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Arnaud Huguet, H el ene Roux De-Balmann, Edith Parlanti. Fluorescence spectroscopy applied to the optimisation of a desalting step by electro dialysis for the characterisation of marine organic matter. *Journal of Membrane Science*, 2009, 326 (1), pp.186-196. 10.1016/J.MEMSCI.2008.09.051 . bioemco-00605321

HAL Id: bioemco-00605321

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To link to this article: DOI:10.1016/J.MEMSCI.2008.09.051
URL: <http://dx.doi.org/10.1016/J.MEMSCI.2008.09.051>

To cite this version: Hugué, Arnaud and Roux-de Balmain, Hélène and Parlanti, Edith (2009) Fluorescence spectroscopy applied to the optimisation of a desalting step by electro dialysis for the characterisation of marine organic matter. *Journal of Membrane Science*, vol. 326 (n°1). pp. 186-196. ISSN 0376-7388

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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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A B S T R A C T

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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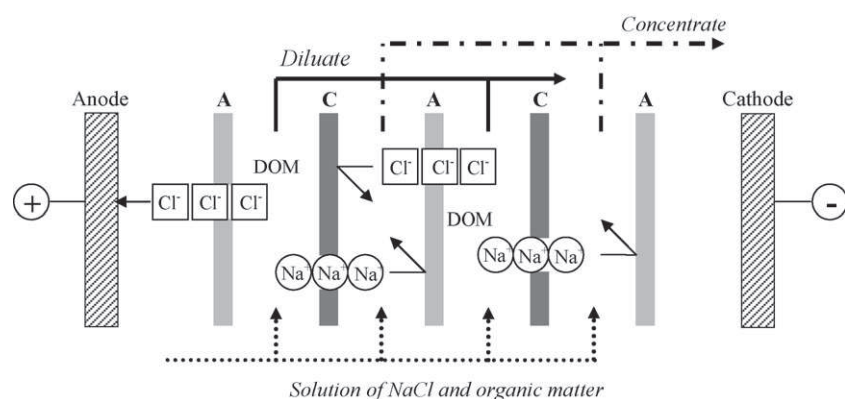


Fig. 1. Schematic representation of the principle of electrodialysis for the desalting of a solution of sodium chloride containing organic matter: A, anionic membrane; C, cationic membrane; DOM, dissolved organic matter.

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. Experi-

ments 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 pre-cleaned 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); $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (10.8 g); Na_2SO_4 (4 g); $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (1.5 g); KCl (0.7 g); NaHCO_3 (0.2 g); KBr (0.1 g); H_3BO_3 (0.03 g); $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (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.

Table 1

Principal characteristics of the artificial and Mediterranean seawater samples (DOC content, pH, conductivity, salinity and ionic concentrations). The uncertainty for the ionic concentrations does not exceed 5%.

	Artificial seawater	Mediterranean seawater
DOC (mg/L)	0.30 ± 0.01	1.00 ± 0.05
pH	7.7 ± 0.1	8.2 ± 0.1
Conductivity (mS/cm)	51.8 ± 0.2	56.9 ± 0.2
Salinity	33.9 ± 0.1	37.2 ± 0.1
Na ⁺ (g/L)	11.7	13.2
K ⁺ (g/L)	0.2	0.3
Mg ²⁺ (g/L)	1.0	1.2
Ca ²⁺ (g/L)	0.3	0.3
Cl ⁻ (g/L)	19.5	22.8
SO ₄ ²⁻ (g/L)	2.2	2.4

The total membrane surface area of any type of membrane, i.e. anionic exchange membrane (AEM) and cationic exchange membrane (CEM), was 0.2 m². The cathode was a stainless steel plate and the anode was platinized titanium mesh. The ED system which was used for this study is equipped with three independent 3-L reservoirs and hydraulic circuits for the diluate, concentrate and electrodes. In order to desalt larger volumes of seawater, the 3-L reservoirs were replaced by an external 20-L tank for the diluate and an external 30-L tank for the concentrate.

Before each run, the equipment was carefully prepared in order to avoid any, even small, contamination of seawater, since it could otherwise modify the quality of DOM present at a very low concentration in the sample. Preliminary experiments were carried out to determine the best cleaning procedure (results not shown), described hereafter. The membranes were first washed by circulating different solutions through the three compartments (diluate, concentrate and electrodes). The sequence was the following: 4 g/L hydrochloric acid solution, tap water, 4 g/L sodium hydroxide solution, tap water. Several rinsings with a 5-g/L NaCl solution were then performed until the pH of the diluate and concentrate solutions remained almost constant. The equipment was further rinsed with ultrapure water until the conductivity in the concentrate and diluate compartments was equal to that of ultrapure water (lesser than 20 µS/cm). At the end of this cleaning procedure, aliquots were collected to test the equipment cleanliness by spectrofluorometry. Finally, the ED pilot was rinsed with seawater: the diluate and concentrate compartments were filled with 2 or 20 L of Mediterranean seawater and the electrode reservoir was filled with 3 L of ultrapure water. Seawater and ultrapure water were allowed to circulate in the pilot for 1 h (without applying an electrical current).

For the seawater desalting, the electrode compartment was fed with a solution of sodium chloride at 9 g/L, the concentrate compartment with a solution of sodium chloride at 10 g/L and the diluate compartment with the solution to be desalted (artificial or Mediterranean seawater). ED experiments were carried out in a batch mode at a constant voltage (14 V).

The concentrate was initially filled with a solution the salinity of which was about three times lower than the one of the diluate. In fact, since ED is performed at a constant voltage, the value of the current intensity varies during the desalting. The latter depends on the ionic concentration in the diluate and concentrate compartments: when the ionic content in the diluate or in the concentrate is low, the resistance of the membrane stack is high and the current intensity value is relatively low. This is due to the relationship existing between the voltage, the current intensity and the resistance of the membrane stack, described by Ohm's law. By initially filling the concentrate compartment with a solution of sufficiently high salinity, the resistance of the membrane stack is minimised and the current intensity can rapidly reach its maximal value. In this way,

the duration of the desalting experiment can be reduced. This point can be particularly important during the desalting of large volumes of seawater.

The temperature, pH and conductivity of both the diluate and the concentrate were monitored over time. The pH was measured with a pH meter pH340 (WTW, Germany). The conductivity was measured with a conductimeter LF537 (WTW, Germany). The experiments were stopped when the conductivity in the diluate reached about 5 mS/cm. A few millilitres of concentrate and diluate were collected regularly. These aliquots were analysed using spectrofluorometry and their DOC concentrations were also determined (see below for details).

Because of the water transported together with the salts, a water flux took place from the diluate to the concentrate, i.e. in the direction of the salt transfer [16]. The volumes were then measured at the end of each experiment.

