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Additional Information

Transport dynamics of atenolol in an electro dialysis cell: membrane sorption and electric field-driven effects

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Abstract

Electrooxidation has proven to be an effective technique to remove pharmaceutical from water and wastewater. However, the low concentration of pharmaceuticals in the environment affects the process, becoming a drawback that needs solution. A new system coupling electrooxidation and electro dialysis was recently proposed for micropollutants removal, since ionic interactions between micropollutants and ion-exchange membranes were already proven. Despite this, the transport of pharmaceutical through ion-exchange membranes under the application of an electric field is still unclear and pathless. To fill this gap, the transport of atenolol (ATL) at under- and overlimiting current conditions was evaluated in an electro dialysis cell for the first time as an initial step to the application of the hybrid process. This study focused on the interaction and transport of ATL through the cation-exchange membrane (CEM), considering ATL cationic aspect. Different current densities (5, 10, 15, 25 mA/cm²) were applied and ion uptake experiments were done. It was found that the transport is mostly driven by this parameter: by applying 15 mA/cm², ≈98% removal rate was achieved, while applying 5 mA/cm² only 7% of ATL was removed. Part of the ATL remained into the CEM structure can be desorbed by applying an electric field at inverse polarity. It occurs because ATL seems to be linked by electrostatic interactions with the functional groups on the CEM matrix. Thus, a hybrid process would be feasible allowing to concentrate and degrade ATL simultaneously, reducing the consumption of chemicals, energy, unitary processes, besides operational costs.

Keywords: Electrodialysis; ion-exchange membranes; organic micropollutants; overlimiting condition; membrane sorption.

1. Introduction

Pharmaceutical compounds of the most varied classes are commonly identified in samples from different water matrices including surface water, groundwater, drinking water and wastewaters. Among them, β -blockers have been detected in different places around the world in concentrations ranging from $\mu\text{g/L}$ to ng/L (Chiffre et al., 2016; Gurke et al., 2015; Lindim et al., 2016; Subedi et al., 2015; Verlicchi et al., 2012). The β -blocker Atenolol (ATL) is among the most sold and consumed drugs worldwide (Patel et al., 2019). In Brazil, this pharmaceutical is included in a social program that provides medication to the population (Brasil, 2006) and, for this reason, it has been detected in water samples from different places within the country (Becker et al., 2020; Pereira et al., 2016; Perin et al., 2021; Sodré et al., 2018; Wilde et al., 2012).

Conventional water and wastewater treatment plants are not designed to remove micropollutants, which implies that the removal efficiencies of pharmaceuticals, for example, are insufficient or even non-existent. In this regard, electrooxidation emerges as technology capable of achieving high removal rates of that compounds. This process presents simple operation and maintenance, and the organic compound is degraded via reactions with electrogenerated reactive species, mainly the hydroxyl radical (Comninellis, 1994).

Despite electrooxidation offers good results in terms of degradation and mineralization of organic compounds, there is an important drawback related to the process: the low concentrations of pharmaceuticals in the environment. In order to be oxidized, the contaminant must reach the anode surface and if it is present in low concentration, the mass transfer from the bulk solution to the anode is hampered (da Silva et al., 2021). To overcome this limitation, new strategies should be investigated (Garcia-Segura et al., 2020). A new reactor setup has been studied to optimize the removal rates by adding an ion-exchange membrane in the system (Sandoval et al., 2022). Therefore, the cathodic reactions are avoided and the contaminant is held near the anode improving its oxidation. This two-compartment reactor has proven to be effective in the removal of different pharmaceuticals despite of the anode material (Carrillo-Abad et al., 2020; Mora-Gómez et al.,

2020). However, some studies have shown that micropollutants can interact with the ion-exchange membranes and some attention should be addressed to this matter (Arola et al., 2019; Roman et al., 2019; Vanoppen et al., 2015).

Most of these studies evaluated the transport and interactions between the pharmaceuticals and membranes, but the experiments were carried out without the application of an electric field or applying a single value of current density and, so, has not evaluated the effect of this operational parameter on the process (Arola et al., 2019; Banasiak and Schäfer, 2010; Pronk et al., 2006; Roman et al., 2019).

