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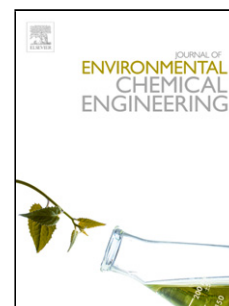
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ELECTRODIALYSIS FOR THE TERTIARY TREATMENT OF MUNICIPAL WASTEWATER: EFFICIENCY OF ION REMOVAL AND AGEING OF ION EXCHANGE MEMBRANES

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HIGHLIGHTS

- Electrodialysis was applied to produce reuse water from samples of municipal sewage.
- Operational parameters were determined and a long term treatment was carried out.
- The treated samples indicated the high efficiency of electrodialysis treatment.
- The membranes did not present damages caused by ageing effects after one year.

ABSTRACT

Electrodialysis was applied as a tertiary treatment for effluents from a Brazilian sewage treatment plant, and the results are discussed in terms of membrane ageing and process efficiency. Current-voltage analysis and electrodialysis (ED) treatment were performed in a bench cell. The treatment was discontinuously carried out for 930 hours within one year. During the experiments, samples were collected for evaluation, and the pH, conductivity and ion concentration were monitored. Thermogravimetric analyses of the membrane were also performed. A reduction in electrical conductivity and the high ion percentage extraction demonstrated the efficiency of the ED treatment, confirming the possibility of using ED as a tertiary treatment for sewage. ED showed 100% effectiveness in terms of meeting the quality standards established by Brazilian legislation on the discharge of effluents. Additionally, important corrosive (Cl^-) and encrusting ions (Ca^{2+} and Mg^{2+}) that limit certain industrial uses of water were satisfactorily removed,

giving the treated effluent a suitable quality for industrial purposes. The treatment did not suffer harmful fouling effects in terms of ion extraction in the membrane ageing study, indicating the possibility of long-term treatment without requiring cleaning for the membranes; however, this needs to be validated by scaling up the process.

Keywords: Electrodialysis; Sewage Treatment; Ion-Exchange Membranes; Water Reuse.

1. INTRODUCTION

The rising demand for water supplies and the misuse of water resources, due mainly to industrialisation and the growth in urban populations, are so intense that the quality of global water resources is under increasing threat.

In addition to contributing to the conservation of water resources, proper management of the effluent from wastewater treatment plants can turn this wastewater into an economic good, and can allow for the possibility of reusing the treated water. Depending on its final characteristics, the treated wastewater can be a substitute for process water for industrial purposes, playing a key role in the planning and sustainable management of water resources. In addition, the concentrate produced by this process may be used as a by-product depending on its composition.

Electrodialysis (ED) is a membrane technology with many applications, such as the desalination of brackish water, wastewater treatment and salt production [1,2]. However, the treatment of effluent from sewage treatment plants is still being researched.

In view of this, recent studies have considered the application of ED in water reuse. Goodman et al. [3] studied the use of a membrane desalination system based on electrodialysis reversal (EDR) to remove salts from treated municipal wastewater and to provide a source of recycled water for agriculture. Hsu et al [4] evaluated two different processes lines (sand filter/ultrafiltration/reverse osmosis and sand filter/electrodialysis reversal) at a municipal wastewater treatment plant in Taiwan in terms of their stability and the quality of the produced water. The results showed that ED is the most cost-effective process. Gotor et al.[5] compared the efficiency of different water qualities in the irrigation of two varieties of banana tree. Electrodialysis reversal (EDR), ultrafiltration and reverse osmosis were applied in a wastewater treatment plant in Spain, and EDR treatment was found to be the most suitable operation for irrigation use [5].

Other studies have recently been conducted of the removal of phosphorous from municipal wastewater [6], including a few studies of phosphorous removal using ED.

Tran et al. [7] used synthetic solutions of water and municipal wastewater to test the competition among ions and the efficiency of the phosphate concentration process. Ebbers et al. [8] investigated the efficiency of simultaneous extraction of heavy metal and phosphorus from wastewater and raw sludge. Electrodialysis has been used for municipal sludge samples obtained at various stages of the conventional wastewater treatment process. Ottosen et al. [9] recovered phosphorous from two different types of sewage sludge ash (SSA) from municipal wastewater treatment plants. The simultaneous recovery of phosphorus and separation of heavy metals from SSA was carried out in a two-compartment ED cell. Higher rates of phosphorous extraction were obtained from both types of SSA compared to chemical extraction at the same pH. Phosphorus salt was produced from the filtrate with a low impurity content, thus allowing further processing for the production of fertiliser.

When ED is applied to sewage demineralisation, the long-term behaviour of ion-exchange membranes must be considered. There are several phenomena that accompany membrane ageing, such as fouling and a reduction in mechanical properties, and these should be investigated. A few studies have addressed membrane ageing in ED treatment [10–12], but none of these have reported on the treatment of domestic sewage. Thus there is considerable room for further research into the behaviour and lifetime of the membrane when EDR treatment is applied to domestic wastewater.

Compared to conventional treatment and other membrane processes, ED is rarely used as treatment method for domestic wastewater. However, this process can offer an interesting alternative for the removal of ions for the purposes of industrial water reuse. In view of the high demand for water in many industrial processes, the use of ED as an alternative method of turning sewage into water of a suitable quality for industrial processes is a valuable topic for research. The use of ED to produce water for cooling towers from petrochemical effluent has already been studied, and the produced water complied with the corresponding standards for reuse in cooling towers [13]. In this work, although the sewage used had already been treated in a municipal wastewater treatment plant using macrophytes, the effluent did not reach the standards established for discharge or reuse. In the light of the above, the present work aims to evaluate the performance of the ED process as a tertiary treatment in a domestic wastewater treatment plant. A membrane ageing study is also carried out in order to assess the properties of the membrane during its lifetime while undergoing ED treatment.

2. MATERIAL AND METHODS

The effluent studied in this work was treated sewage from a domestic wastewater treatment plant (WWTP) located in Novo Hamburgo, Southern Brazil. This WWTP uses a pilot treatment system using macrophytes (*Typha domingensis*). Samples of the treated effluent were collected from the outlet of the macrophytes tank.

The current-voltage curves (CVCs) were constructed and the ED treatment performed using a bench ED cell; this contained five acrylic compartments, separated by cation-exchange (CEM) and anion-exchange (AEM) membranes arranged alternately, as shown in Fig. 1. The structure of the cell was similar to a filter press, and corresponded to a small-scale industrial ED stack. The membranes were provided by Hidrodex® and had an area of 16 cm². The characteristics of these membranes are shown in Table 1.

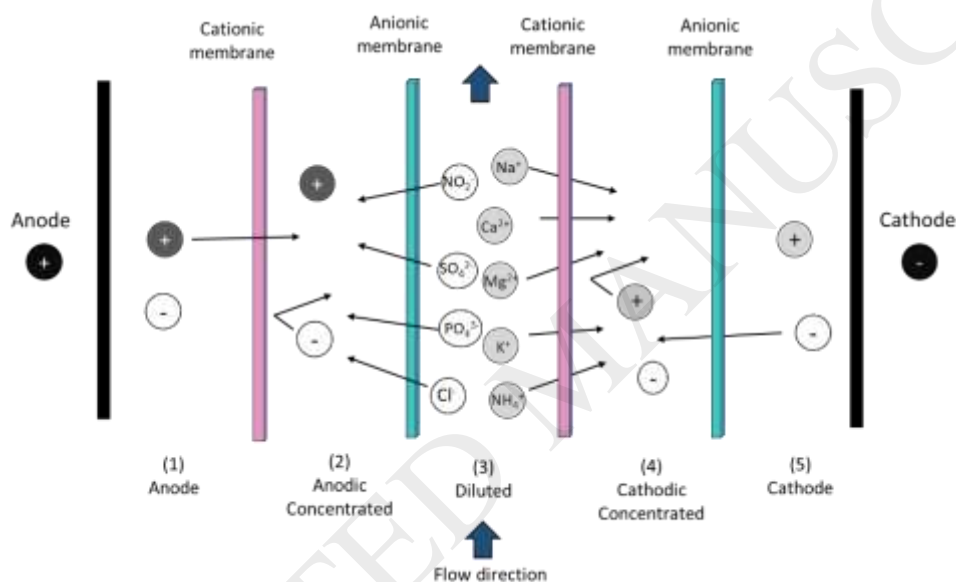


Fig. 1 Layout of the electrodiolysis lab cell used in the treatment of the studied solutions

The anodic and cathodic concentrated compartments were fed with 0.5 g.L⁻¹ Na₂SO₄ solution (with a conductivity similar to that of the effluent). The electrode compartments (cathode and anode compartments) were filled with a 4 g.L⁻¹ Na₂SO₄ solution and connected to the same reservoir, in order to reduce the electrical resistance and to avoid changes in pH and potential in the ED system [15]. The diluted compartment was fed with the effluent.

The reservoir of each compartment was connected to the ED stack by centrifugal pumps, and the solutions were recirculated with a flow rate of 80 L.h⁻¹. Titanium sheets coated with titanium and ruthenium oxides (Ti/Ti_{0.7}Ru_{0.3}O₂) and with an area of 16 cm²

were used as electrodes [15]. All ED treatments were performed in galvanostatic mode using an adjustable power supply (ICEL Manaus PS – 7000).

2.1 Initial Assessment

The effluent for the preliminary studies was stored in plastic drums of 50 L. Current-voltage curves (CVCs) were constructed in order to define the work parameters, and ED tests were conducted in order to verify the efficiency of the treatment.

The WWTP carried out monthly monitoring of the effluent, collected from the outlet of the macrophytes tank. Based on these data, a high variation in the concentration of organic matter is observed: the biochemical and chemical oxygen demand was $100 < \text{BOD} < 180 \text{ mg.L}^{-1}$ and $200 < \text{COD} < 350 \text{ mg.L}^{-1}$, respectively. These concentrations of organic matter can cause blockages in the membranes. In view of this, CVC and ED tests were carried out for two effluent conditions: treated effluent (as collected) and filtered treated effluent (treated effluent after a filtration step performed with cellulose membranes with pore sizes of $0.45 \mu\text{m}$, supplied by Merck Millipore®).

The reservoirs for each compartment of the bench cell contained 500 mL of solution. The central compartment (diluted, Fig. 1) was fed with treated effluent (TE) or with filtered treated effluent (FTE).

The limiting current density (LCD) for the bench ED system was determined following a method described in the literature [14, 16]. The initial electric current applied was 3 mA, and this was increased in increments of 3 mA to 60 mA. The potential of the membranes was measured using a voltmeter connected to platinum wires, placed on both sides of the anion and cation exchange membranes in the diluted compartment. These tests were performed in triplicate.

In order to carry out the ED test, the membranes were equilibrated with the solutions for 24 hours. Following this, the solutions were replaced with new ones and the pumps were turned on for 30 minutes, the solutions flowing through the system without an applied electrical current. Then, 15 mL samples were taken from each reservoir, and these were defined as the initial samples. ED treatment was carried out until the diluted solution reached an electrical conductivity of around $200 \mu\text{S.cm}^{-1}$ (a similar value to that of Brazilian tap water). Tests were performed in triplicate.

2.2 Membrane-Ageing Study

A membrane-ageing study was performed in order to evaluate the lifetime of the ED membranes and to verify the extent to which the presence of fouling harms the

performance of the ED process as a tertiary treatment for sewage. Figure 2 summarises the methodology used in this test.

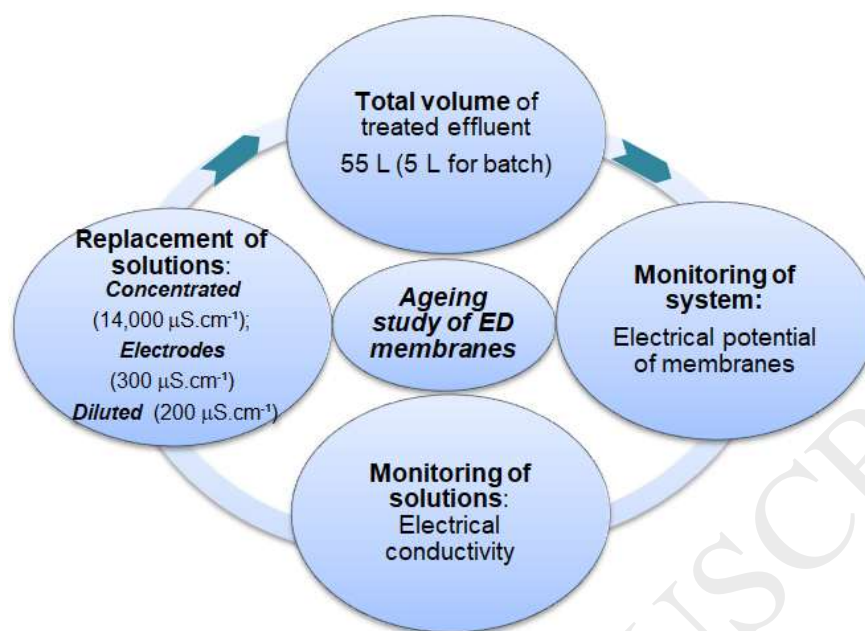


Fig. 2. Flowchart summarising the methodology adopted for the membrane-ageing test

The study was carried out over one year. Samples of treated domestic sewage were collected directly from the outlet of the municipal WWTP for tertiary treatment by ED in the bench scale cell described above. Five litres of effluent were used to fill the reservoir of the diluted compartment in the ED cell (see Fig. 1), while the other compartments were filled with four litres of sodium sulphate solution. The concentrate compartments contained $0.5 \text{ g.L}^{-1} \text{ Na}_2\text{SO}_4$ (with a conductivity similar to that of the effluent) and the electrode compartment contained a $4 \text{ g.L}^{-1} \text{ Na}_2\text{SO}_4$ solution.

The system was stabilised for 24 hours with the respective work solutions. Following this, all solutions were replaced with new ones, and the ED treatment was then performed.