2.3. Salinity

During all the ED experiments, the salinity of both the diluate and the concentrate were regularly measured. Salinity is used by oceanographers as a measure of the total salt content of seawater. The practical salinity (*S*) of a seawater sample is determined through measurements of a ratio between the electrical conductivity of seawater and the electrical conductivity of a standard solution (see [17] for more details). The electrical conductivity of seawater changes with temperature and pressure. Thus, the practical salinity of seawater, which is directly proportional to the conductivity, also depends on these two parameters. For the experiments carried out in this study, the salinity *S* was determined by using the following relation, $S = (37/56.6) \times \sigma$, where σ is the conductivity at 20 °C, expressed in mS/cm.

2.4. DOM characterisation

Dissolved organic carbon measurements and fluorescence spectroscopy were used to characterise the organic material present in water samples.

DOC measurements were achieved using a Shimadzu Total Organic Carbon Analyser (TOC-V CSN). The instrument was run in non-purgeable organic carbon (NPOC) mode. The apparatus was calibrated using a standard solution of potassium hydrogen phthalate C₆H₄(COOK)(COOH), diluted to different concentrations according to the estimated DOC content of the samples. For each sample, the DOC value was the mean of at least three analyses providing a standard deviation of less than 0.1 and a variation coefficient of less than 2%. The experimental uncertainty on the DOC value was estimated to be lower than 0.05 mg/L. It is important to keep in mind that at such low DOC values, such as those of seawater samples (see Table 1), any contamination may have an impact. The mass balance, i.e. the total organic content in terms of DOC, was then calculated for all experiments and all sampling. This will be discussed in Section 3.

In order to detect any change in the DOM composition, three-dimensional excitation-emission matrix (EEM) spectroscopy was also used. This technique presents the advantages of being fast, non-destructive, and sensitive to low concentrations of fluorescent compounds, as it is the case with seawater. It has been largely applied over the last 15 years to the study and characterisation of DOM in marine and fresh waters (e.g. [18–21]).

The fluorescence spectra were recorded with a Fluorolog FL3-22 SPEX Jobin Yvon Fluorometer. This spectrofluorometer is equipped with double monochromators both at the excitation and the emission sides. Samples were contained in a 1-cm path length fused silica cell (Hellma), thermostated at 20 °C.

The fluorescence EEM spectroscopy involved scanning and recording of 17 individual emission spectra (260–700 nm) at sequential 10 nm increments of excitation wavelength between 250 and 410 nm as previously described [18]. Experiments were run in ratio mode with a 0.5-s integration time, a 1-nm emission wavelength increment and a 4-nm bandwidth for both excitation and emission. The spectra were obtained after subtracting a blank spectrum, obtained with ultrapure water (Milli-Q, Millipore) under the same conditions, in order to eliminate water Raman and Rayleigh scattering peaks. The 17 scans were used to generate three-dimensional contour plots of fluorescence intensity as a function of excitation and emission wavelengths. To make the graphs readable, the topographic and contour EEM plots are presented in this paper with excitation and emission wavelength increments of 10 and 5 nm, respectively. Although the resolution in the plots is lower, the positions and intensities quoted in the text correspond to the original line spectra. The uncertainty for the measurement of the fluorescence intensities is about 1%.

The ratio mode (sample/reference) selected as the acquisition mode produced spectra corrected for variations in lamp intensity with respect to time. They were obtained by performing the ratio of the photomultiplier signal to the reference signal measured with a photodiode.

In addition, the emission spectra were electronically corrected for instrumental response [22,23]. The emission correction factors were obtained by using a reference tungsten lamp and were applied to all the spectra of this paper. The excitation correction was not applied to the spectra. However, the comparison of spectra obtained with the same instrument was correct as regardless of whether or

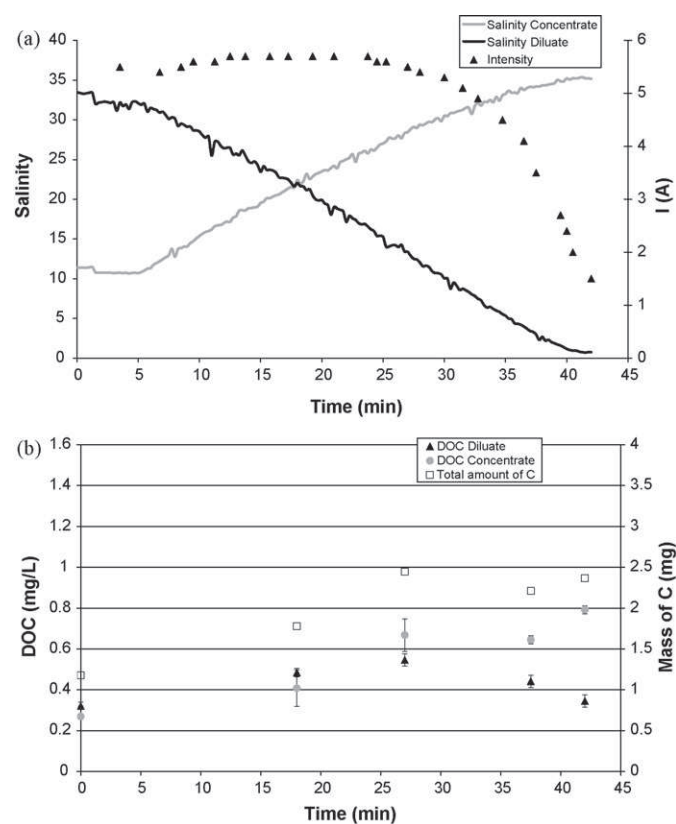


Fig. 2. Variations of the current intensity and of the salinity in the diluate and concentrate compartments during the desalting of 2 L of artificial seawater by electro dialysis (a). Variations of the dissolved organic content (DOC) (expressed in mg/L) in the diluate and the concentrate compartment and values of the total amount of carbon (expressed in mg) present in the system (b).