Roman et al. (2020) evaluated the effect of different current densities but emphasized the discussion on the effect of pH on the organic micropollutants transport through IEM. Also, Vanoppen et al. (2015) evaluated different current densities in a solution containing a concentration of salt 6 orders of magnitude greater than organic ones and stated that the transport of the latter occurs only when the salt is depleted from the solution.

Besides that, recent studies have proven that is possible to couple electro dialysis and electrooxidation in a single batch reactor to treat solutions containing micropollutants by concentrating and oxidizing them simultaneously (Llanos et al., 2018; Raschitor et al., 2020, 2017). These studies have focused on pesticides so far and, for this reason, our group intends to investigate this integrated technique on the removal of pharmaceutical contaminated water and wastewater.

The purpose of this work is to evaluate the transport of ATL through ion-exchange membrane and establish the interactions that occurs between them, aiming a hybrid process in the future. This hybrid process integrates both electro dialysis and electrooxidation, allowing to concentrate and oxidize ATL simultaneously. So, the present work is focused on an initial study of how the electric field can affect the transport and in which conditions this concentration would be optimized. The investigation consists of electro dialysis experiments with a 0.375 mM ATL as a model pollutant evaluating four different current density conditions (5, 10, 15 and 25 mA/cm²). The interactions

between the ATL and the ion-exchange membrane were also elucidated by ion uptake and reverse polarity experiments.

2. Experimental

2.1. Chemicals, ion exchange membranes and solutions

ATL active compound (99%) was purchased in a local drugstore. Na_2SO_4 , KCl and H_2SO_4 of analytical grade were also utilized for the preparation of electrolytic solutions. IONSEP-HC-C and IONSEP-HC-A membranes were used as cation-exchange membrane (CEM) and anion-exchange membrane (AEM), respectively. The properties of these membranes are reported elsewhere (Martí-Calatayud et al., 2020; Rotta et al., 2019).

A working solution containing 0.375 mM of ATL and 0.021 M of Na_2SO_4 was used in ED and in ion uptake experiments. Databases of the speciation of ATL and literature indicate that its pKa is near 9.7. Below this value, it is positively charged whereas above it has no charge (Amirdehi et al., 2017; ChemAxon, 2019). Considering that the pH of most water matrices tends to be neutral, an initial pH near 6 was chosen in this study, so that the solution pH was adjusted to 6 ± 0.2 by adding a 0.5 M H_2SO_4 solution. For the electrodialysis experiments, two other electrolyte solutions were prepared with 0.021 M and 0.035 M of Na_2SO_4 and were used in the concentrate compartments and as electrode rinse, respectively. For the ion uptake experiments, a 0.1 M of KCl solution was also used. Distilled and deionized water was employed to prepare electrodialysis and ion uptake solutions, while Milli-Q[®] Direct water was used to prepare analytical and standards solutions.

2.2. Ion uptake experiments

First, pieces of membranes of the same size were cut and equilibrated in two different solutions for 24 h, under stirring condition: (i) 0.375 mM of ATL and (ii) 0.375 mM ATL + 0.021

M Na₂SO₄. After this, these membranes were washed with distilled water several times and put into equilibration in 0.1 M KCl solution for another 24 h, also under stirring condition. Finally, the ATL content in this soak solution was measured. The mass of the dry membranes was measured on an analytical balance. A schematic representation can be found in Fig S1 in supplementary material.

2.3. Experimental setup, limiting current density and ED experiments

A lab-scale cell with five compartments was used in the experiments (Fig S2, in supplementary material). The compartments were separated by two CEM and two AEM membranes alternately arranged. The effective area of the membranes was 16 cm². The electrodes consisted of 4 × 4 cm plates of commercial Ti/70%TiO₂+30%RuO₂.