A continuous and fixed electrical current density of 1.65 mA.cm^{-2} was applied. This value corresponds to 80% of the limiting current density obtained for the anion exchange membrane in the current-voltage curve test described in Section 2.1 above.

ED treatment was performed discontinuously during one year, treating 5 L of effluent in each batch. As the effluent became diluted, it was replaced by a new 5 L sample when the conductivity reached an established limiting value of 200 µS cm^{-1} . A total of 55 L of treated effluent was obtained.

The membranes were in contact with the solutions for 12 months, and the total treatment time was 930 hours.

The electrical potential of the membranes and of the ED system was monitored over the testing period of 12 months in order to analyse any system disturbance. Two platinum wires, placed one on each face of the CEM and AEM in the diluted compartment, allowed measurements to be taken of the potential difference for each membrane (the same measurement was made in the CVC tests, as described above and reported elsewhere [16, 18]).

During the ED treatment, samples were collected from all compartments in order to analyse the ion transport and demineralisation, and to evaluate the ion percentage extraction. When the electrical conductivity of the concentrated solutions was very high ($14,000 \mu\text{S cm}^{-1}$), these solutions were also replaced by new Na_2SO_4 solutions with concentration, pH and conductivity equal to the initial samples. For the electrode solutions, replacement was carried out when they showed a conductivity lower than $300 \mu\text{S cm}^{-1}$, with the aiming of re-establishing the initial conditions. These conductivities ($14,000$ and $300 \mu\text{S cm}^{-1}$) were selected as the critical values because they correspond to an increase in the system potential, which is associated with a concentration of the polarisation and higher energy consumption.

At the end of the test (after 930 hours), the stack was opened for an evaluation of the condition of the membranes. The membranes were washed with deionised water, and a soft sponge was used to remove the layer deposited on their surfaces. Following this, membranes were submitted to thermogravimetric analysis (TGA and DTG) and microscopy analysis (SEM with EDS) in order to verify the occurrence of blockages in the membrane channels after cleaning.

2.3 Analytical Methods

During the experiments, samples were collected for evaluation of the desalination rate and pH, and the conductivity of all working solutions was monitored with a pH meter (DM-22 Digimed) and a conductivity meter (AZ8361).

Ion concentration (fluoride, chloride, nitrite, phosphate, sulphate, sodium, ammonium, potassium, magnesium and calcium) was measured using the Ion Chromatograph DIONEX ICS-3000 with conductivimetric detection, using IonPac® AS22 and CS12A columns for anions and cations, respectively.

Analyses of the total phosphorus were performed using the ascorbic acid method from the Standard Methods for the Examination of Water and Wastewater [17]. The reproducibility of the analytical method was evaluated based on a representative sample.

These analyses enabled us to check the transport of ions through the membrane, the ionic concentration and the percentage extraction.

Thermogravimetric analysis (TGA and DTG) was accomplished using a TGA Q50, TA Instruments, and SEM and EDS analysis using EVO MA10.

2.4 Data Analysis

The percentage extraction (PE%) for the main ions detected in the diluted solution was evaluated using Equation 1:

$$PE\% = [(1 - (M_t \div M_0))]. 100 \quad (1)$$

where M_0 is the ion concentration in the effluent at the beginning of the experiment, and M_t is the concentration in the effluent at the end of the experiment.

3. RESULTS AND DISCUSSION

3.1 Initial Assessments

In the preliminary studies, ED was carried out for three hours on both the treated effluent (TE) and the filtered treated effluent (FTE). The effluents are summarised in Table 2.

Table 2 shows that the initial concentrations for some of the analysed ions (F^- , Cl^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ and Ca^{2+}) are slightly different for treated and filtered effluents, meaning that the filtration, in addition to removing organic compounds, retained some salts on the surface and/or inside the micropores of the membrane.

3.1.1 Evaluation of the Limiting Current Density

The limiting current density (LCD) was determined before and after the ED experiments, which were conducted for three hours. The LCD was first measured for the anion exchange membrane, and this value was then used to define the current density applied in the ED experiments.

Current-voltage curves for the anion exchange membranes are shown in Fig. 3; these were carried out in order to determine the LCD value associated with the treatment of both effluents (treated effluent and filtered treated effluent) and for new and used membranes.

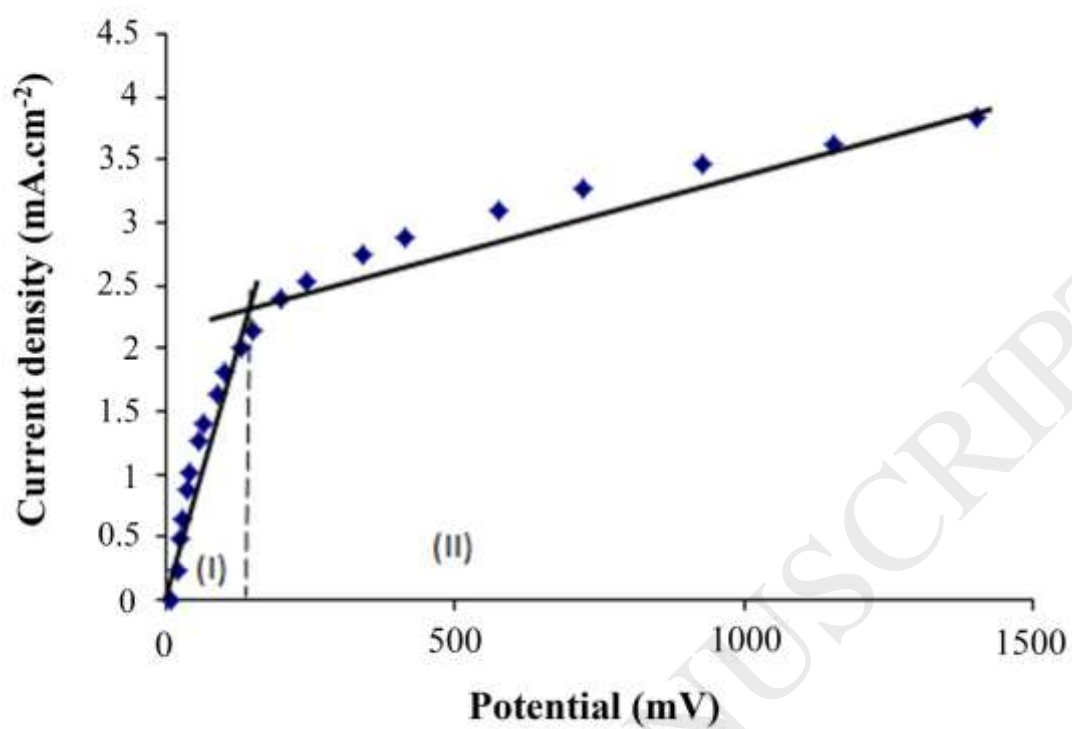
Potential and electric current data were plotted in order to identify the first and second regions and the inflection point equivalent to the limiting current (I_{lim}). Two well-defined regions can be observed in the CVCs. Region (I) shows an almost steady state at the membrane/solution interface, where the system resistance can be attributed to the ion

transport through the membrane. In region (II), where the current density shows only small variation and high potential increments, the concentration polarisation becomes more evident. The ion concentration in the boundary layer of the membrane on the diluted compartment side decreases, and consequently the resistance increases.

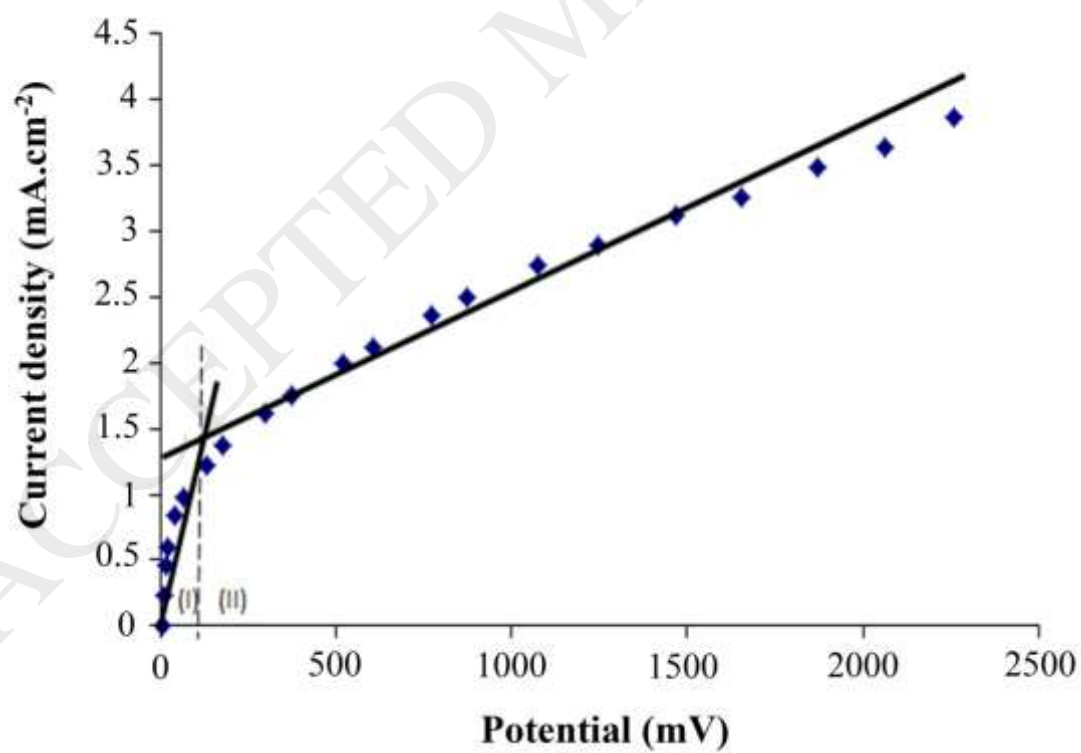
The value of the LCD obtained in the first test (Fig. 3a), in which a new membrane (NM) was used, was $2 \text{ mA}\cdot\text{cm}^{-2}$. In the second test (Fig. 3b), with reused membranes (UM), the limiting current was $1.4 \text{ mA}\cdot\text{cm}^{-2}$. This decrease in the LCD can be explained by an increase in the electrical resistance of the membrane-solution system; this is caused by fouling, which reduces the efficiency of the process over time. Organic substances typically cause fouling in the AEM, since the AEM has a positive charge while most organic foulants present in natural waters and effluents are negatively charged [18, 19]. This fouling causes a loss of membrane selectivity and a reduction in the diffusing capacity of the ions due to the deposition of organic material inside the channels or on the membrane surface. Fouling of ED membranes by organic solutes is a well-known problem and has been reported by other researchers [20–22].

A new membrane was used for the test with FE and following this, the same membrane was reused, resulting in LCDs of 2.2 and $2 \text{ mA}\cdot\text{cm}^{-2}$, respectively, as shown in Figs. 3c and 3d. These results indicate that the value of the limiting current for the FE (Fig. 3c) was close to that obtained for the unfiltered one (treated effluent – Fig. 3a) using a NM.