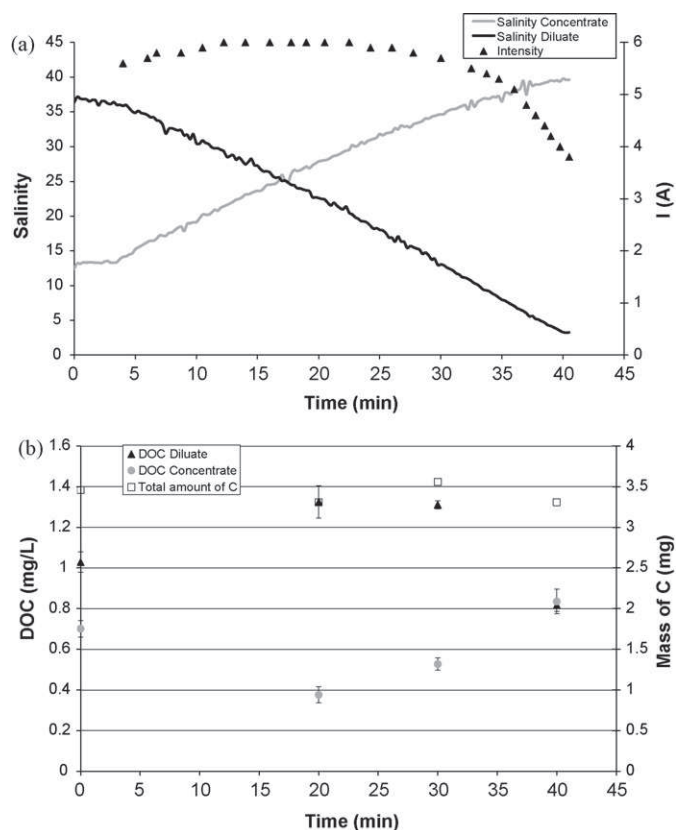


Fig. 3. Variations of the current intensity and of the salinity in the diluate and concentrate compartments during the desalting of 2 L of Mediterranean seawater by electro dialysis (a). Variations of the DOC content (expressed in mg/L) in the diluate and the concentrate compartment and values of the total amount of C (expressed in mg) present in the system (b).

not the corrections are made, the spectra from a single instrument are internally consistent.

3. Results and discussion

Experiments were first carried out with 2 L of seawater, using artificial and natural seawater. These experiments are later presented as “small scale experiments”. Then, larger volumes (20 L) of both waters were treated in the same conditions. The corresponding experiments are presented as “larger scale experiments”. The small and large scale experiments performed with artificial seawater were considered as blank experiments.

3.1. Small scale experiments

3.1.1. Artificial seawater

The current intensity and the salinity variations of the diluate and concentrate versus time are presented in Fig. 2(a). The current intensity was approximately constant during the first 25 min (about 5.6 A) and then it decreased until the end of the ED. This variation of the current intensity was due to the progressive decrease of the ion concentration in the diluate compartment, which was responsible for an increase of the total resistance in the ED stack. Since the voltage was kept constant, the current intensity logically decreased.

Because of the water carried out by the salts transferring from the diluate to the concentrate, the concentrate volume increased whilst that in the diluate decreased (the total volume was checked to remain constant). The variation was found to be linear versus time and the total volume change in one compartment was about

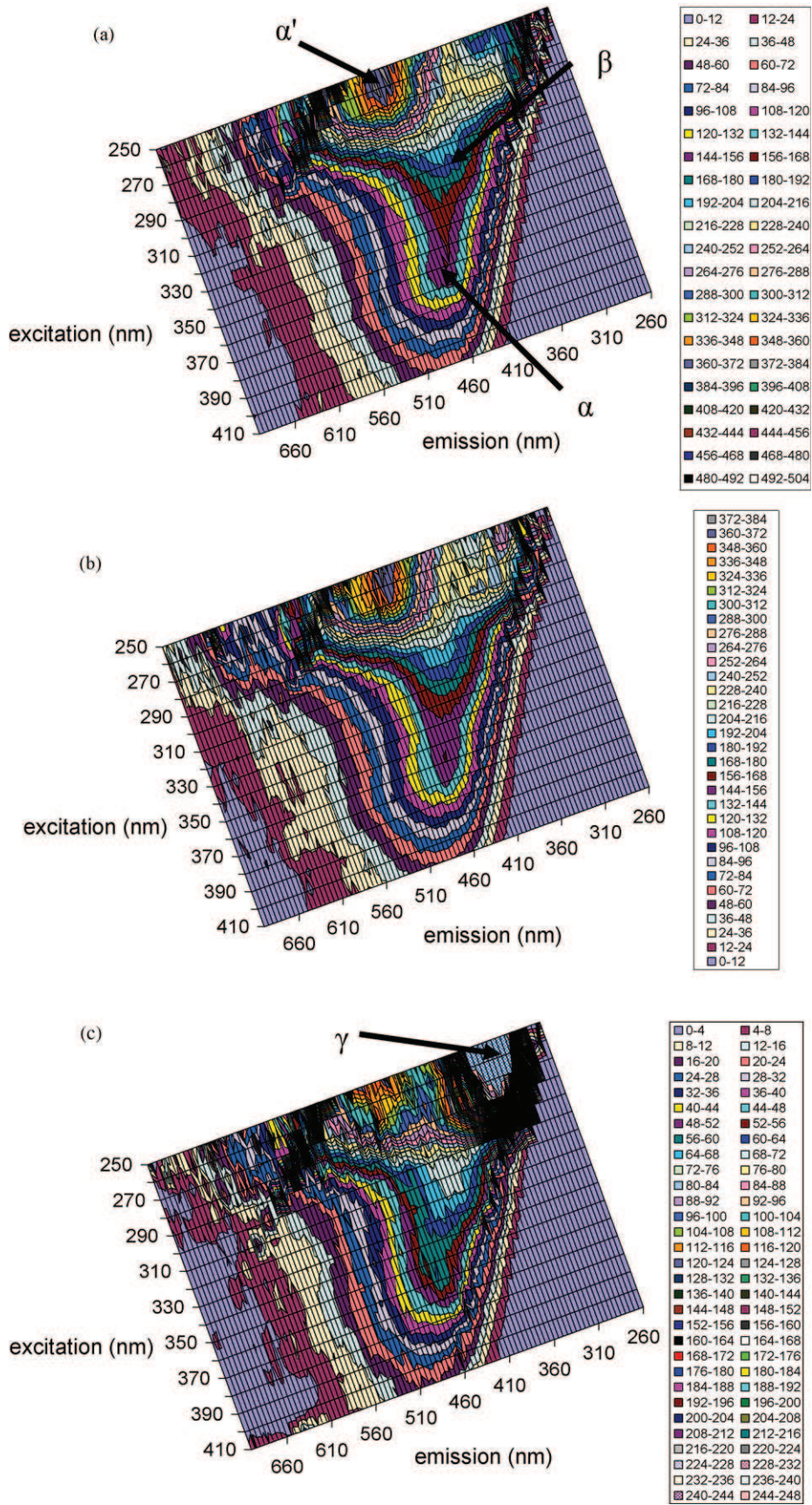


Fig. 4. Contour excitation–emission matrix plots of the initial Mediterranean seawater sample (a), of the diluate with a salinity of 22.9 (b) and of the diluate at the end of the electrodesalting (c) (desalting of 2 L of Mediterranean seawater). Fluorescence intensity scales identical for (a) and (b). Intensity scale three times smaller for (c) than for (a) and (b).

Table 2

Major fluorescence bands observed in seawater, with the notations used in this paper and the nomenclature proposed by Coble (1996) [19].