The limiting current density of the CEM ($i_{lim,CEM}$) was estimated by applying successive increasing current densities in steps of 2 mA every 30 s, according to the procedure described in other studies (Mahendra et al., 2014; Rotta et al., 2019). The membrane potential was measured with platinum wire electrodes coupled to digital multimeters.

Electrodialysis experiments were performed at room temperature in galvanostatic mode at a constant current density value, with isolated recirculation in each compartment at batch mode and at a flow rate of 85 L/h. Initially, a sequence of individual experiments was performed evaluating four different current densities (5, 10, 15 and 25 mA/cm²). In these experiments, the working solution containing ATL was fed only in the central compartment, while the concentrate compartments were fed with the 0.021 M of Na₂SO₄ solution (Fig S3, in supplementary material). Before each experiment, the solutions were left in the system for a 24 h equilibration period and triplicates were done for all evaluated conditions. After that, a single electrodialysis experiment was conducted applying an inverse polarity and using Na₂SO₄ solutions without ATL in all compartments (Fig S4, in supplementary material). The main objective of this experiment was to evaluate the release of ATL possibly sorbed in the membrane during the previous experiments.

Finally, to better understand the ATL transport through the CEM, a singular batch of continuous experiments was performed using a new set of membranes. For that, the same electro dialysis setup was used (Fig S3, in supplementary material), and the same current condition was applied repeatedly.

2.4. Analysis

During the electro dialysis experiments the cell potential, pH and conductivity of all solutions were monitored. Aliquots were collected at pre-established times and ATL concentration was determined by high-performance liquid chromatography (HPLC) using a Thermo Scientific DIONEX ICS-3000 associated to a Thermo Scientific Ultimate 3000. The equipment was fitted with a C18 DIONEX column 120 Å, 4.6 × 10 mm and 3 µm. Phosphate buffer of pH 3 and acetonitrile (40:60) were used as mobile phase, with a flow rate of 0.75 mL/min. A sample volume of 20 µL was injected into the equipment for analysis. The photodiode array detector was fixed at $\lambda = 225$ nm, and under these conditions the ATL retention time was 2 min.

An analysis of the membrane morphology was performed using a scanning electron microscope Phenom ProX (ThermoFisher), operated at 10 kV. For this purpose, the membrane was placed in a sampler without prior metallization, to avoid any surface modification.

3. Results and discussion

3.1. ATL/CEM interaction and determination of limiting current density

Interactions and attractive/repulsive forces between membranes and organic molecules determine their transport in electro dialysis systems. To evaluate the ion exchange between the membrane used in this study and ATL, ion uptake experiments were carried out. For that, two solutions were evaluated: one containing only ATL and the other a mixture of ATL and Na₂SO₄. In the first one, the calculated loading of ATL in the membrane was 0.08 meq/g while in the second it

was 0.03 meq/g. This decrease in the number of ATL molecules exchanged in the membrane with the presence of Na⁺ ions indicates that the Na⁺ interact more easily with the membrane and, therefore, will be more easily transported when compared to ATL. This may be also associated with the fact that Na⁺ ions are in much higher concentration than the ATL and because they are smaller in size (Vanoppen et al., 2015). Furthermore, the IEC provided by the manufacturer is 2.0 meq/g and the difference in the values obtained experimentally with ATL may also be related to the presence of protons in solution, as a function of pH adjustment, what involves that not all fixed charges of the membrane can be equilibrated with ATL.

Fig. 1a shows the polarization curve obtained for the CEM placed in the central compartment and surrounded by the working solution. At low current densities, the membrane potential increases linearly with the increase in the current density value, presenting a quasi-ohmic behavior. By increasing the current density, concentration gradients develop near the membrane interface, involving the dilution of ions on one side of the membrane (diluted compartment) and an accumulation of ions on the other (cationic concentrate compartment).

The formation of concentration gradients is a consequence of the higher cation permeation rates through the membrane phase, as compared with their motion across the bulk solution. When the concentration of ions near the diluted side of the membrane approaches zero, a change in the slope is observed increasing the system resistance. The current density corresponding to the beginning of this limiting state, named as limiting current density ($i_{lim,CEM}$), appears close to 13 mA/cm². Commonly a third region appears in the polarization curves, which is characterized by an increase in the slope because of the activation of mass transport mechanisms typical of overlimiting conditions, but in this particular case the third region cannot be seen within the evaluated voltage range.