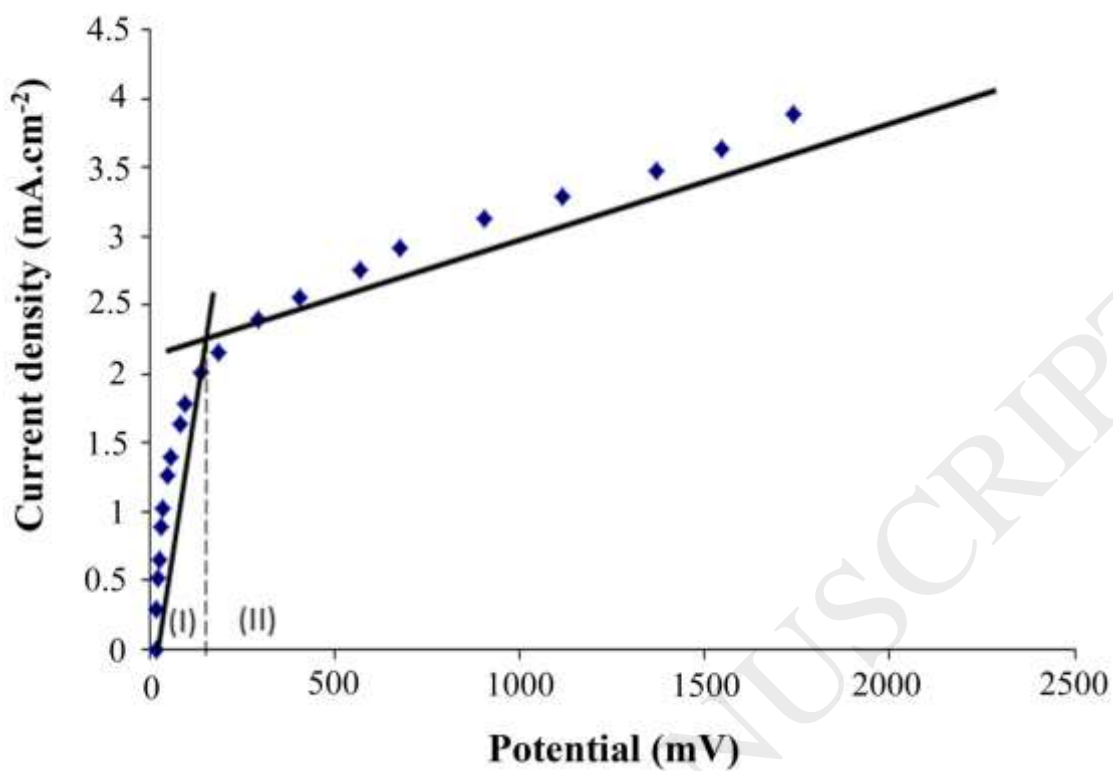
a



b



c



d

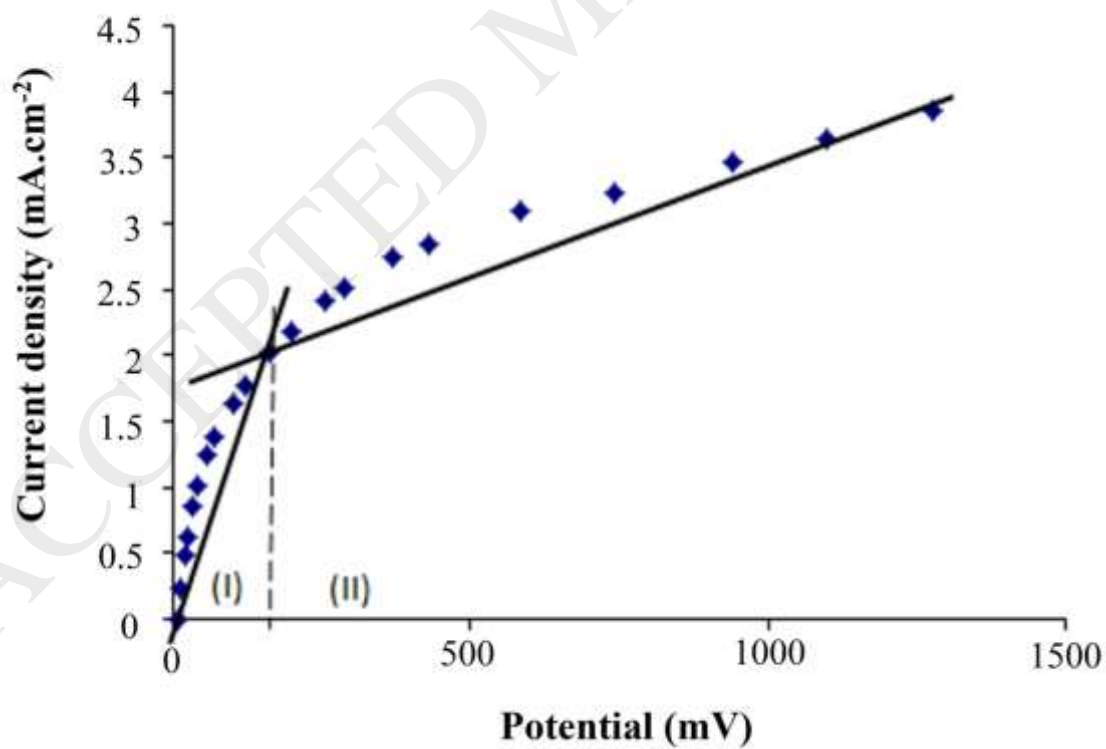


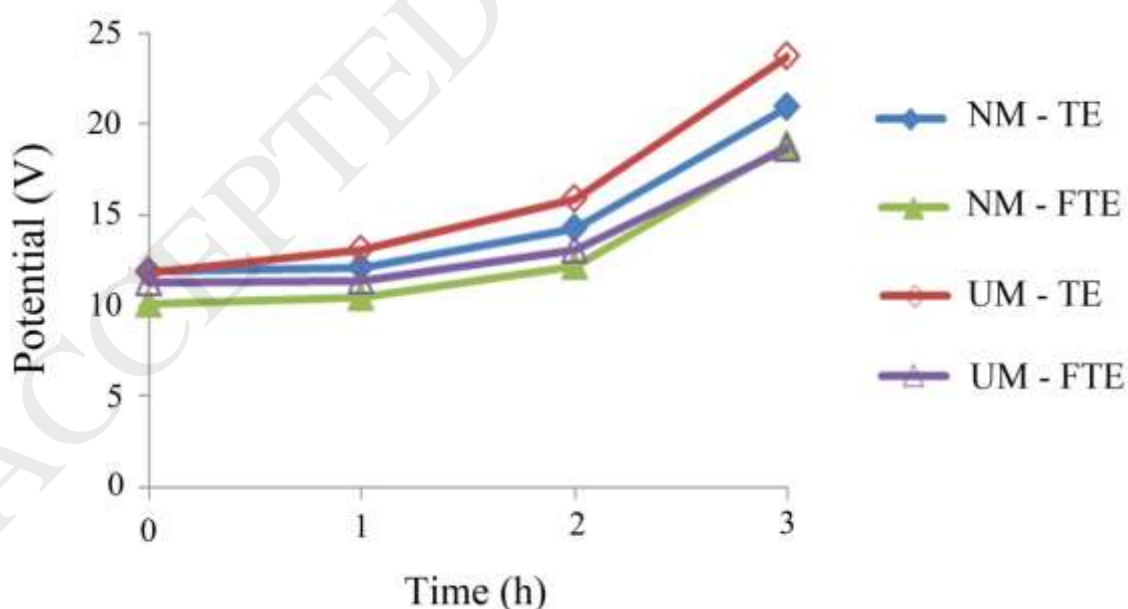
Fig. 3 Current-voltage curves (CVCs) for the anion exchange membrane in contact with the treated effluent (TE) or with the filtered treated effluent (FTE): (a) TE with a new membrane (NM); (b) TE with an used membrane (UM); (c) FTE with a new membrane (NM); (d) FTE with an used membrane (UM)

Although there was a visible material deposit on the AEM in both experiments using treated sewage and filtered effluent, when reusing the membranes, the values of the limiting current showed that the filtration step enabled the LCD to be maintained following the ED process (Figs. 3c and d).

3.1.2 Electrodialysis and Ions Removal

ED was carried out until the diluted solution achieved a conductivity of $200 \mu\text{S}\cdot\text{cm}^{-1}$. The tests were performed in galvanostatic mode with $1.65 \text{ mA}\cdot\text{cm}^{-2}$, a value based on data obtained from the CVCs, in order to avoid problems with concentration polarisation. The monitoring data for both the electrical potential of the ED cell and that measured on the new and used membranes are shown in Fig. 4.

a



b

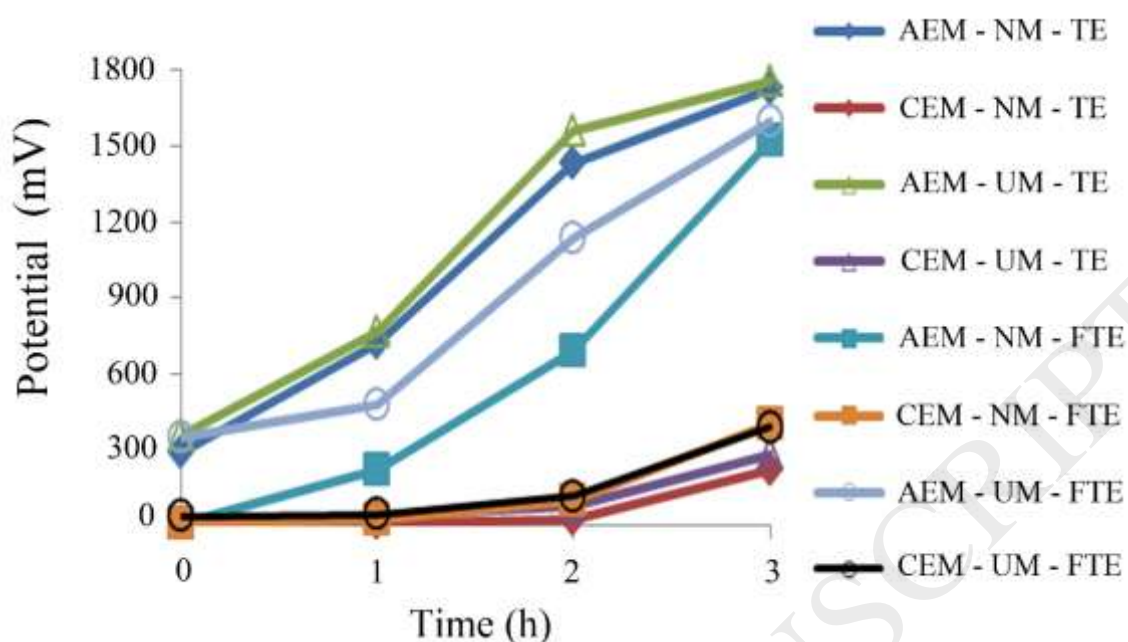


Fig. 4 Electrical potential during the ED treatments using treated effluent (TE) and filtered treated effluent (FTE): (a) of the electro dialysis cell for new (NM) and used membranes (UM) (b) of the anion (AEM) and cation (CEM) exchange membranes using new (NM) and used membranes (UM)

It was observed that both the total cell potential and the potential of the membranes increased throughout the treatment period. The AEMs had an increase in electrical potential that was much higher than that of the CEMs, which can be attributed to the deposition of organic matter on the membrane causing an increase in electrical resistance.

A linear decrease in the conductivity of the diluted solution (DC - central compartment) was observed during the ED treatment for TE and FTE. This is due to the migration of ions from this compartment into the anodic and cathodic concentrates, which consequently showed an increase in their conductivities, as illustrated in Fig.5.

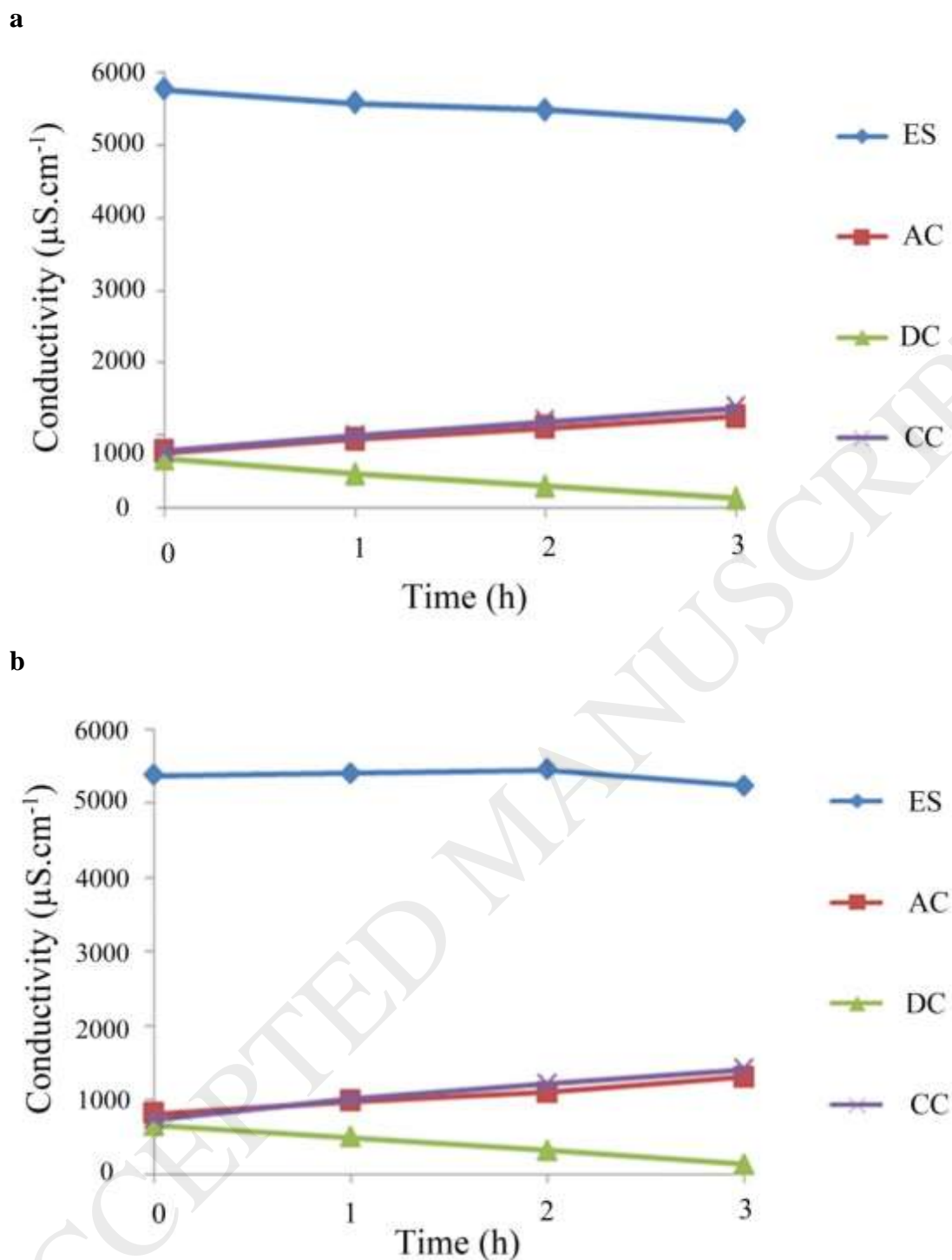
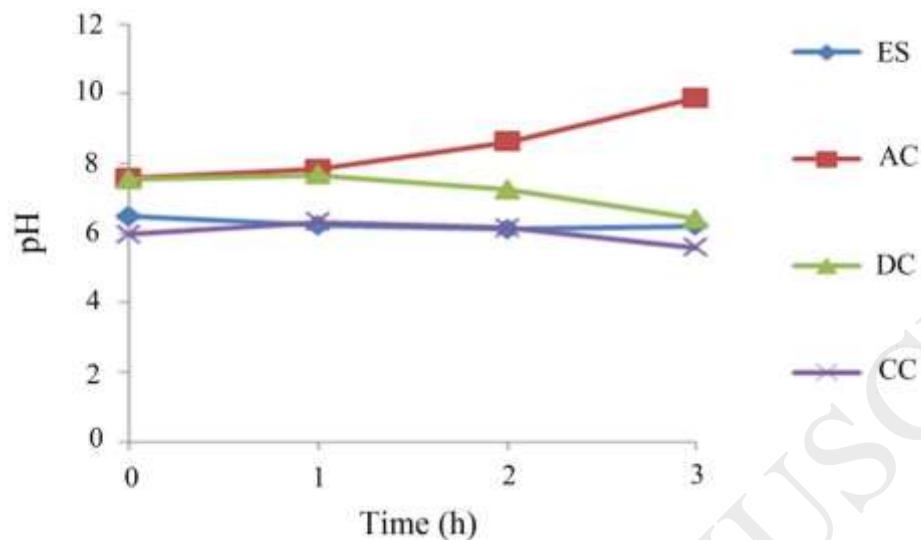