Band	Excitation max (nm)	Emission max (nm)	Type of compounds	Letter used by Coble (1996)
α	330–370	420–480	Humic-like material	C
α'	230–260	380–480	Humic-like material + recent material	A
β	310–320	380–420	Autochthonous production	M
γ	270–280	300–340	Protein-like material and bacterial activity	B

0.2 L over the ED duration. The temperature increased from 26 to 30 °C during the desalting process.

The variation of DOC concentration is plotted versus time in Fig. 2(b). DOC content varied between 0.3 and 0.8 mg/L during the ED. The mass balance, expressed in g of C, was calculated and the values are reported in Fig. 2(b). It can be observed that the mass of C present in the system increased with time, especially during the first part of the ED process. Even though the ED pilot was carefully and thoroughly cleaned before and between each desalting experiment (see the optimised procedure in Section 2.2), a slight contamination was observed during the desalting of artificial seawater.

3.1.2. Mediterranean seawater

Subsequently, 2 L of Mediterranean seawater were desalted under the same conditions as those used for artificial seawater (constant voltage of 14 V).

No significant shift in pH was observed during the experiment, the pH of the diluate (desalted seawater) varying only between 8.1 and 8.5. It is essential to check this point, since a significant variation of pH could lead to irreversible modifications of spectral DOM properties.

Current intensity and salinity variations of the diluate and concentrate versus time are presented in Fig. 3(a). As expected, these graphs are very similar to those reported in Fig. 2, obtained with artificial seawater. The temperature increase (25–30 °C) and volume variations (about 0.2 L over the ED duration) were also similar.

The DOC content variations for both the diluate and the concentrate can be seen in Fig. 3(b). The total amount of C present in the system is also plotted in the same graph. It remained almost constant, the variation not exceeding 5%. Despite the slight changes observed in the two compartments, these variations can be considered to be not significant. These results show that no significant

contamination or global loss of DOM occurred during the desalting of natural seawater.

There was a noticeable decrease in DOC content of the diluate after 30 min of ED and the DOC concentration of the concentrate increased at the same time. This may be due to the fact that at the end of the ED a large amount of inorganic solutes had already been extracted from the diluate and that organic anions (constituting DOM) began to be transferred from the diluate to the concentrate. In this experiment the transfer of DOM seemed to take place for salinity in the diluate below 15, i.e. for a desalting ratio higher than 60%.

In order to detect modifications or losses of DOM during the desalting process, the different diluate aliquots collected during ED were analysed using spectrofluorometry. The contour EEM plots of three of them, i.e. initial Mediterranean seawater sample ($S=37.2$), diluate at a salinity of 22.9 and diluate collected at the end of the ED ($S=3.3$), are presented in Fig. 4(a)–(c), respectively. In order to aid the detection of any spectral modification, different intensity scales were chosen for the three contour plots. The intensity scale for the diluate collected at the end of the ED (Fig. 4(c)) is three times smaller than the one used for the other spectra (Fig. 4(a) and (b)). Different bands were observed in fluorescence spectra and are listed in Table 2. They are in accordance with what has been previously reported in the literature by several authors [18,19,21,23–25].

The EEM plot of artificial seawater is also presented in Fig. 5, using the same intensity scale as the one of the initial Mediterranean sample (Fig. 4(a)). Artificial seawater only contains residual organic matter. Despite this residual content, the fluorescence intensity of the artificial seawater sample is significantly lower than the one of the natural seawater sample.

The spectra of the initial Mediterranean seawater sample (Fig. 4(a)) and of the intermediate diluate sample ($S=22.9$) (Fig. 4(b)) have a similar shape, which means that the organic

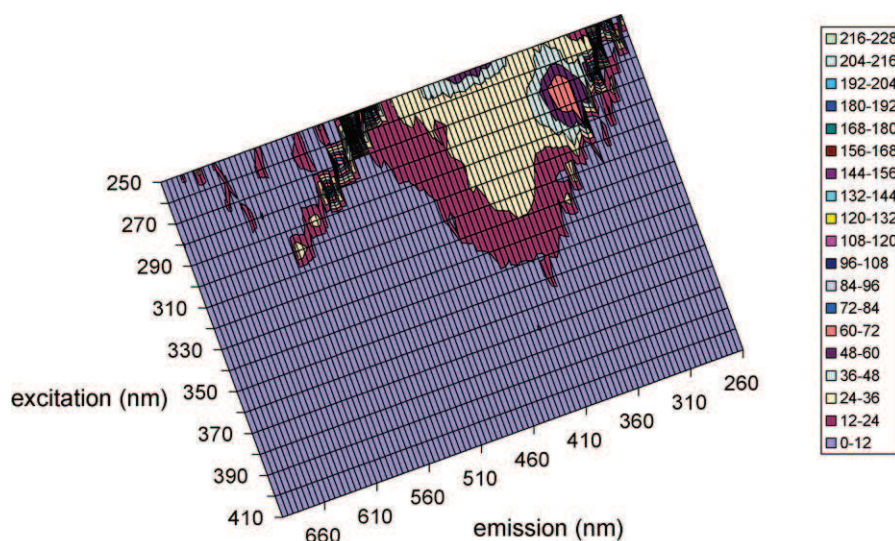


Fig. 5. Contour excitation–emission matrix (EEM) plot of the artificial seawater sample. Fluorescence intensity scale identical as the one of the spectrum of the initial Mediterranean seawater sample (Fig. 4(a)).

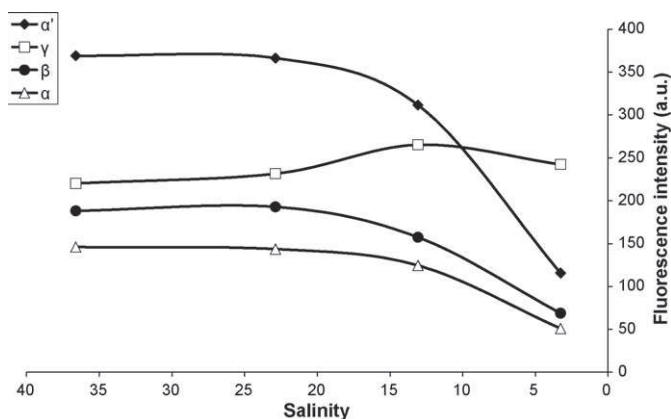


Fig. 6. Variations of the fluorescence intensities of the four main fluorophores characteristic of DOM (α' , α , β and γ) in the diluate as a function of the salinity (desalting of 2 L of Mediterranean seawater). The uncertainty for the measurement of the fluorescence intensities is about 1%. The error bars are not visible in the graph due to the very low value of the random error.

matter was not modified during the first part of the ED. Nevertheless, the spectrum of the diluate collected at the end of the experiment shows that fluorescent DOM was not only less concentrated (lower in fluorescence intensity), but also modified during the last part of the ED, particularly in the region of the bands γ (associated to the fluorescence of proteins) and β .