After determining the $i_{lim,CEM}$, electro dialysis experiments were carried out to evaluate the ATL transport at underlimiting and overlimiting conditions. The experimental time was fixed at a maximum of 4 h. In general, the ions scarcity promoted by their migration from the diluted to

adjacent compartments causes an increase in the cell potential values (U_{cell} , Fig. 1b). At underlimiting conditions, a linear behavior was observed when applying 5 mA/cm², when the U_{cell} value remained constant. The same behavior was observed when applying 10 mA/cm², but only up to an experimental time of 2 h, when there is a trend change with a sudden exponential increase of the U_{cell} . This could be linked to a concentration polarization effect caused by the scarcity of ions near the membrane/solution interface, situation in which the $i_{\text{lim,CEM}}$ is reached, or also just to the gradual dilution of the central compartment. Regarding overlimiting conditions (15 and 25 mA/cm²), U_{cell} presented an exponential raise linked to a faster depletion of ions near the membrane surface, increasing the system electric resistance notoriously (Nikonenko et al., 2014). In these two cases, the experimental time was limited by the voltage of the power supply.

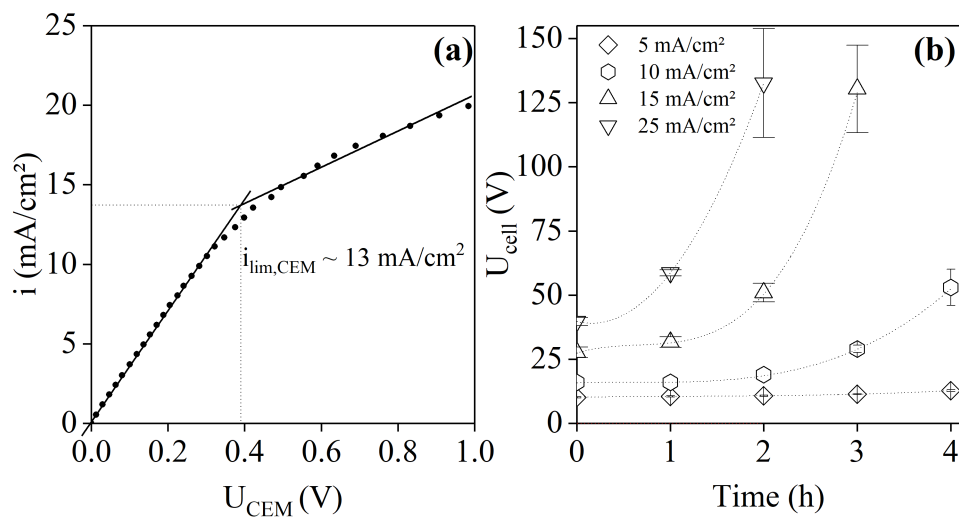


Fig. 1. (a) Polarization curve for cation-exchange membrane in contact with 0.375 mM ATL + 0.021 M Na₂SO₄ solution and (b) Cell potential during the experiments. Where the U_{CEM} represents the CEM potential measured with the platinum wires and multimeter and U_{cell} the cell potential.

3.2. Conductivity behavior and pH evaluation during the experiments

The conductivity of aqueous solutions is an important parameter to be evaluated in the electro dialysis process. It is associated with the presence of ions in solution and ensures the proper

application of an electrical field within an electro dialysis cell. Although ATL presents charge at the selected pH, it does not have the ionic strength to influence the conductivity of the solution. All initial solutions presented the same conductivity (Table 1) regardless of the presence of ATL, so this parameter is associated with the ionic conductivity of Na^+ and SO_4^{2-} ions. Besides that, these two ions are in a much higher concentration than ATL.