Fig. 5 Electrical conductivity during the ED treatment of the work solutions (ES – electrode solution, AC – anodic compartment, DC – diluted compartment and CC – cathodic compartment): (a) Treated Effluent (TE); (b) Filtered treated effluent (TFE)

Fig. 6 shows the pH behaviour over the ED treatment period. The pH of the diluted solution (DC) decreased due to the transport of the hydroxyl ions into the anodic concentrate solution (AC), where the pH increased. In the cathodic concentrated solution

(CC) the pH was slightly reduced by the transport of H^+ ions from the dilute to the CC. As all measurements were performed in the bulk solution, it is necessary to consider that the pH value in the membrane interfaces during the ED treatment may be different.

a



b

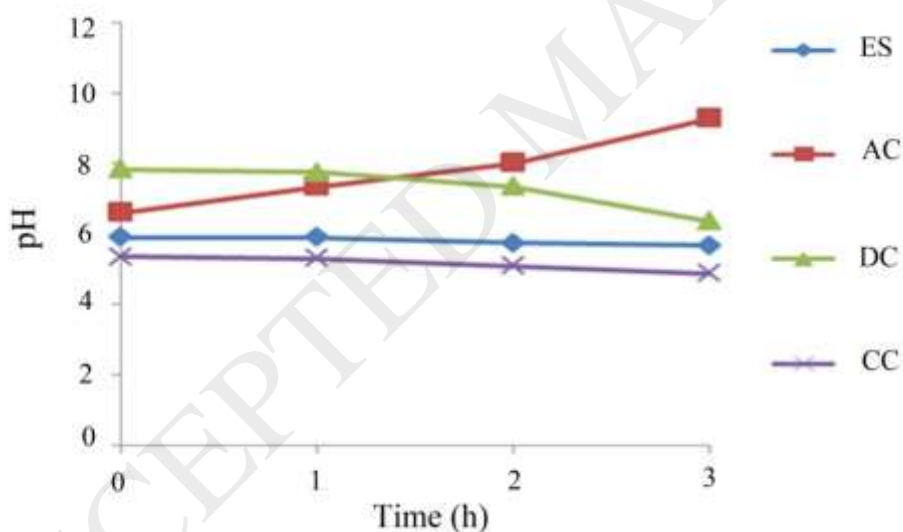


Fig. 6 pH monitoring during the ED treatments on the work solutions: (ES – electrode solution, AC – anodic concentrated, DC – diluted compartment and CC – cathodic concentrated): (a) Treated Effluent (TE); (b) Filtered treated effluent (TFE)

Fig. 7 shows that after treating the effluent with ED, the ionic PE% from the diluted to the concentrated compartments was higher than 70% for most of the ions

evaluated. Exceptions were the sulphate and phosphate ions, for which the percentage extraction ranged from 30% to 40%.

Although the PE% of sulphate was low, it is important to highlight that the initial sulphate concentration was much higher in the electrode compartments, as well as in the anodic concentrated and cathodic concentrated, since these were fed with Na_2SO_4 , than in the diluted solution. The same effect was seen for sodium extraction, where the PE% for both effluents was around 74%, the lowest cations extraction.

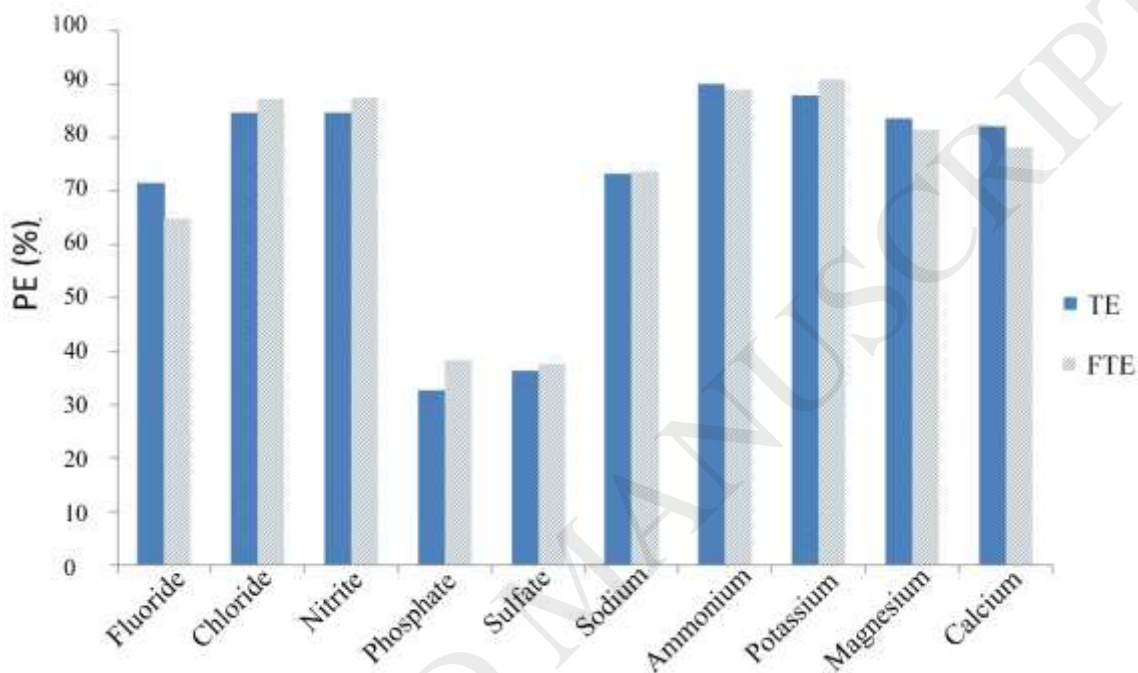


Fig. 7 Ionic percent extraction (PE%) by the electro dialysis treatment of the treated effluent (TE) and the filtered treated effluent (FTE).

Table 3 presents the ionic concentrations before and after the ED experiments in all compartments.

During the ED treatment, transport of fluoride and chloride ions took place from the diluted solution to the anodic concentrated solution for both effluents, as expected. Cl^- is a critical parameter in water reuse for industrial purposes, since it is related to the corrosive properties of water. In all samples, ED reduced the chloride concentration by around 85%, improving the water quality sufficiently for industrial purposes.

Nitrites naturally occur as intermediate products in bacteria-mediated processes (nitrification and denitrification) involving transformations of nitrogen in water and soil media. After the ED treatment of the treated sewage, NO_2^- shows a PE% of 87%. However, this extraction cannot be considered effective, since the nitrite was not detectable in the anodic concentrated solution, as expected. There are two possible reasons for this: ions may have been retained on the surface and/or within the membrane channels, or NO_2^- may have undergone oxi-reduction reactions. At the same time, the presence of organic matter in non-filtered sewage may interact with nitrites to form complex species and/or chelates, which are large and are therefore unable to pass through the membrane. However, following the ED treatment of the filtered effluent samples, the PE% of nitrite was around 88%; it was observed that most of the nitrite concentration migrated through the AEM to the anodic compartment, as expected.

For ammonium, the PE% for both effluents was around 90%, and some of the NH_4^+ ions extracted from the diluted samples were detected in the CC, as expected. Some ammonium may have been converted to unionised ammonia or to other nitrogen compounds.

The phosphate concentration showed PE% of 30% and 38% for treated effluent and filtered effluent, respectively. A chromatographic analysis of these ions gave important information; the PE% was not as efficient as that found for the other ions analysed in this work. This extraction was apparently ineffective, since phosphate ions were not detectable in any solutions following the ED treatment. It is likely that phosphate ions were retained on the surface of the membrane or its channels, or underwent chemical reactions to produce other compounds, thus making their identification as phosphate ions impossible. Analyses of the total phosphorus were performed for samples from the diluted (DC), cathodic (CC) and anodic concentrated (AC) solutions, in order to check the behaviour of phosphate ions. Total phosphorus concentration did not change during the ED treatment, and was detected mainly in the DC and in the AC, as shown in Table 4.

Based on the ionic concentration in the sewage (the “initial” data presented in Table 3), it is possible to construct chemical speciation diagrams using software such as HydraMedusa® [22]. For the effluent studied here, the phosphate ion may form complexes with other ions, forming negatively and positively charged complexes, as shown in Fig 8.

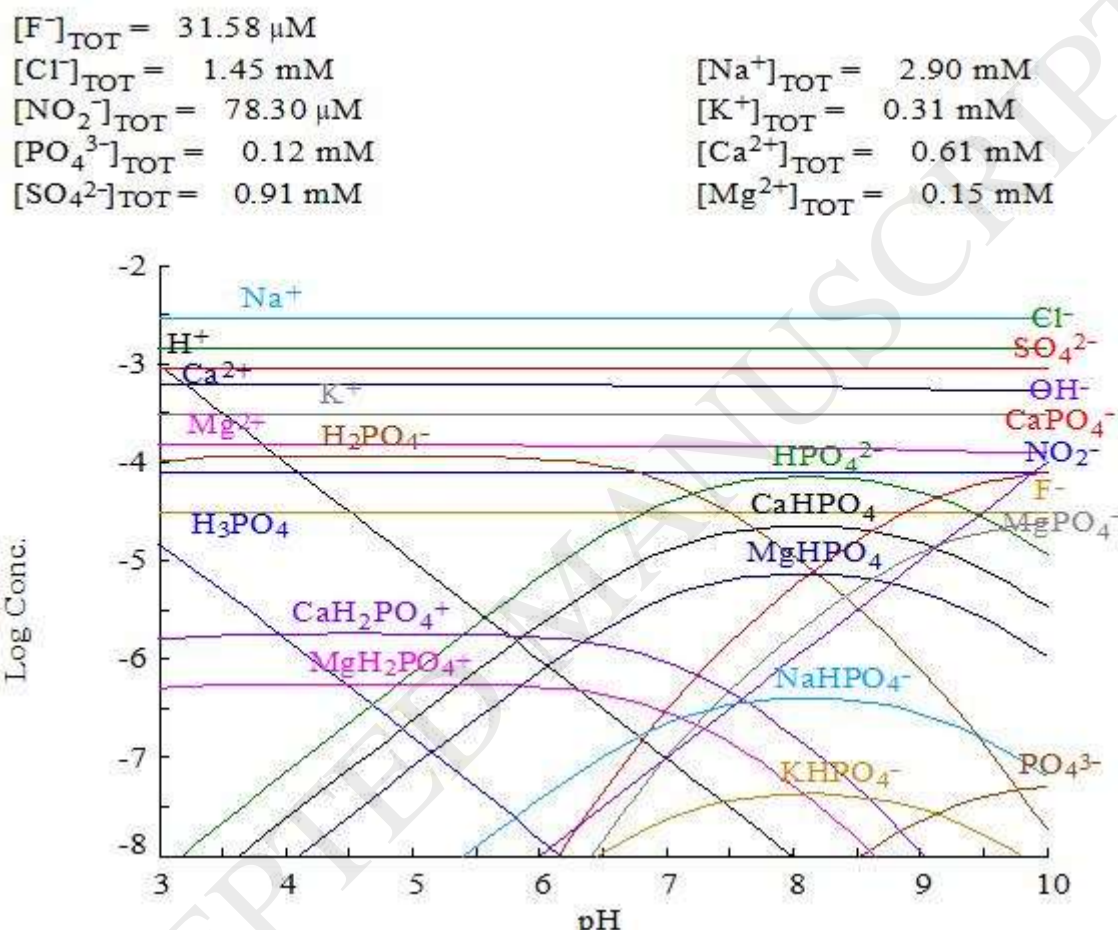


Fig. 8 Chemical equilibrium diagram for ionic species present in the studied effluent

Considering the pH of the diluted solution during the ED treatment, that varied from values around 8.0 to 6.0 in the bulk solution (Fig. 6), the effluent may present different P-containing species. Anionic species as HPO_4^{2-} and $H_2PO_4^-$ (in concentration around 10^{-4} M) and $CaPO_4^-$, $MgPO_4^-$, $NaHPO_4^-$ and $KHPO_4^-$ (in concentration lower than 10^{-5} M) that could be transferred to the anionic concentrated (AC) solution through the anion exchange membrane. This transference can explain the value of total phosphorus detected in the AC solution (Table 4). On the other hand, complexes species as $CaH_2PO_4^{4+}$

and $\text{MgH}_2\text{PO}_4^+$ (in concentration lower than 10^{-6} M) could be transported through the cation exchange membrane. However, the cationic and anionic complexes species probably have low mobility both within the solution and through the membrane, since they have a larger ionic radius than ions such as chloride (1.81 Å) and fluoride (1.36 Å) and sodium (0.95 Å) [23,24]. From an analysis of the diagram (Fig. 8) and the data presented in Table 4, it seems likely that cationic complexes remain in the dilute solution or become attached to the cationic membrane. Additionally, the non-charged species MgHPO_4 and CaHPO_4 (in concentrations around 10^{-6} to 10^{-5} M) probably remain in the dilute solution, explaining the values detected for phosphate (Table 3) and total phosphorous (Table 4) concentration in the diluted solution.

Potassium showed very similar PE% of around 89% and 91% for treated sewage and filtered effluent, respectively, and ions extracted from the DC were detected in the CC, as expected.

For cations, the primary focus in industrial uses of water is the concentration of magnesium and calcium, which indicate the encrustation potential. Precipitated salts of these ions can damage tanks and pipelines, triggering severe problems in heat exchangers and boilers.