In order to aid detections of changes in DOM fluorescence during ED, variations of fluorescence intensities of the diluate for the four main fluorophores (α' , α , β and γ) were plotted as a function of the diluate salinity (Fig. 6). The fluorescence intensities were determined at excitation wavelengths of 260, 280, 310 and 370 nm for α' , γ , β and α bands, respectively.

We can see that the fluorescence intensities of the bands α , α' and β showed similar variations. For salinities down to about 20, the intensity remained almost constant. Then, for lower salinities, the fluorescence intensities of the three bands began to decrease. This decrease seems more significant for the fluorophore α' (associated with humic-like + more recent material). A different behaviour was observed for the fluorescence intensity of the band γ compared to the other fluorophores, since a slight increase was observed with decreasing salinities.

DOC measurements and fluorescence analyses both showed that DOM modifications and losses occurred for salinities below 20, probably because of the transfer of organic matter from the diluate to the concentrate. The results obtained from DOC measurements and fluorescence analyses are complementary and clearly show the relevance of spectrofluorometry in order to characterise DOM quality, and not only DOM quantity, during the desalting process.

3.2. Larger scale experiments

After having developed the desalting step by ED with small volumes of seawater, the feasibility of desalting larger volumes to recover larger amount of DOM was tested. The main target was again to check DOM quality along the desalting process.

3.2.1. Artificial seawater

Current intensity and salinity variations in the diluate and concentrate during the desalting of 20 L of artificial seawater are shown in Fig. 7(a). The average current intensity remained constant and comprised between 5 and 6 A during the first part of the ED.

With the exception of the time-scale, the observed variations are similar to those obtained during small scale experiments. The time required to achieve a given desalting ratio was 10 times that

observed in small-scale experiments since the volume, and thus the mass of ions to remove, is 10 times higher. The volume variation was about 2 L over the experiment duration, i.e. 10 times that observed during small scale experiments. The temperature increased from 14 to 30 °C.

Fig. 7(b) gives the variation of the DOC content in each compartment versus time. The total amount of C is also plotted on the same graph. The DOC content of the diluate remained relatively low and almost constant during all the ED (between 0.2 and 0.35 mg/L), and was comparable to the initial DOC concentration of artificial seawater (0.3 mg/L). The DOC variations in the diluate are similar to those obtained during small scale ED (0.3–0.5 mg/L; Fig. 2(a)). As for the DOC content in the concentrate, it increased slightly but continuously, from 0.2 to 0.5 mg/L (Fig. 7(b)). This increase is lower than that observed during small scale ED, where DOC varied from 0.25 up to 0.8 mg/L (see Fig. 2(b)). The total DOC content increased continuously (see the DOC mass balance in Fig. 7(b)). This is also in agreement with what was observed during small scale experiments. This increase is relatively difficult to explain and could be due to a slight contamination.

3.2.2. Mediterranean seawater

20 L of Mediterranean seawater were then desalted exactly in the same way as the 20 L of artificial seawater. The pH of the diluate, i.e. the desalted seawater, was found to remain almost constant, between 8.2 and 8.8.

Current intensity and salinity variations of the diluate and concentrate versus time are shown in Fig. 8(a). The variations are

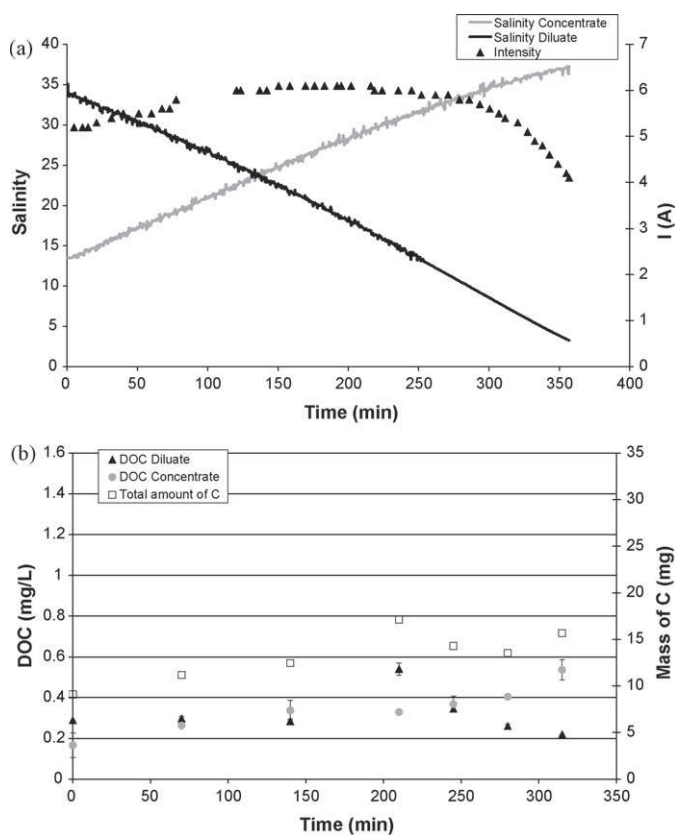


Fig. 7. Variations of the current intensity and of the salinity in the diluate and concentrate compartments during the desalting of 20 L of artificial seawater by electrodialysis (a). Variations of the DOC content (expressed in mg/L) in the diluate and the concentrate compartment and values of the total amount of carbon (expressed in mg) present in the system (b).

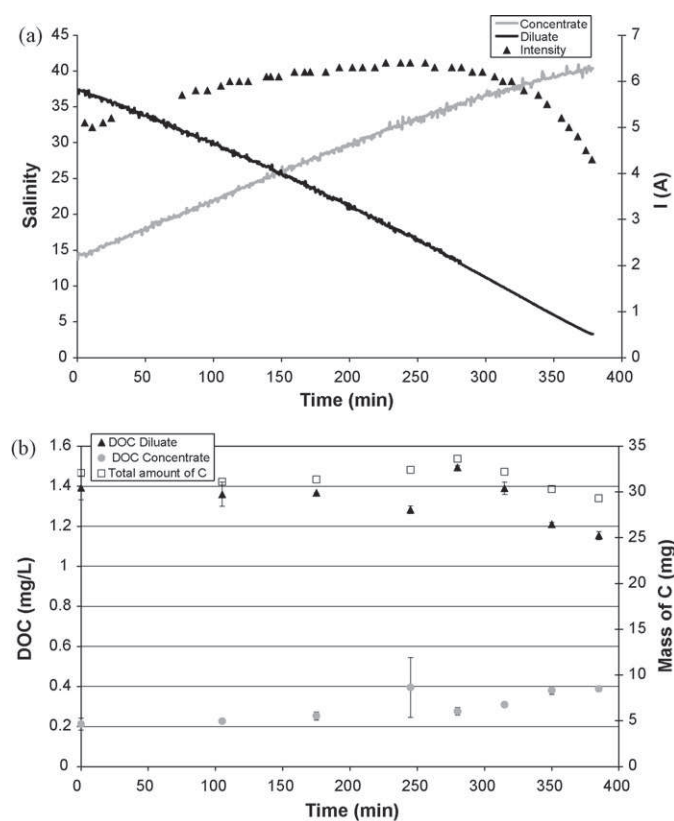


Fig. 8. Variations of the current intensity and of the salinity in the diluate and concentrate compartments during the desalting of 20 L of Mediterranean seawater by electrodesalination (a). Variations of the DOC content (expressed in mg/L) in the diluate and the concentrate compartment and values of the total amount of carbon (expressed in mg) present in the system (b).

again very close to those obtained with the artificial seawater (see Fig. 7(a)).