As discussed above, when ions from the diluted compartment migrate towards the concentrate ones, the process is limited by the high resistivity of the medium. As expected, the conductivity of the diluted compartment dropped with time, reaching low values, limiting the process mainly when operated under overlimiting conditions. Likewise, the conductivity of the cathodic and anodic concentrate compartments increased, not only due to the ions that migrated from the diluted compartment but also from the rinse solution flowing through the electrode compartments.

Table 1. Conductivity (mS/cm) of initial and final solutions of the compartments under the application of different current densities. Final experimental times of 4 h (5 mA/cm²), 4 h (10 mA/cm²), 3 h (15 mA/cm²) and 2 h (25 mA/cm²).

Compartment	Initial	5 mA/cm²	10 mA/cm²	15 mA/cm²	25 mA/cm²
Diluted	5.3	1.8	0.4	0.1	0.2
Cathodic concentrate	5.3	7.6	9.7	11.3	11.3
Anodic concentrate	5.3	7.6	9.9	12.8	12.9

The solution pH is also expected to play an important role in the process considering that the ATL molecule presents different charges as a function of pH. To ensure that ATL was positively charged, an initial pH value of 6 was chosen in this study, typical of natural sources of water. The evolution of pH was monitored in the different compartments (Fig. 2).

The pH in the cathodic compartment decreased and in the anodic compartment increased with time, except for the condition of 5 mA/cm² when the pH values did not change. As expected, at overlimiting conditions (Fig. 2 c and d) this effect was more noteworthy. This may be linked to the

water dissociation phenomenon, characteristic of systems operated above the i_{lim} , in which water molecules are dissociated into H^+ and OH^- ions at the membrane surface (Nikonenko et al., 2010).

The OH^- ions generated in the CEM remain in the diluted compartment while the H^+ permeate through it towards the cathodic concentrate compartment, causing the drop in the pH of this solution over time. In contrast, the water dissociation in the anion-exchange membrane (AEM) causes the H^+ to remain in the diluted compartment and the OH^- to permeate it, leading to an increase in the pH of the anionic concentrate compartment. The water dissociation phenomena occur more easily on AEM as compared to CEM (Tanaka, 2010) and that is why the pH of the diluted compartment tends to decay with time.

Besides that, when applying 10 mA/cm^2 (Fig. 2b) there is a shift in the behavior of the anodic concentrate curve at the time of 2 h, when a sudden increase in the pH values occurred. This finding agrees with what was previously discussed, indicating that after this time, at this current density, the system starts to operate above the $i_{lim,CEM}$, favoring the water dissociation. Finally, in all experimental conditions, the pH of the diluted compartment was always below the pKa value. Thus, it can be ensured that ATL was positively charged in the bulk solution during the experiments.

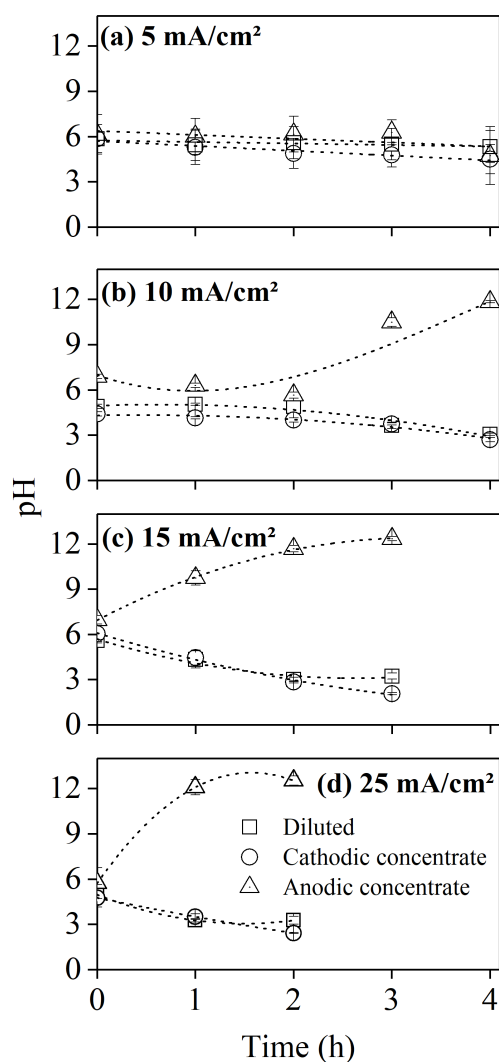


Fig. 2. Evolution of pH in the different compartments during the experiments at underlimiting (a, b) and overlimiting (c, d) conditions.

