranes (Ralex), were used. The working channels dimensions were 4 × 16 cm (width and length) and the intermembrane distance (channel height) was kept constant by 0.8 mm thick polyethylene spacers. In the two first experiments, Atlantic Ocean water, collected in Fonte da Telha (Almada, Portugal), and Lisandro river water, taken in Cheleiros (Mafra, Portugal), were used respectively as concentrated and dilute saline streams. In the third experiment, synthetic aqueous solutions were used; as dilute stream: 1.03 g/L NaCl solution with 40.4 mg/L of commercial humic acids (Fluka 53680) and, as concentrated stream: 31.0 g/L NaCl solution. The RED process was operated with recirculation of the two saline solutions, using flow rates ranging between 20 and 70 ml/min. Differential pressure sensors (Honeywell, model