The total amount of C (Fig. 8(b)) remained almost constant until the 300th min; a slight decrease was then observed for salinities lower than 10. The variation, however, did not exceed 4%. Therefore, global DOC losses were negligible during the desalting process, which confirms the results obtained with 2 L of natural seawater.

DOC values determined for both compartments did not change very much during the desalting process, at least during the first 300 min. During this time, the DOC concentration in the diluate remained constant (about 1.4 mg/L). As for the DOC content in the concentrate, it was similar to the one obtained with artificial seawater (Fig. 7(b)). This suggests that the DOC content measured in the concentrate during the demineralisation of both Mediterranean and artificial seawater samples (0.2–0.3 mg/L) can at least be partly considered as the blank due to the system.

After 300 min of ED, the DOC in the diluate decreased slightly to 1.15 mg/L. At the same time, the DOC in the concentrate increased slightly to 0.4 mg/L. This indicates that at the end of the desalting process, DOM was transferred from the diluate to the concentrate. Indeed, as the salinity decreases, less and less mineral ions are present and organic ions (constituting DOM) begin to carry the electrical current and to pass through the membranes. Increasing desalting factor is thus expected to give higher DOM losses, because of higher migration of DOM from the diluate to the concentrate.

The diluate aliquots collected during the ED were also analysed using spectrofluorometry, as explained in Section 3.2. The contour EEM plots (a) of the initial Mediterranean seawater sample ($S=37.2$), (b) of the diluate with a salinity of 23.5 and (c) of the dilu-

ate collected at the end of the ED ($S=3.3$) are presented in Fig. 9. The spectrum of the diluate collected at the end of the ED (Fig. 9(c)) is 1.5 times less intense than the spectrum of the initial seawater sample and than the one of the intermediate diluate (Fig. 9(b)), which shows that fluorescent DOM was slightly lost during the second part of the ED. This result is in good agreement with DOC losses observed at the end of the ED. However, fluorescent DOM represents only a part of the DOC (up to 70% of DOM in natural waters; [26,27]). As a result, the concentrations in fluorescent DOM and DOC do not necessarily vary in the same proportion.

The shapes of the fluorescence spectra of the initial seawater sample (Fig. 9(a)) and of the intermediate diluate (Fig. 9(b)) were similar, which shows that no significant modification of fluorescent DOM occurred during the first part of the ED. The organic material was only very slightly modified at the end of the desalting, more particularly in the region of the γ and β bands, as can be seen in the spectrum of the diluate corresponding to the lowest salinity (Fig. 9(c)). These modifications were clearly much smaller in extent than those observed during the small scale ED (Fig. 4(c)). The small and large scale ED experiments were carried out with the same membrane surface area. The ratio between the volume of water to be desalted and the membrane surface area was ten times higher during the desalting of the 20 L of seawater than during the desalting of the 2 L of water. This suggests that qualitative modifications of fluorescent DOM can be decreased by increasing this ratio.

The diluate fluorescence intensity variations were plotted versus diluate salinity for the four main fluorophores (α' , α , β and γ) (Fig. 10(a)). The comparison with Fig. 6, obtained for small scale experiment, shows that the variations of the fluorescence intensities are similar. Indeed, we can see in Fig. 10(a) that the intensity of the band γ , contrary to those of the other fluorophores, increased slightly for salinities between 37 and 15. The increase of the intensity of the band γ was already observed during the desalting of 2 L of Mediterranean seawater (Fig. 6). It could be related to a slight contamination of the sample by the membranes, the pipes or the system, occurring despite an optimised cleaning of the membranes and of the pilot, as described in Section 2.2. The membranes or the other elements of the pilot may release some organic compounds fluorescing more intensely in the region of the band γ . It should be noted that the temperature increased from 14 °C at the beginning of the ED to 31 °C at the end of the desalting. This increase could explain the increase in the intensity of the fluorophore γ , associated with protein-like material and bacterial activity. A cooling system should be added to the pilot for future experiments in order to avoid temperature variations of water samples.

As for the other fluorophores, their fluorescence intensities remained constant for salinities down to about 20 or 15. For lower salinities, the intensity decreased. This decrease is much more pronounced for the α' band compared to the α and β bands. Furthermore, it seems that the decrease of the fluorescence intensities, which are proportional to the concentration of fluorescent molecules, was less pronounced in the case of the desalting of 20 L of seawater compared with that of 2 L. This is probably due to the fact that a higher seawater volume (20 L instead of 2 L) was desalted with the same membrane surface area. This result confirms the one obtained for the fluorescence spectra of diluate samples collected during ED, i.e. a higher ratio between the volume of water to be desalted and the membrane surface area reduced fluorescent DOM modifications, in both qualitative and quantitative terms. Thus, the volume of sample which has to be desalted could be chosen in function of the membrane surface area (and conversely) in order to limit DOM modifications and losses during ED. In any case, a compromise has to be found between the volume of seawater to desalt, the duration of the desalting, and the membrane surface area.