3.3. Influence of current density condition on ATL transport

A previous study by Vanoppen et al. (2015) points out that the transport of charged organic molecules in electro dialysis processes is mostly driven by diffusion and is inversely proportional to the current density. This would happen due to the longer experimental time achieved when lower current densities are applied and, with that, the molecule would have more time to diffuse. However, this behavior was not observed in this study.

The evolution of ATL with time in the diluted and cathodic concentrate is shown in Fig. 3. All current density conditions promoted ATL transport from the diluted to the concentrate

compartments. At underlimiting conditions, when applying 5 mA/cm², there was a removal of only 7% after 4 hours, but this value increases up to 84% by applying 10 mA/cm² (Fig. 3a and b). At this current density, as previously discussed, the system shifts from under- to overlimiting conditions during the electro dialysis experiment, and this could improve the ATL transport.

It looks as if when the $i_{lim,CEM}$ is reached, Na⁺ ions may have been depleted and the ATL starts to cross the membrane faster. When the system was operated at overlimiting conditions, the removal of ATL from the diluted compartment was almost complete (Fig. 3c and d), achieving removals of 98% and 96% when applying 15 mA/cm² and 25 mA/cm², respectively. Thus, contrary to what the literature indicates, an increase in the current density accelerates the transport of ATL. This finding can be confirmed by the ionic flux (J), calculated by the following equation (1) (Kikhavani et al., 2014; Liu et al., 2017).

$$J (mg/cm^2 h) = V \times (C_t - C_0) / A_m \times t \quad (1)$$

where: V is the volume of the compartment (L), C_t is the final concentration (mM), C_0 is the initial concentration (mM), A_m is the effective membrane area (cm²) and t is the time (h).

The ionic flux calculation is an important parameter that can be used to shed light on the fate of ATL within the electro dialysis cells, since the evaluated current densities were applied during different experimental times. An important increment in ATL ionic flux in both compartments was observed when the current density was increased (Table 2). It must be noted that the flux in the diluted compartment is negative, according to the decreasing concentration with time. By that, it can be inferred that the ionic flux of ATL and the applied current density are clearly related to each other.

Table 2. Ionic flux (J , $\times 10^{-3}$ mM/cm² h) values calculated for the different compartments at the final experimental time (5 mA/cm²: 4 h; 10 mA/cm²: 4h; 15 mA/cm²: 3 h; 25 mA/cm²: 2 h).

Compartment	5 mA/cm ²	10 mA/cm ²	15 mA/cm ²	25 mA/cm ²
Diluted	-0.26 ± 0.01	-2.46 ± 0.44	-3.63 ± 0.13	-6.18 ± 0.17
Cathodic concentrate	0.61 ± 0.01	1.24 ± 0.23	1.47 ± 0.23	2.21 ± 0.48

Despite the almost total removal of ATL from the diluted compartment, its concentration in the cathodic concentrate could not reach concentrations higher than 0.150 mM. This difference in the mass balance between the compartments suggests that part of ATL is retained in the membrane.

Roman et al. (2019), indicate that positively charged pharmaceuticals can interact with IEM by electrostatic forces and π - π interactions, promoting their strong adsorption on the membrane and, therefore, presenting low transport rates through them. However, the Na⁺ ions in the solution are at a much higher concentration than ATL, have a smaller size and greater mobility, which promotes a preferential interaction of the membrane with these ions in relation to ATL, as demonstrated in the ion uptake experiments. This could explain how the concentration of ATL in the diluted compartment drops almost to zero while in the cathodic concentrate it increases slowly.