The magnesium PE% was effective for both effluents, with similar percentages of around 84% and 81% for treated sewage and filtered effluent, respectively. However, the magnesium concentration in the CC solution was lower than the expected value, indicating that scaling probably occurred.

For calcium, in the treated sewage and filtered effluent, the PE% was about 82% and 78%, respectively. Calcium can bind with other ions to form negatively charged complexes (for example as CaPO_4^- , as shown in Fig. 8) that are therefore also transported through the anion-exchange membrane.

The results of these preliminary studies show that reuse of the membranes caused a decrease in the limiting current density for the treated effluent, while for the filtered effluent, this effect was not observed. This may indicate a cumulative effect from the foulant compounds from the treated sewage. Despite this, the data obtained from the ED treatments did not show significant variations in PE% values for the treated and filtered effluent. It is important to highlight that the ED tests were carried out over short treatment periods, meaning that the influence of foulant compounds was not observed. Longer

treatment times were therefore used and a follow up study of membrane ageing performed to verify the efficiency of the ED treatment and investigate the fouling effects.

3.3. Membrane Ageing Study

The study was conducted on various collected samples without previous filtration. During the test, it was observed that the electrical conductivity of the electrode solution and the treated effluent decreased. There was a transport of ions to the AC and the CC, as demonstrated in the initial assessment, causing an increase in ED cell potential or loss of efficiency in the system, due to the low concentration of ions.

For the sewage samples (treated effluent), the initial and final electric conductivity values measured during the test, before and after the replacement of the solution in the cell, are shown in Fig. 9. A mean value for the conductivity decrease of $18 \mu\text{S}\cdot\text{cm}^{-1}$ per hour was obtained in the diluted compartment over all experiments.

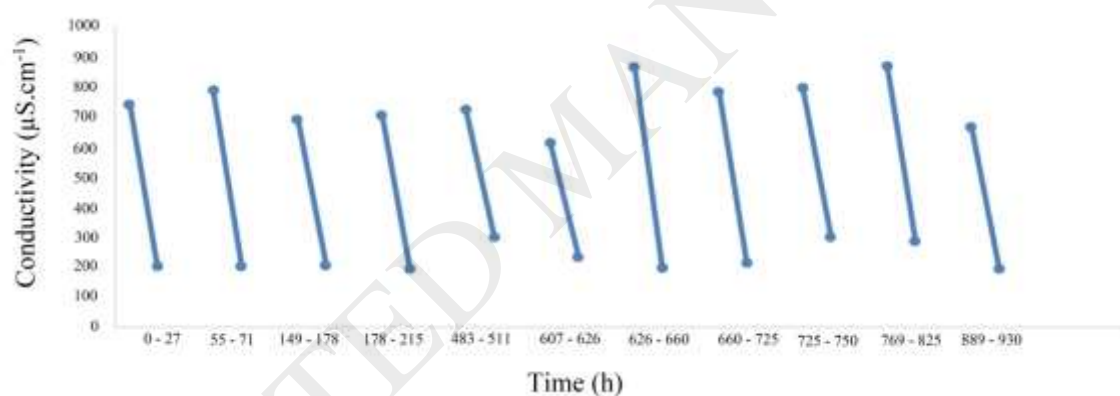
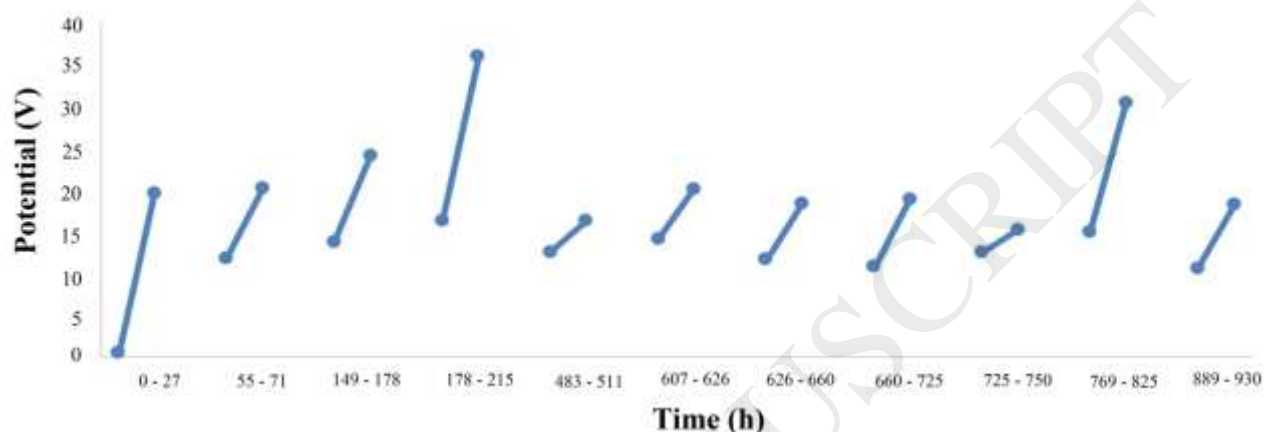


Fig. 9 Initial and final electrical conductivities of the treated effluent for each replacement of the diluted solution

The electrical potential of the ED system was monitored, and the results are presented in Fig. 10a. An increase in the electrical potential was shown for each replacement of the effluent in the central compartment. This increase in electrical potential is directly related to the loss of ED efficiency, associated with the low conductivity of the diluted solution. Two points in Fig. 10a show a higher increase in potential compared to the other points. This may be due to the low concentration of ions in the electrode compartment, leading to the replacement of the electrode solution in order to restore normal system operation.

The electrical potential for the AEM and the CEM is presented in Fig. 10b. As expected, the highest potential was obtained in the AEM, following the behaviour observed in the studies of CVCs; this may be related to the deposition of organic matter on the membrane [25], increasing the resistance to ion transport and reducing the efficiency of anion removal.

a



b

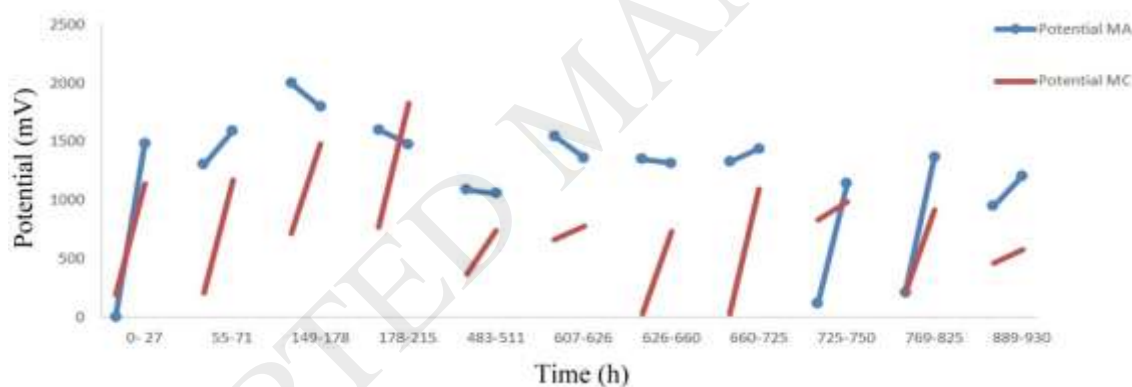


Fig. 10 Electrical potential during the membrane ageing study: (a) of the ED system; (b) of the anion-exchange membrane (AEM) and the cation-exchange membrane (CEM)

The behaviour of the pH was also monitored during the treatment. In the same way as for the electrical conductivity, the pH of the diluted compartment decreased. This behaviour (shown in Fig. 11) repeats that observed in the previous short-term tests described in Section 3.1.2.

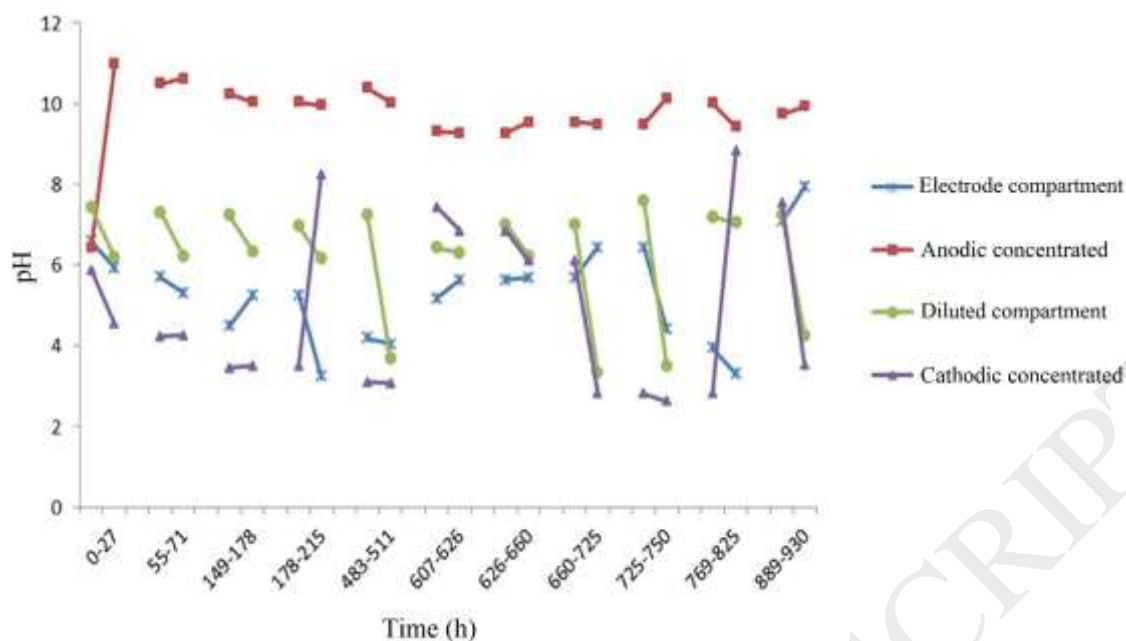
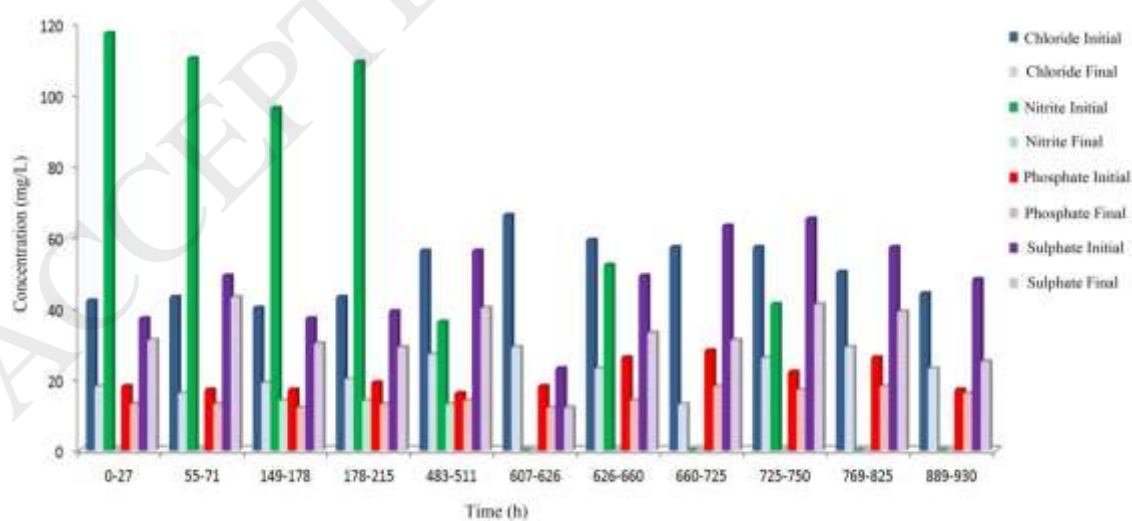


Fig. 11 Variation in pH during the treatment period for ED work solutions

Chromatography analyses were performed to verify the ion PE% and the efficiency of the ED system during the test. Initial and final concentrations of the cations and anions in the effluent were measured each time a new effluent was fed and when the effluent was treated and replaced by a new one. The effluent was considered to be fully treated when it reached the conductivity established as standard ($200 \mu\text{S}\cdot\text{cm}^{-1}$). The ion concentrations are shown in Fig. 12.