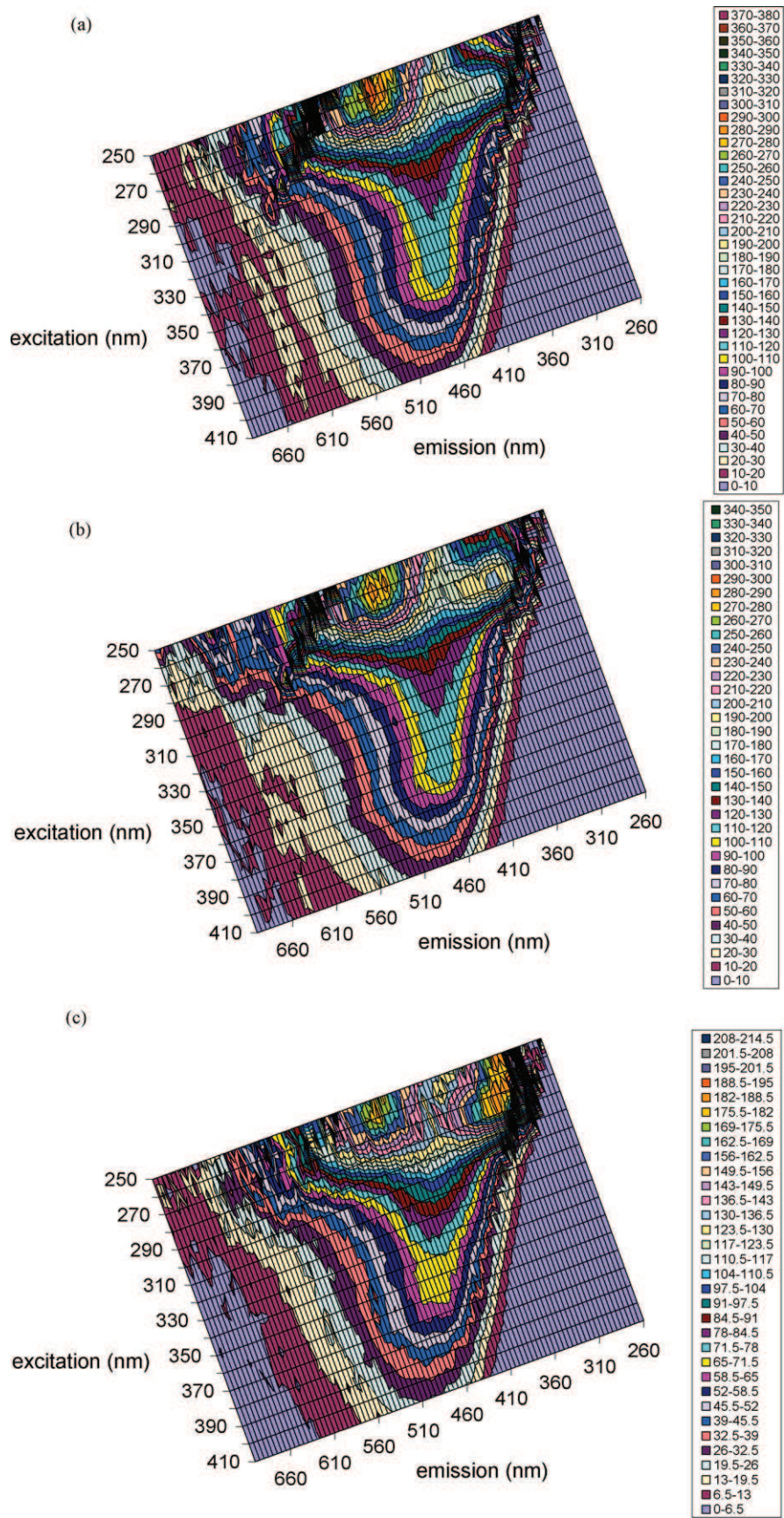


Fig. 9. Contour EEM plots of the initial Mediterranean seawater sample (a), of the diluate with a salinity of 23.5 (b) and of the diluate at the end of the electrodesalting (c) (desalting of 20 L of Mediterranean seawater). Fluorescence intensity scales identical for (a) and (b). Scale one and half times smaller for (c) than for (a) and (b).

The intensity ratios $I_{\alpha'}/I_{\alpha}$, I_{β}/I_{α} and I_{γ}/I_{α} were calculated in order to follow the variation of the different bands with respect to each other. They were plotted versus salinity (Fig. 10(b)). The intensity ratios were almost constant for salinities from 40 to 10, and then increased slightly. The increase was more pronounced for the ratio I_{γ}/I_{α} and was correlated with the increase of the intensity of the γ band at the end of the ED (Fig. 10(a)). These results clearly show that fluorescent DOM was modified only slightly during the desalting step by ED and that the modifications principally occurred during the last part of the desalting (salinity lower than 10).

In order to monitor the transfer of fluorescent DOM from the diluate to the concentrate during ED, the fluorescence intensities of all the aliquots collected in the diluate and the concentrate compartments were divided by the fluorescence intensities of the initial seawater sample. The fluorescence intensities were determined at excitation wavelengths of 260 nm (fluorophore α') and 370 nm (fluorophore α). The intensity ratios were plotted versus salinity in diluate. As can be seen in Fig. 11, the ratios remained almost constant in the two compartments for salinities higher than 20. Then, fluorescent DOM began to be transferred from the diluate to the concentrate. For a desalting ratio of 75% (salinity of 10), 80% of fluorescent DOM still remained in the diluate, whereas at the end of the ED (desalting ratio of 90%), about 40% of fluorescent organic matter was transferred to the concentrate. It can be noticed that, whatever the salinity, the results obtained in the two compartments are in total agreement, i.e. the fluorescent organic material lost in the diluate appears in the concentrate. As expected, transfer of DOM from

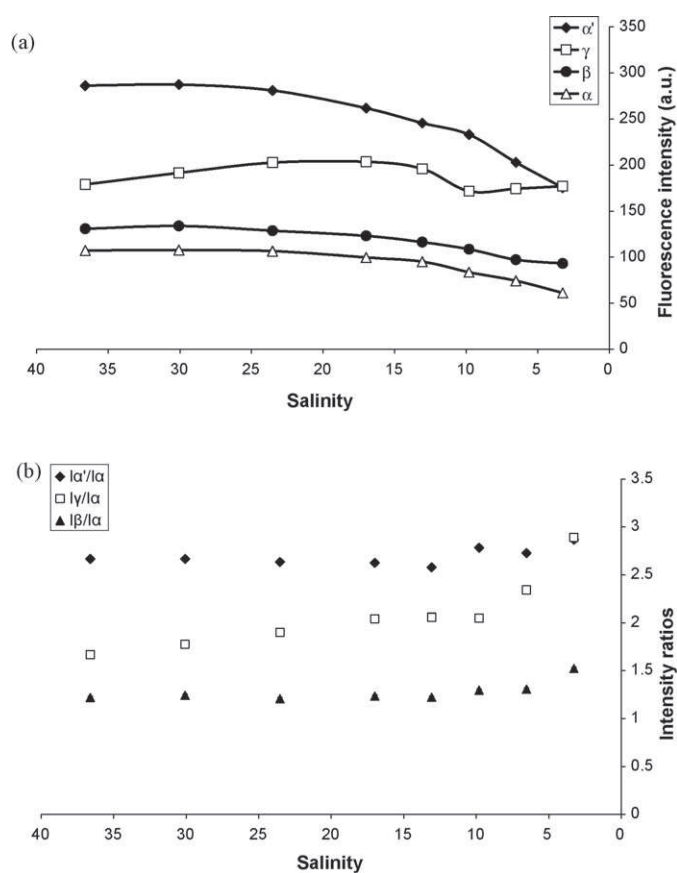


Fig. 10. Variations of the fluorescence intensities of the fluorophores α' , α , β and γ in the diluate as a function of the salinity (a). Variations of the fluorescence intensity ratios $I_{\alpha'}/I_{\alpha}$, I_{γ}/I_{α} and I_{β}/I_{α} as a function of the salinity (desalting of 20 L of Mediterranean seawater) (b). The uncertainty of the calculation of these ratios did not exceed 1%, which explains why the error bars are not visible in the chart.