The results obtained when applying 5 mA/cm² (Fig. 3a) were quite unexpected, since the removal of ATL in the diluted compartment (0.026 mM) is smaller than the increase in concentration in the cathodic concentrate (0.086 mM). This could indicate that the ATL detected in the cathodic concentrate is related to a content that was initially inside the membrane matrix, rather than in the central (diluted) compartment.

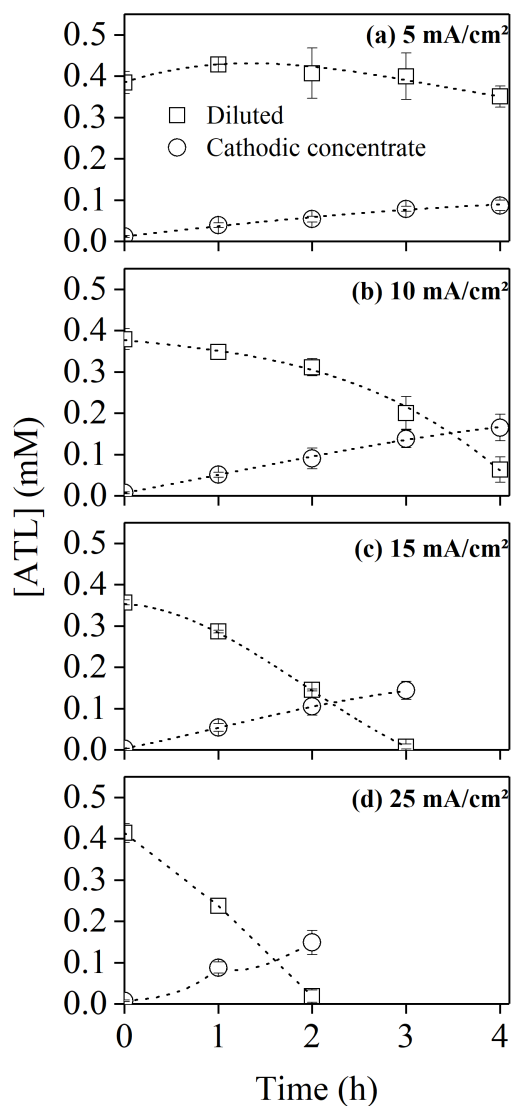


Fig. 3. ATL concentration profiles by applying different current densities.

3.4. Dynamics of ATL transport through CEM

Since IEM are subject to the occurrence of fouling/poisoning when exposed to solutions containing organics, an experiment with inverse polarity was carried out. For this experiment, the central compartment was fed with the same solution used in the concentrate ones (0.021 M Na₂SO₄, without ATL), and a current density of 15 mA/cm² was applied for 3 hours (Fig S4, in supplementary material).

All solutions were left in the system for 72 h before the electrical current application, which corresponds to the aliquot analyzed at the time of 0 h (Fig. 4). Just after the equilibration time with the Na₂SO₄ solution without the application of a current density, 0.089 and 0.095 mM of ATL were measured in diluted and cathodic concentrate compartments, respectively. This content is related to the detachment of ATL that is most likely adhered by ionic interactions to the surface of the CEM that separates the two compartments.

After applying an electric field in reversed bias, the ATL in the cathodic concentrate compartment migrates to the diluted one. At the final time, 0.338 mM of ATL was detected in the diluted compartment (central), while in the cathodic concentrate no content was observed. The difference in the values between the two compartments indicates that the ATL retained inside the membrane also migrates towards the central compartment.

At the anodic concentrate compartment no ATL was observed, as expected, since it is positively charged and cannot interact with the positively charged functional groups of the AEM. However, considering that in the previous electro dialysis experiments both AEM and CEM from the central compartment (diluted) were left in equilibration with the working solution containing ATL and that both membranes have the same polymeric matrix. It indicates that ATL molecules may link to the membrane by electrostatic interactions with the functional groups rather than by adsorption on the membrane matrix, as other studies suggests (Roman et al., 2020, 2019).

