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Fluorescence spectroscopy applied to the optimisation of a desalting step by electrodialysis for the characterisation of marine organic matter

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ABSTRACT

The isolation and characterisation of marine dissolved organic matter (DOM) are still not readily achieved today. The study of this chemically complex material is particularly difficult, especially as it is hindered by the high salinity of seawater. It is therefore essential to develop a method in which a sufficient quantity of marine organic matter can be collected for structural analyses. Reverse osmosis (RO) is often used for the concentration of DOM from freshwaters, due to the fact that DOM is not modified during RO and that DOC recoveries are high (about 80%). Unfortunately, RO cannot be used directly to isolate marine DOM, since both salts and organic matter are concentrated during the process. Therefore, marine samples have to be desalted before their concentration by RO.

Our aim was to develop a desalting step of seawater by electrodialysis (ED), whilst minimising DOM modifications and losses. The process was first developed with small volumes (2 L) of artificial and Mediterranean seawater and was then applied to larger volumes. We showed that 20 L of Mediterranean seawater could be rapidly desalted (in less than 7 h) and, by monitoring the quality of DOM in desalted subsamples collected during ED using spectrofluorometry, that the quality of DOM was not significantly modified. It was concluded that desalted samples were still representative of the initial seawater samples. It should be noted, however, that care has to be taken in choosing the ratio of the volume of water to be desalted over the membrane surface area in order to limit DOM modifications and losses.

Electrodialysis efficiently removed up to 75% of the salts present in the seawater samples whilst recovering most of unaltered DOM. ED and RO could then be combined in order to isolate, concentrate and characterise marine organic matter.

1. Introduction

The isolation and characterisation of aquatic dissolved organic matter (DOM) are still representing a real challenge today, especially in marine waters. The study of the fate and composition of organic matter in the oceans is of significant interest since organic matter is believed to play a key role in the biogeochemical cycles, notably the carbon cycle. The amount of dissolved organic carbon in seawater (685 Gt C; [1]) is comparable to the mass of inorganic carbon present in the atmosphere (750 Gt C) and to the amount of carbon contained in the terrestrial biomass (570 Gt C; [2]). Changes in marine DOM production or consumption may have a significant effect on the carbon cycle even over time scales as short as years. The study of DOM is therefore essential, particularly in coastal waters, where substances are transferred from the terrestrial to the marine environment.

But advanced analytical techniques can hardly be used to characterise marine DOM because of the difficulty in collecting significant amounts (between 20 and 100 mg; [3]) of this highly dilute material and because DOM is usually in high saline solution. Two techniques have been widely used to isolate marine DOM over the last 30 years: separation on XAD resins [4,5] and tangential ultrafiltration (UF; [6] and references therein). However, it has been demonstrated that these two techniques lead to a fractionation of the organic matter: DOM components are separated according to their relative hydrophobicity during extraction on XAD resins and according to their size during UF. Moreover, only a small fraction of marine organic matter is recovered when using these two techniques: about 20% (mainly humic substances) when XAD resins are used [7] and about 30% (the high molecular

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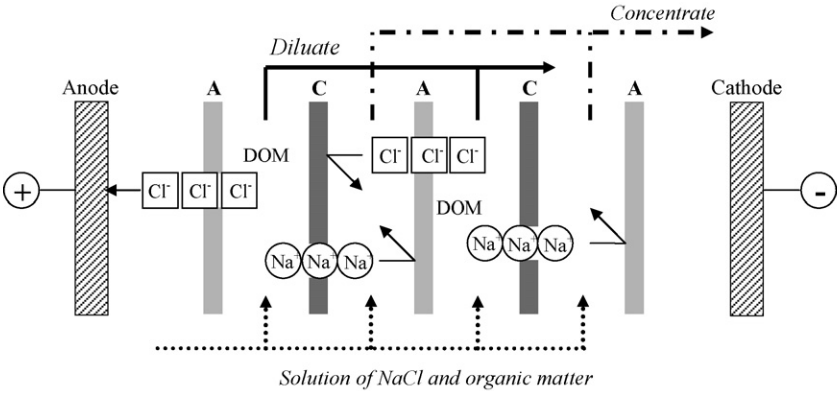

Fig. 1. Schematic representation of the principle of electrodialysis for the desalting of a solution of sodium chloride containing organic matter: A, anionic membrane; C, cationic membrane; DOM, dissolved organic matter.

weight (MW) fraction, fraction of MW higher than 1000 Da) by UF [6].