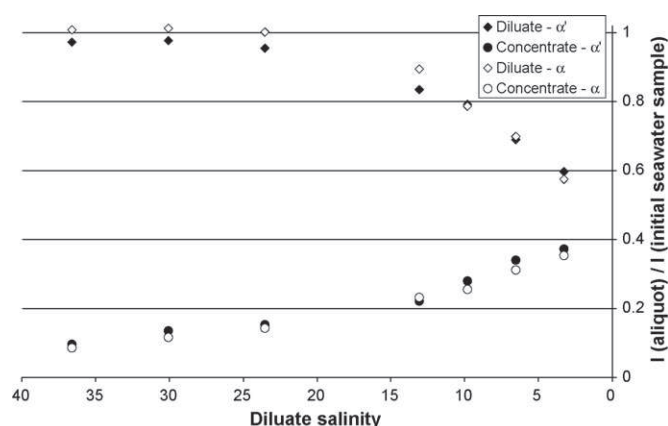


Fig. 11. Ratios of the fluorescence intensities of the aliquots collected in the diluate and in the concentrate over the fluorescence intensities of the initial Mediterranean seawater sample as a function of the diluate salinity (desalting of 20 L of natural seawater). These ratios were determined at an excitation wavelength of 260 nm (fluorophore α') and 370 nm (fluorophore α).

the diluate to the concentrate is the main mechanism responsible of DOM losses at the end of the desalting.

Previous studies dealing with the desalting of salted waste waters containing organic pollutants have demonstrated that achieving high desalting ratios can lead to increased organic matter loss [13]. Neither significant modifications nor losses of marine DOM were observed during the first part of the desalting of Mediterranean seawater. By desalting 20 L of natural seawater down to a salinity of 10 (which corresponds to a desalting ratio of 75%), the DOC to salinity ratio was increased by a factor 4. At the same time, it has to be underlined that DOM losses occurred for salinities of 20 until the end of desalting, but they were limited and non-specific, at least down to salinities of 10 (Fig. 10(b)).

For a desalting ratio of 90%, the DOC content in the diluate was only slightly lower (about 1.2 mg/L) than the initial value of 1.4 mg/L and the DOC to salinity ratio was increased by a factor 6, with a very high DOC recovery about 85%. Nevertheless, slight alterations and significant losses of fluorescent DOM (about 40%) by transfer to the concentrate were observed for such a high desalting ratio. When high degrees of desalination are reached, organic matter, which is negatively charged, probably competes with inorganic ions to carry the current through anion-exchange membranes.

About 75% of inorganic salts were removed from the 20 L of Mediterranean seawater without altering DOM or significantly modifying the DOC and fluorescent DOM contents of the sample. During the ED of 2 L of natural seawater, slight DOM modifications and losses began to occur at a desalting ratio of about 60%. Therefore, the results obtained in this study seem to suggest that the degree of desalting which can be reached without altering DOM depends on the ratio of the volume of water to be desalted over the membrane surface area.

4. Conclusions

Contrary to freshwater DOM, marine organic matter cannot be directly concentrated by RO, due to the presence of salts in high amounts in seawater. A desalting step has to be carried out prior RO and one of the most promising processes for DOM concentration today probably lies in the coupling of ED, for demineralisation, and RO, for concentration.

The objective of this study was to optimise a desalting step of seawater by ED for a reliable process which does not lead to DOM modification or contamination. New insights were provided

into potential changes of the organic matter during ED separation using 3D fluorescence spectroscopy. Specific cleaning procedures were first developed in order to avoid any contamination that could modify the initial DOM composition of seawater samples.

Thanks to the procedures developed in this work, it was possible to remove up to 75% of the inorganic salts from 20 L of a natural seawater sample whilst greatly minimising fluorescent DOM modifications and DOC losses. The DOC to salinity ratio was increased by a factor 4. Fluorescence spectroscopy showed that slight changes of DOM occurred at the end of the ED, i.e. for higher desalting ratios. The necessity to carry such specific characterisation of DOM, in order to identify modifications that might go undetected by DOC measurements only, was clearly established. This is the first time that ED has been evaluated for marine DOM desalting by a method other than simple DOC measurement.

The ED process could still be improved in order to avoid the slight fluorescent DOM modifications that were observed at the end of the desalting. This could be achieved by further investigating the influence on DOM quality of the process parameters (current, duration, temperature, membrane conditioning, system cleaning, etc.). We have already shown that the ratio between the volume of water to be desalted and the membrane surface area has to be carefully chosen to limit DOM modifications and losses.

In order to further decrease DOM losses during the ED, testing of other membranes, such as monovalent-selective ion exchange-membranes, could be considered. In this work, standard electro dialysis membranes were used. Contrary to standard membranes, monovalent-selective ion exchange-membranes preferentially retain multivalent ions. Since organic matter behaves like a polyelectrolyte in solution, the use of monovalent-selective anion-exchange membranes could minimise the transfer of DOM from the diluate to the concentrate compartment. The research work carried out by Drewes et al. [10] seems to confirm this hypothesis. These authors wanted to combine ED and RO to concentrate organic matter from freshwaters. They tested five pairs of cation- and anion-exchange membranes. The best results were obtained with the ACS/CMS combination with which 92% of DOC was retained in the diluate (against only 59% with AMX/CMX membranes).

Finally, ED appears to be a fast and efficient technique for desalting seawater samples whilst minimising, and even avoiding, DOM modifications. It may therefore be a reliable solution for overcoming the problems encountered with other processes, like ultrafiltration or XAD resins for instance, used for marine DOM extraction/concentration. The combination of ED and RO should allow the isolation and concentration of marine organic matter from large volumes of seawater and then the structural analyses of the organic material. By combining ED and RO, the characterisation of marine DOM should be improved and a more detailed knowledge of the nature and physicochemical characteristics of DOM in seawater should be acquired over the short term.

Acknowledgments

The authors want to thank Dr. Ernest Casademont for his help during ED experiments and acknowledge the CNRS, the Regional Council of Aquitaine and the French MONALISA research project coordinated by the IFREMER (Grant No.03/1214910/T) for their financial support. The interesting comments of the anonymous reviewers were helpful in improving the manuscript. We are also most grateful to Dr. N. Nunan and Dr. S. Derenne from UMR CNRS 7618 BioEMCo in Paris, France, for their improving remarks on the manuscript.

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