a



b

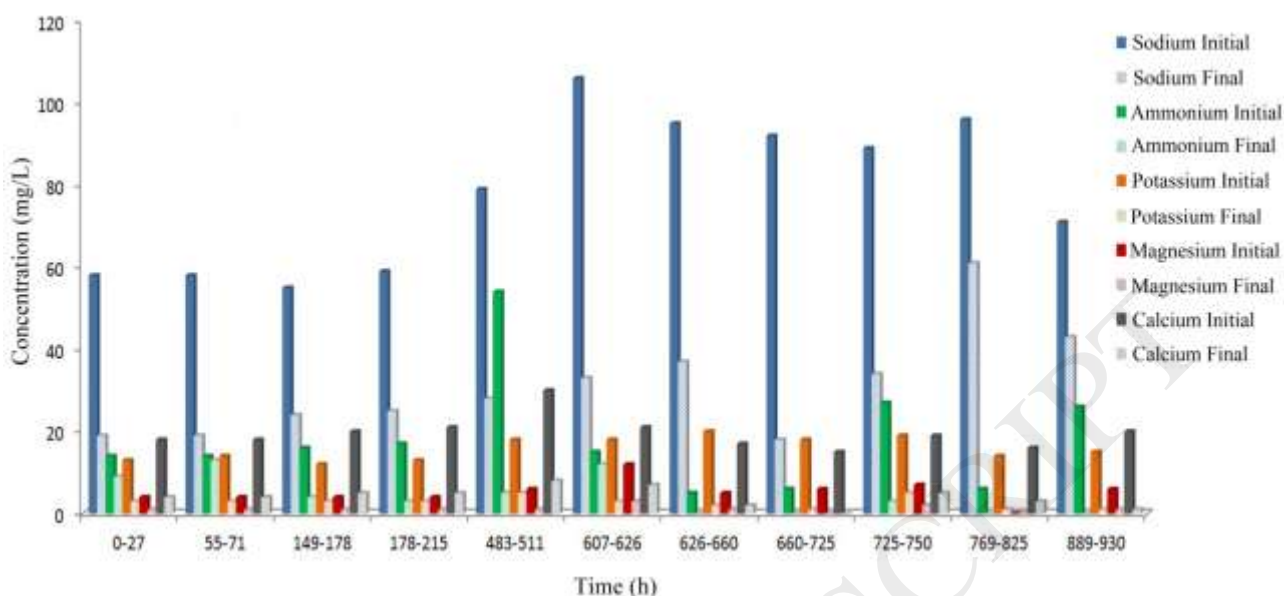
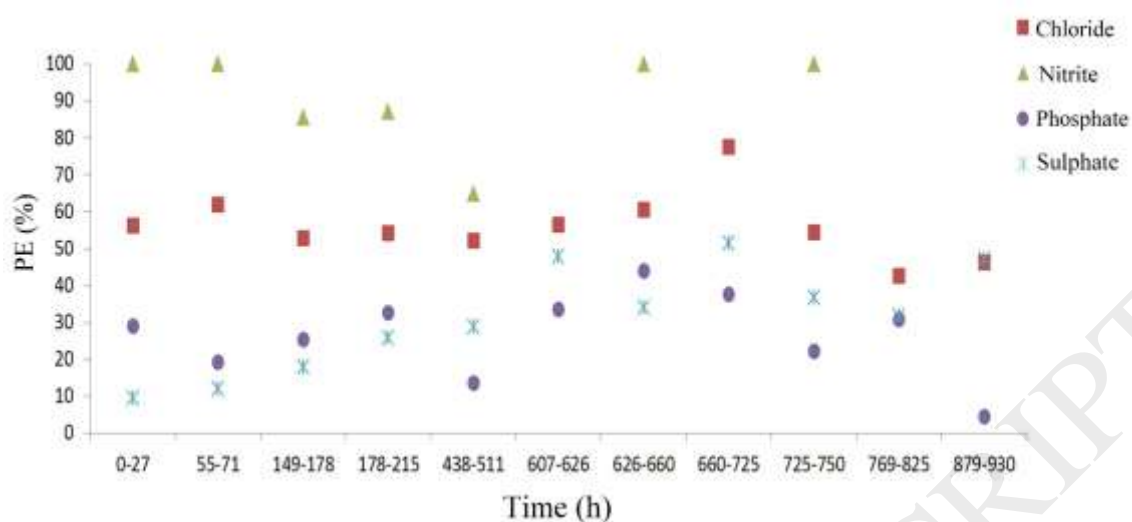


Fig. 12 Ionic concentration in the effluent samples over the 930 hours of the ED membrane-aging test: (a) anion concentration; (b) cation concentration

Fig. 12 shows that the interval between effluent replacements was about 30 hours. During the 930 hours of the ED membrane-aging test, the ion concentration did not undergo significant changes. This suggests that impediments to the ion transfer through the membranes did not occur.

The ion removal efficiency, measured as PE%, was analysed at certain points in the effluent replacement in order to identify whether there was a reduction in the efficiency of the ionic transport through the membranes over the ED ageing test. The obtained data are presented in Fig. 13.

a



b

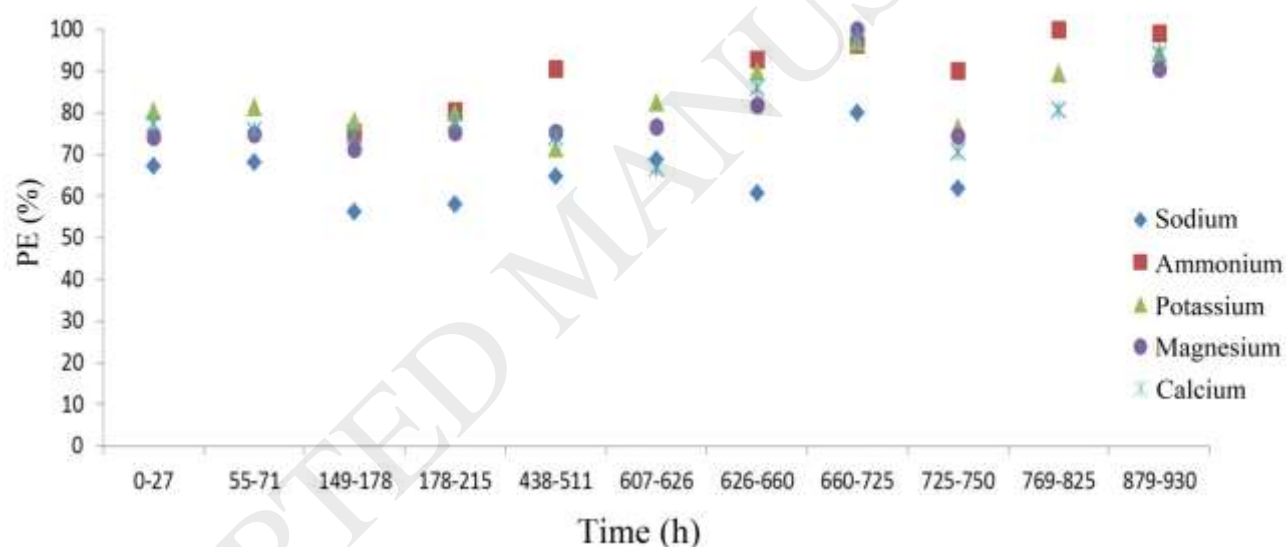


Fig. 13 Ion removal efficiency as percentage extraction: (a) anions; (b) cations

After 930 hours of assay, the ED cell was opened in order to verify and analyse the membranes. After surface cleaning of the membranes, they underwent thermogravimetric and microscopy analysis. Figure 14 shows the membranes and the acrylic plate of the central compartment (i.e. the location where the effluent was fed), indicating deposition of organic matter.

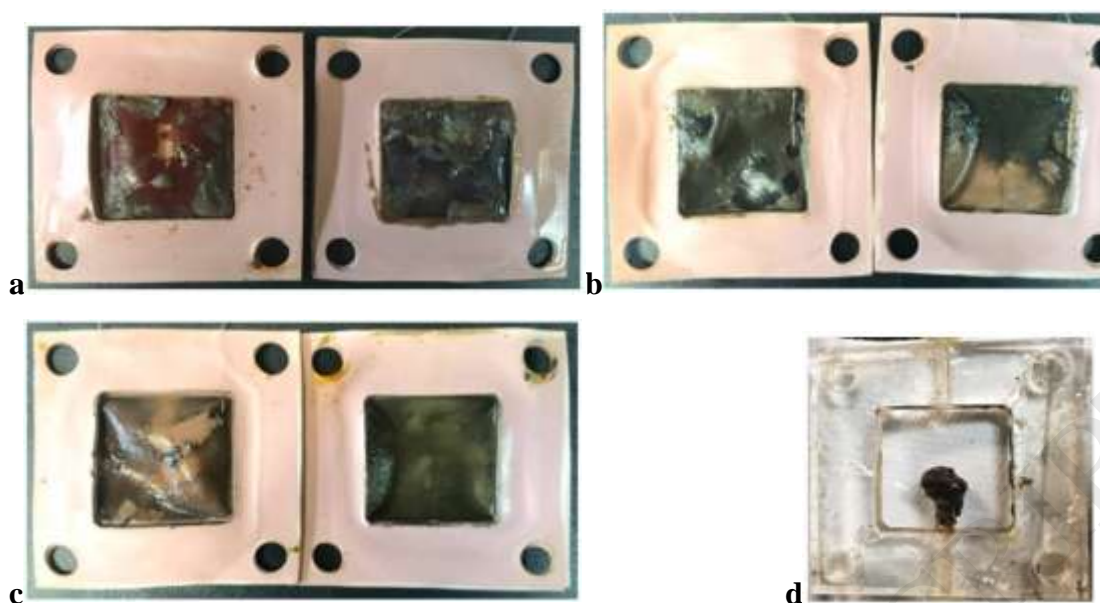
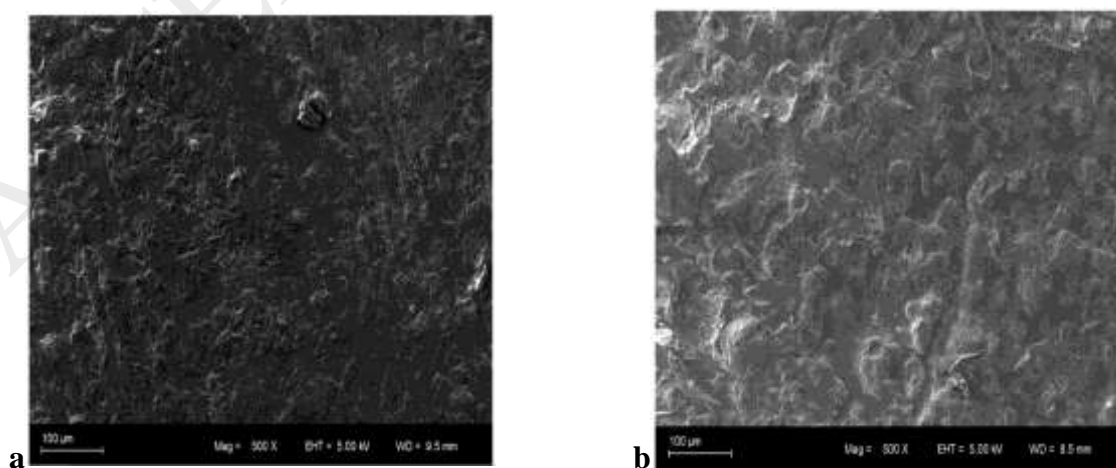


Fig.14 Cation and anion-exchange membranes: (a) in contact with the solution of the anodic concentrate; (b) in contact with the treated effluent; (c) in contact with the solution of the cathodic concentrate and (d) image of the acrylic plate from the central compartment (fed by the effluent) after 930 hours

Figs. 15 and 16 present images obtained by scanning electron microscopy (SEM) of the surface of the ionic membranes. These demonstrate that the membranes were not damaged in terms of their structures after 930 hours of assay. The membranes also underwent EDS analysis, in which two different voltages were applied (5 and 15 keV). The EDS analysis showed only carbon and oxygen elements in all samples analysed, indicating that there was no presence of residues on the membrane surface.



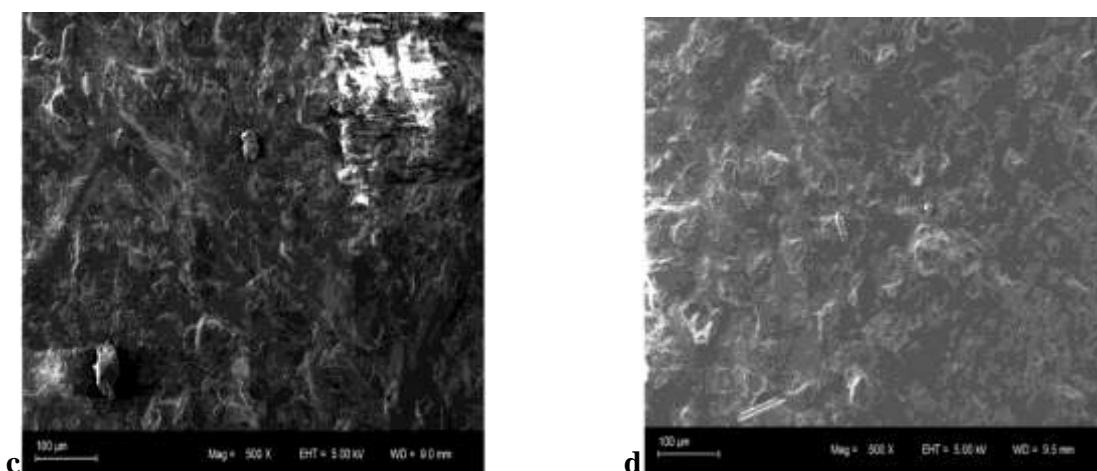


Fig.15 Scanning electron microscopy of the cation-exchange membranes (CEM) of the ED system: a) new CEM; b) CEM of anodic concentrated; c) CEM of central compartment; d) CEM of cathodic concentrated