Reverse osmosis (RO) may be an interesting alternative for isolating marine DOM without fractionation. It has been shown that freshwater DOM is not modified during RO and that the yields of dissolved organic carbon (DOC) are generally high (about 80%; [8]). Unfortunately, RO cannot be directly used to concentrate marine DOM because salts and organic matter are co-concentrated during RO. Therefore, in order to obtain high yields of DOM from saline waters, a pre-treatment is necessary to demineralise seawater before, or during, the RO concentration step.

This can be achieved by electrodialysis (ED). ED is a gentle electrochemical process allowing the separation of ionic species from aqueous solutions by using an applied direct current potential through anion- and cation-exchange membranes. The principle of ED for the demineralisation of a solution of sodium chloride containing organic matter is depicted in Fig. 1. Using this technique one obtains a demineralised solution containing the organic matter (diluate compartment) and a solution containing the extracted salts (concentrate compartment). Over the last 10 years, ED has been used in several studies to desalt freshwater [9–11] and more recently seawater [12] samples. It is a valuable tool for desalting water samples, since the losses of DOC during the whole process were relatively low (less than 25% for freshwater samples). Moreover, it has been shown that this yield depends on the desalting ratio, so that higher recovery can be expected if the operating conditions and system are appropriate [13].

The technological improvement in marine DOM isolation offered by the coupling of reverse osmosis and electrodialysis (RO/ED) is highly promising. It has recently been shown that up to 95% of marine DOM can be recovered by combining RO and ED, compared to ~10–40% for previous techniques [11,12]. To date, the only DOC recovery was considered in these studies. But DOC is a bulk parameter, which does not provide any insight into the qualitative characteristics of DOM. Therefore, it still remains to be proved that DOM recovered using ED/RO is representative of the organic material present in the initial sample. It is essential to pay attention to the quality of concentrated and desalted organic matter: preliminary studies showed that water samples can be significantly modified or contaminated during the concentration and desalting steps and that these processes have to be controlled to minimise DOM losses and alterations [14,15]. It is also established that spectrofluorometry is a valuable tool for the qualitative control of DOM, allowing direct analyses of organic matter without preconcentration of water samples.

The objective of this work was to investigate ED as a seawater desalting technique prior to any DOM concentration step. Experiments were first carried out to optimise experimental conditions and methods, using small volumes of seawater. Then, the feasibility of the process was tested and demonstrated with larger volumes. Different seawater samples, i.e. artificial and natural ones, were desalted in order to compare the progress of ED with these two types of water. The study was focused on the characterisation of DOM during the demineralisation. In addition to DOC measurements, spectrofluorometry was used to characterise any change in the DOM quality that could not be identified from simple DOC analysis.

2. Materials and methods

2.1. Seawater samples

Natural and artificial seawater samples were used in this work.

200 L of Mediterranean seawater were collected in October 2006 from the Bay of Balaguier in Toulon (South Eastern France). This sampling was carried out so as to minimise any contamination of the DOM content. The pump and the pipes were made of Teflon and the water was pumped directly from the sea through a 0.45-μm in-line Teflon filter (Polycap 75 TF, Whatman). Each filter was precleaned with methanol and pure water and pre-treated by filtering water from the sampling site. Samples were then stored in the dark at 4 °C. They were analysed by fluorescence spectroscopy and for their DOC content just after sampling and before the desalting by ED. The analyses showed that neither qualitative nor quantitative modification of DOM occurred during storage.

Artificial seawater was prepared by dissolving inorganic salts in ultrapure water, so as to have an ionic composition as close as possible to that of the natural water sample. The following salts (analytical grade, Acros Organics) were added to 1 L of ultrapure water (Milli-Q, Millipore): NaCl (23.9 g); $MgCl_2 \cdot 6H_2O$ (10.8 g); Na_2SO_4 (4 g); $CaCl_2 \cdot 2H_2O$ (1.5 g); KCl (0.7 g); $NaHCO_3$ (0.2 g); KBr (0.1 g); H_3BO_3 (0.03 g); $SrCl_2$, $6H_2O$ (0.025 g); NaF (0.003 g).

The characteristics and composition of both seawater samples are provided in Table 1. The DOC content of artificial seawater (0.3 mg/L) corresponded to the residual organic carbon content of ultrapure water and salts.

2.2. Electrodialysis experiments

The electrodialysis set up used in this work was described in detail in a previous paper [16]. The ED stack (Eurodia Industrie SA) consisting of 10 cell pairs was equipped with AMX and CMX membranes (Tokuyama Corp., Japan). New membranes were installed to avoid any residual contamination from earlier experiments.