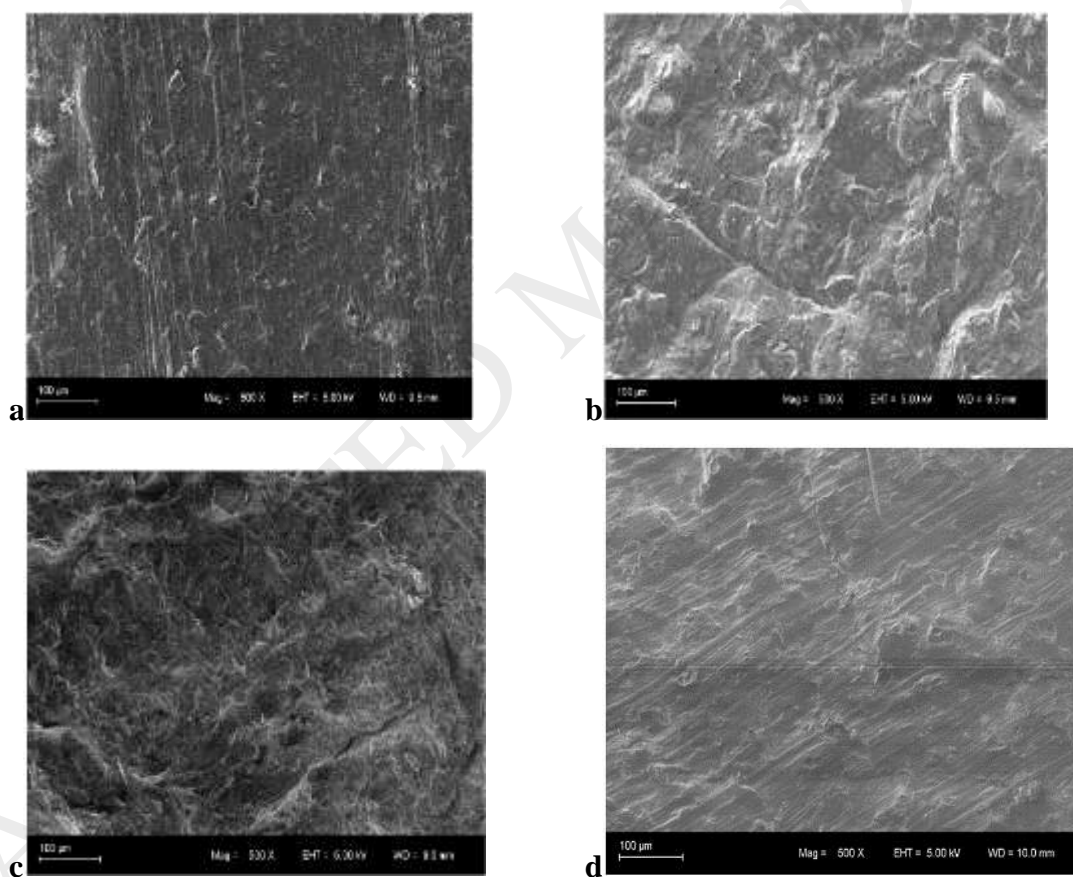
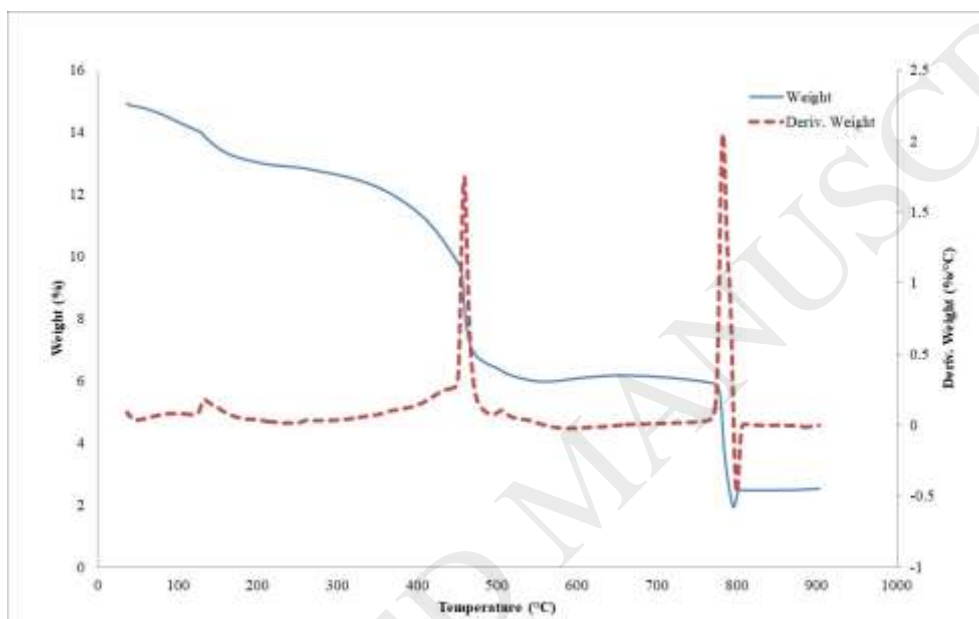


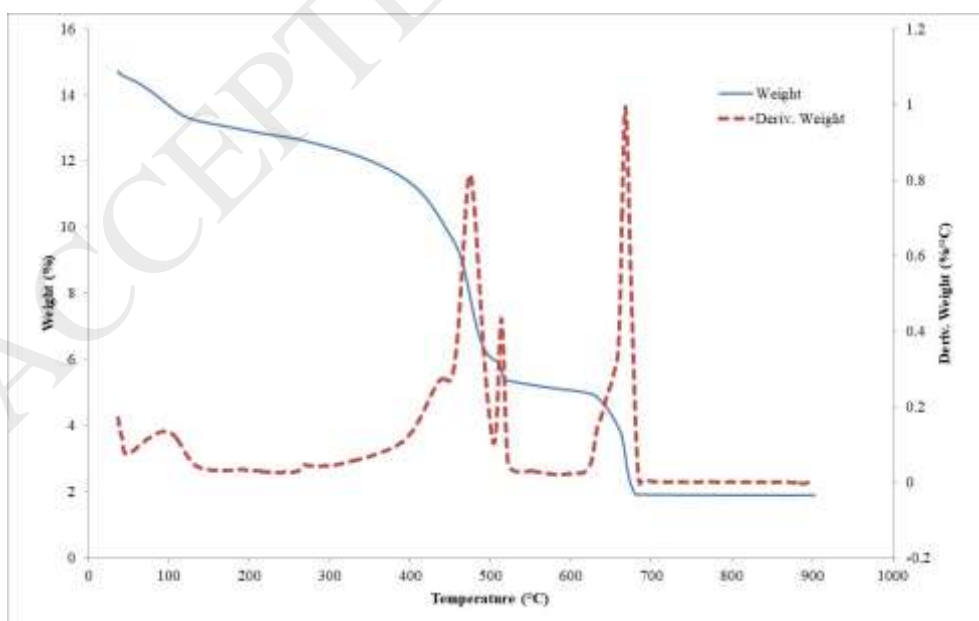
Fig.16 Scanning electron microscopy of the anion-exchange membranes (AEM) of the ED system: a) new AEM; b) AEM of anodic concentrated; c) AEM of central compartment; d) AEM of cathodic concentrated.

Fig. 17 presents TGA analyses of the new and used (after 930 h) ion exchange membranes, indicating that these membranes are unmodified after use. In the CEM, a large loss of mass was observed at 420°C, probably due to the degradation of the sulphonated groups [26]. The literature reports a variable temperature range for the decomposition of these groups, and this variation may be due to the composition and thermal stability of each material [27]. Above this temperature, degradation of the main chain polymer is likely to occur [26].

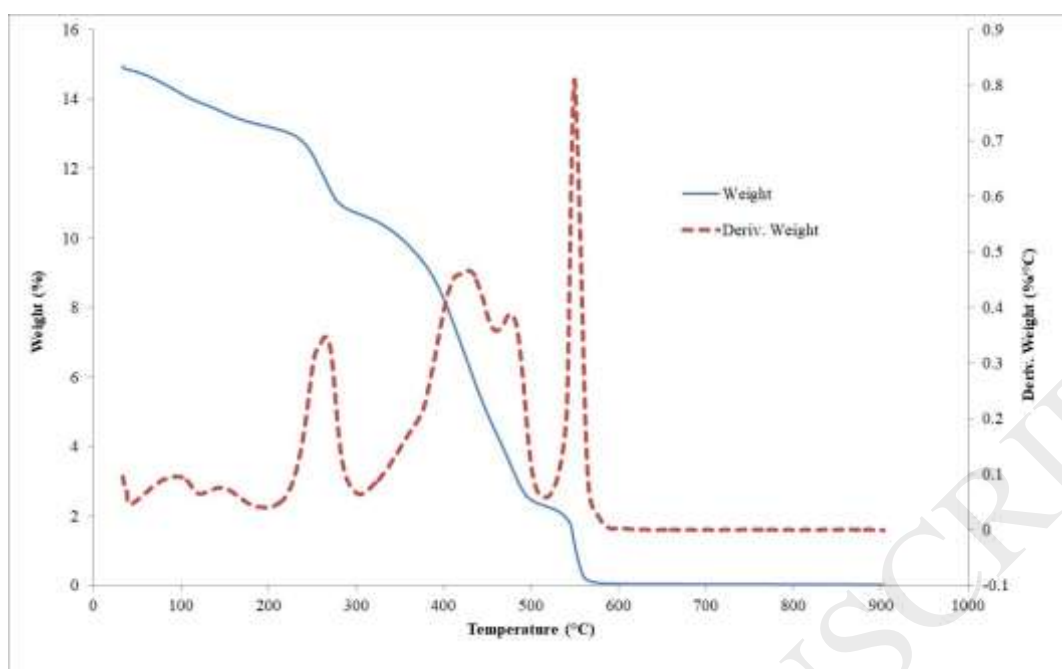
a



b



c



d

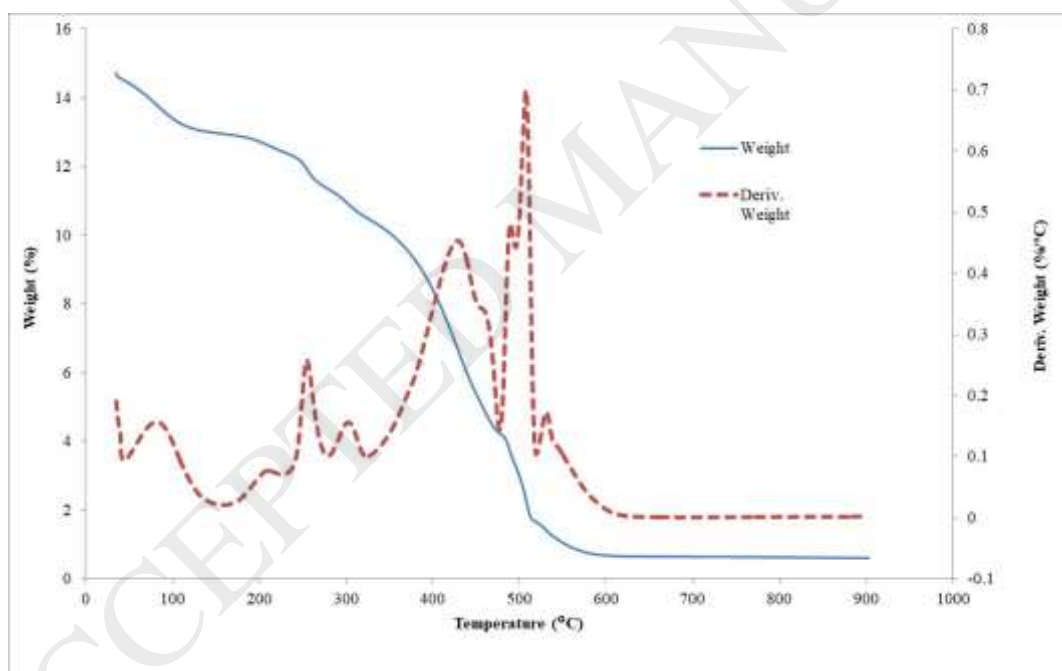


Fig.17 Thermogravimetry of the new and used cation (CEM) and anion-exchange membranes (AEM) after 930 hours of use over a period of 12 months: a) new CEM; b) used CEM; c) new AEM; d) used AEM

The new cation-exchange membrane showed residues of around 15% for both the new and used membranes. The similarity in the values for the new and used membranes suggests that the cleaning of the membrane after use (with deionised water and a soft

sponge) was efficient, and there was no permanent precipitation on its surface and/or channels.

In the AEM, a large loss of mass was observed at a temperature of around 400°C in both samples, and this was attributed to the decomposition of the quaternary ammonium groups of the membranes [29, 30]. Above 450 °C, the loss of mass is attributed to the decomposition of the main polymer chains [30, 31].

For the new AEM, it was observed a value of 0.16 % for the residue, while 4 % was detected for the used membranes. Detection of the latter quantity of residue in the thermal analysis of AEMs after washing indicates the formation and permanence of residues in the membrane structure. These are likely to be scaling-type residues (inorganic material), since the component does not volatilise and does not lose mass even at temperatures above 600 °C. It is known that the loss of organic matter by volatilisation occurs mainly in a temperature range above 500 °C [17]. According to Tay et al. [31], the volatile material deposited on the membrane is mainly composed of organic substances, while the non-volatilising material is composed of inorganic substances.

The higher value of residuals on the used AEM was expected, since in the CVC assay, the used AEM showed a lower LCD than the new one, indicating the presence of deposits on the membrane.

4. CONCLUSION

In this study, it is demonstrated that ED can be applied as a tertiary treatment for domestic sewage, and that it is able to produce reusable water for industrial use, such as in cooling towers. The composition of the sewage can cause problems related to fouling and scaling, reducing the ED efficiency, as shown by the LCD values of the microfiltered effluent and the non-filtrated samples and by the residue detected through thermogravimetric analysis. However, no significant loss in anion-exchange capacity was observed when the treatments of filtered and non-filtered effluent were compared, either during the ED treatment or after the membrane-ageing test. The reduction in the electrical conductivity and the high PE% for the analysed ions demonstrated the efficiency of this membrane separation process. This is due mainly to minimisation of the concentration of important corrosive (Cl^-) and encrusting ions (Ca^{2+} and Mg^{2+}) that limit industrial uses. This work confirms the possibility of applying ED in the treatment of real effluents to turn the sewage into a water source for industrial use.

Acknowledgements

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REFERENCES

- [1] H. Strathmann, L. Giorno, E. Drioli, Introduction to membrane science and technology, Weinheim, 2011.
- [2] C. Xu, Tongwen; Huang, Modeling and simulation of the polymeric nanocapsule formation process, *AIChE J.* 54 (2008) 3147–3159.
- [3] N.B. Goodman, R.J. Taylor, Z. Xie, Y. Gozukara, A. Clements, A feasibility study of municipal wastewater desalination using electro dialysis reversal to provide recycled water for horticultural irrigation, *Desalination.* 317 (2013) 77–83. doi:10.1016/j.desal.2013.02.010.
- [4] Y.-C. Hsu, H.-H. Huang, Y.-D. Huang, C.-P. Chu, Y.-J. Chung, Y.-T. Huang, Survey on production quality of electro dialysis reversal and reverse osmosis on municipal wastewater desalination, *Water Sci. Technol.* 66 (2012) 2185–2193.
- [5] A.G. Gotor, S.O. Pérez Baez, C.A. Espinoza, S.I. Bachir, Membrane processes for the recovery and reuse of wastewater in agriculture, *Desalination.* 137 (2001) 187–192. doi:10.1016/S0011-9164(01)00217-X.
- [6] L. Egle, H. Rechberger, J. Krampe, M. Zessner, Phosphorus recovery from municipal wastewater: An integrated comparative technological, environmental and economic assessment of P recovery technologies, *Sci. Total Environ.* 571 (2016) 522–542. doi:10.1016/J.SCITOTENV.2016.07.019.
- [7] A.T.K. Tran, Y. Zhang, J. Lin, P. Mondal, W. Ye, B. Meesschaert, L. Pinoy, B. Van Der Bruggen, Phosphate pre-concentration from municipal wastewater by

electrodialysis: Effect of competing components, *Sep. Purif. Technol.* 141 (2015) 38–47. doi:10.1016/j.seppur.2014.11.017.

[8] B. Ebberts, L.M. Ottosen, P.E. Jensen, Electrodialytic treatment of municipal wastewater and sludge for the removal of heavy metals and recovery of phosphorus, *Electrochim. Acta.* 181 (2015) 90–99. doi:10.1016/j.electacta.2015.04.097.

[9] L.M. Ottosen, P.E. Jensen, G.M. Kirkelund, Phosphorous recovery from sewage sludge ash suspended in water in a two-compartment electrodialytic cell, *Waste Manag.* 51 (2016) 142–148. doi:10.1016/j.wasman.2016.02.015.

[10] L. Dammak, C. Larchet, D. Grande, Ageing of ion-exchange membranes in oxidant solutions, *Sep. Purif. Technol.* 69 (2009) 43–47. doi:10.1016/j.seppur.2009.06.016.

[11] R. Ghalloussi, L. Chaabane, C. Larchet, L. Dammak, D. Grande, Structural and physicochemical investigation of ageing of ion-exchange membranes in electrodialysis for food industry, *Sep. Purif. Technol.* 123 (2014) 229–234. doi:10.1016/j.seppur.2013.12.020.

[12] W. Garcia-Vasquez, L. Dammak, C. Larchet, V. Nikonenko, D. Grande, Effects of acid-base cleaning procedure on structure and properties of anion-exchange membranes used in electrodialysis, *J. Memb. Sci.* 507 (2016) 12–23. doi:10.1016/j.memsci.2016.02.006.

[13] C.D. Venzke, A. Giacobbo, J.Z. Ferreira, A.M. Bernardes, M.A.S. Rodrigues, Increasing water recovery rate of membrane hybrid process on the petrochemical wastewater treatment, *Process Saf. Environ. Prot.* 117 (2018) 152–158. doi:10.1016/j.psep.2018.04.023.

[14] D.C. Buzzi, L.S. Viegas, M.A.S. Rodrigues, A.M. Bernardes, J.A.S. Tenório, Water recovery from acid mine drainage by electrodialysis, *Miner. Eng.* 40 (2013) 82–89. doi:10.1016/j.mineng.2012.08.005.

[15] S.D. Bittencourt, L. Marder, T. Benvenuti, J.Z. Ferreira, A.M. Bernardes, Analysis of different current density conditions in the electrodialysis of zinc electroplating process solution, *Sep. Sci. Technol.* 6395 (2017). doi:10.1080/01496395.2017.1310896.

[16] T. Benvenuti, G. Haubert, G. Fensterseifer Jr, M.A.S. Rodrigues, A.M. Bernardes,

J. Zoppas-Ferreira, Electrodialysis for the nickel electroplating industry from Sinos River Basin, in: 3rd Int. Conf. Ind. Hazard. Waste Manag., Technical University of Crete, Greece, Chania, Crete, 2012: pp. 1–8. <http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=16510>.

[17] APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, Stand. Methods. (2012) 541. ISBN 9780875532356.

[18] D.A. Vermaas, D. Kunteng, M. Saakes, K. Nijmeijer, Fouling in reverse electrodialysis under natural conditions, *Water Res.* 47 (2012) 1289–1298. doi:10.1016/j.watres.2012.11.053.

[19] S. Mulyati, R. Takagi, A. Fujii, Y. Ohmukai, T. Maruyama, H. Matsuyama, Improvement of the antifouling potential of an anion exchange membrane by surface modification with a polyelectrolyte for an electrodialysis process, *J. Memb. Sci.* 417–418 (2012) 137–143. doi:10.1016/j.memsci.2012.06.024.

[20] Q. Wang, P. Yang, W. Cong, Cation-exchange membrane fouling and cleaning in bipolar membrane electrodialysis of industrial glutamate production wastewater, *Sep. Purif. Technol.* 79 (2011) 103–113. doi:10.1016/j.seppur.2011.03.024.

[21] V. Lindstrand, G. Sundström, A.S. Jönsson, Fouling of electrodialysis membranes by organic substances, *Desalination.* 128 (2000) 91–102. doi:10.1016/S0011-9164(00)00026-6.

[22] L.E. Bacher, C. de Oliveira, A. Giacobbo, T. Benvenuti, A.B. Lacerda, A.M. Bernardes, M.A.S. Rodrigues, Coupling coagulation using tannin-based product with electrodialysis reversal to water treatment: A case study, *J. Environ. Chem. Eng.* 5 (2017) 6008-6015. doi:10.1016/j.jece.2017.11.002.

[23] T. Sata, Studies on anion exchange membranes having permselectivity for specific anions in electrodialysis — effect of hydrophilicity of anion exchange membranes on permselectivity of anions, *J. Membr.Sci.* 167 (2000) 1–31. doi:10.1016/S0376-7388(99)00277-X.

[24] T. Sata, T. Yamaguchi, K. Matsusaki, Effect of hydrophobicity of ion exchange groups of anion exchange membranes on permselectivity between two anions, *J. Phys. Chem.* 99 (1995) 12875–12882. doi:10.1021/j100034a028.

- [25] M.A.S. Rodrigues, F.D.R. Amado, J.L.N. Xavier, K.F. Streit, A.M. Bernardes, J.Z. Ferreira, Application of photoelectrochemical–electrodialysis treatment for the recovery and reuse of water from tannery effluents, *J. Clean. Prod.* 16 (2008) 605–611. doi:10.1016/j.jclepro.2007.02.002.
- [26] D. Lu, H. Zou, R. Guan, H. Dai, L. Lu, Sulfonation of polyethersulfone by chlorosulfonic acid, *Polym. Bull.* 54 (2005) 21–28. doi:10.1007/s00289-005-0361-x.
- [27] W. Cui, J. Kerres, G. Eigenberger, Development and characterization of ion-exchange polymer blend membranes, *Sep. Purif. Technol.* 14 (1998) 145–154. doi:10.1016/S1383-5866(98)00069-0.
- [28] M. Kumar, S. Singh, V.K. Shahi, Cross-Linked Poly (vinyl alcohol) - Poly (acrylonitrile-co-2-dimethylamino ethylmethacrylate) based anion-exchange membranes in aqueous media, *J. Phys. Chem. B.* 114(1): (2010) 198-206. doi: 10.1021/jp9082079.
- [29] S. Singh, A. Jasti, M. Kumar, V.K. Shahi, A green method for the preparation of highly stable organic-inorganic hybrid anion-exchange membranes in aqueous media for electrochemical processes, *Polym. Chem.* 1 (2010) 1302–132. doi:10.1039/C0PY00084A
- [30] K. Wu, Y. Zhang, W. Hu, J. Lian, Y. Hu, Influence of ammonium polyphosphate microencapsulation on flame retardancy, thermal degradation and crystal structure of polypropylene composite, *Compos. Sci. Technol.* 81 (2013) 17–23. doi:10.1016/j.compscitech.2013.03.018.
- [31] J.-H. Tay, J. Liu, D.D. Sun, Quantification of membrane fouling using thermogravimetric method, *J. Memb. Sci.* 217 (2003) 17–28. doi:10.1016/S0376-7388(02)00554-9.

Table 1. Characteristics of the cation-exchange (CEM) and anion-exchange (AEM) membranes [14]

| Parameter | Unit | HDX100 (CEM) | HDX200 (AEM) |
|----------------------|------|-------------------------------|-------------------------------|
| Ionic group attached | — | -SO ₃ ⁻ | -NR ₃ ⁺ |

| | | | |
|---|----------------------------|-------------------------|---------------------------|
| Water content | % | 35–50 | 30–45 |
| Ionic exchange capacity | mol.kg ⁻¹ (dry) | ≥2.0 | ≥1.8 |
| Membrane surface resistance (0.1 mol NaCl) | Ohm.cm ⁻² | ≤20 | ≤20 |
| Permselectivity (0.1 mol KCl/0.2 mol KCl) | % | ≥90 | ≥89 |
| Burst strength | MPa | ≥0.6 | ≥0.6 |
| Dimension change rate (longitudinal, lateral) | % | ≤2 | ≤2 |
| Water permeability | mL.h.cm ⁻² | ≤0.1 (below 0.2 MPa) | ≤0.2 (below 0.035 MPa) |

Table 2. Initial characteristics of the treated effluent (as collected) and the filtered treated effluent (treated effluent after filtration with a 0.5 μm cellulose membrane)

| Parameter | Treated effluent (mg.L ⁻¹) | Filtered treated effluent (mg.L ⁻¹) |
|-------------------|---|--|
| Fluoride | 0.6±0.0 | 0.5±0.0 |
| Chloride | 51.4±10.6 | 42.5±3.5 |
| Nitrite | 3.6±0.5 | 13.2±1.9 |
| Phosphate | 11.2±0.4 | 10.6±0.9 |
| Sulphate | 42.0±4.0 | 39.0±0.1 |
| Sodium | 66.7±16.2 | 58.1±4.6 |
| Ammonium | 68.5±1.9 | 58.4±4.7 |
| Potassium | 12.0±1.1 | 11.4±0.4 |
| Magnesium | 3.7±0.1 | 4.0±0.0 |
| Calcium | 24.4±1.1 | 25.7±0.5 |
| pH | 7.16 | 7.85 |
| Conductivity (μS) | 669 | 666 |

Table 3. Ion concentrations in the initial and final ED solutions

| | mg.L ⁻¹ | Treated Effluent | | | | Filtered Treated Effluent | | | |
|-----------|--------------------|--------------------|---------------------|---------|-----------------------|---------------------------|---------------------|---------|-----------------------|
| | | Electrode solution | Anodic concentrated | Diluted | Cathodic concentrated | Electrode solution | Anodic concentrated | Diluted | Cathodic concentrated |
| Fluoride | Initial | <0.02 | <0.02 | 0.6 | <0.02 | <0.02 | <0.02 | 0.5 | <0.02 |
| | Final | <0.02 | 0.5 | 0.2 | <0.02 | <0.02 | 0.6 | 0.2 | <0.02 |
| Chloride | Initial | 9.9 | 14.1 | 51.4 | 6.0 | 1.8 | 7.6 | 42.5 | 2.4 |
| | Final | 10.3 | 53.1 | 7.6 | 9.2 | 6.7 | 51.7 | 5.4 | 6.0 |
| Nitrite | Initial | <0.05 | <0.05 | 3.6 | <0.05 | <0.05 | <0.05 | 13.2 | <0.05 |
| | Final | <0.05 | <0.05 | 0.5 | <0.05 | <0.05 | 10.3 | 1.6 | <0.05 |
| Phosphate | Initial | <0.11 | <0.11 | 11.2 | <0.11 | <0.11 | <0.11 | 10.6 | <0.11 |
| | Final | <0.11 | <0.11 | 7.5 | <0.11 | <0.11 | 0.3 | 6.6 | <0.11 |
| Sulphate | Initial | 2738.1 | 341.0 | 42.0 | 352.5 | 2688.7 | 314.0 | 39.0 | 327.5 |
| | Final | 2607.9 | 377.4 | 26.5 | 612.7 | 2485.9 | 370.8 | 24.3 | 620.1 |
| Sodium | Initial | 1592.4 | 219.9 | 66.7 | 214.8 | 1586.4 | 200.4 | 58.1 | 194.4 |
| | Final | 1475.5 | 349.6 | 17.2 | 245.2 | 1470.2 | 355.2 | 15.2 | 260.7 |
| Ammonium | Initial | <0.07 | <0.07 | 68.5 | <0.07 | <0.07 | <0.07 | 58.4 | <0.07 |
| | Final | <0.07 | <0.07 | 6.8 | 20.1 | <0.07 | <0.07 | 6.5 | 19.1 |
| Potassium | Initial | <0.04 | <0.04 | 12 | 0.1 | <0.04 | <0.04 | 11.4 | <0.04 |
| | Final | <0.04 | <0.04 | 1.4 | 9.3 | <0.04 | <0.04 | 1 | 10.4 |
| Magnesium | Initial | <0.02 | <0.02 | 3.7 | <0.02 | <0.02 | <0.02 | 4 | <0.02 |
| | Final | <0.02 | <0.02 | 0.6 | 0.8 | <0.02 | <0.02 | 0.7 | 0.6 |
| Calcium | Initial | 11.4 | 2.5 | 24.4 | 2.7 | 11.5 | 1.3 | 25.7 | <0.03 |
| | Final | <0.03 | 10.8 | 4.4 | 10 | <0.03 | 9.3 | 5.6 | 11.8 |

Table 4. Total phosphorus concentration in the work solutions before and after electro dialysis

| Sample | Mean (mg.L ⁻¹) and standard deviation |
|-----------------------|---|
| Initial | 2.50 ± 0.3 |
| Final (diluted) | 1.44 ± 0.3 |
| Cathodic concentrated | 0.02 ± 0.0 |
| Anodic concentrated | 1.02 ± 0.2 |

ACCEPTED MANUSCRIPT