Finally, the detachment of the ATL without the application of an electric field can possibly indicate that these electrostatic interactions with the CEM functional groups are weak (Ma et al., 2018). The ATL content that remains inside the membrane can easily cross it when a current density is applied again.

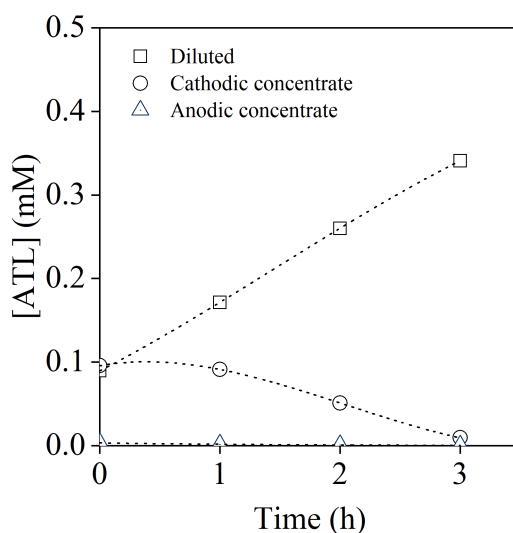


Fig. 4. ATL concentration during a reverse electro dialysis experiment.

To obtain more information regarding the dynamics of ATL transport through the membrane and to elucidate the reason why the mass balance between the flux of ATL in the diluted and cathodic concentrate compartments did not match (Table 2), another singular batch of experiments was done using the cell configuration demonstrated in Fig S3 in supplementary material.

A new set of membranes was employed in a continuous experiment, in which the same condition of 15 mA/cm² was evaluated repeatedly. Before each cycle, the membranes were left out in an equilibration time of 24 h, just like in the previous experiments. According to Roman et al. (2020), positively charged drugs adsorb almost completely and immediately when in contact with IEM, but probably would not penetrate its polymeric structure, i.e., the adsorption would only take place on the surface layer of the membrane.

However, in all experiments, shown in Fig. 5, the ATL concentration decreased in the central compartment from the beginning of the experiments, whereas an increase in ATL concentration in the cathodic concentrate compartment could only be noticed after the third experiment conducted in sequence. Another study evaluated the transport of ATL through IEM and also found that its transport occurs only after a certain time of current application (Arola et al., 2019). This may indicate that the ATL detected in the cathodic concentrate compartment is not only associated with

the amount that is transported during the experiment itself, but also with a content present inside the membrane due to the equilibration and previous experiments, which ends up permeating the membrane with the application of an electric field, as discussed before. This could justify why the ATL concentration in the cathodic concentrate is higher than the removal from the diluted compartment when applying 5 mA/cm² (Fig. 3a), as previously mentioned.

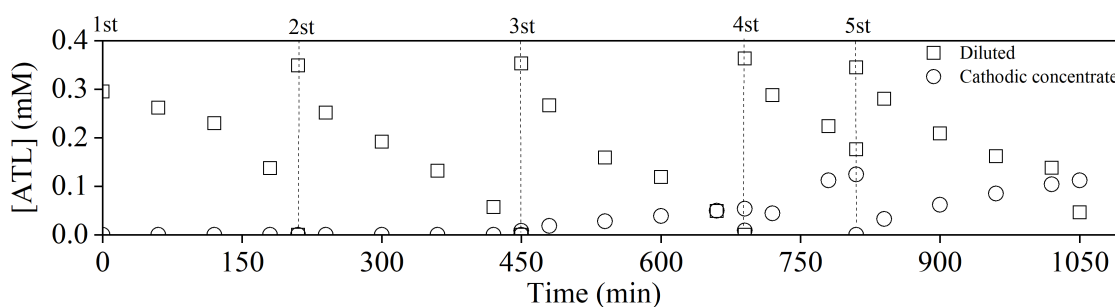


Fig. 5. ATL concentration during continuous experiments at overlimiting condition.

3.5. Evaluation of CEM before and after experiments

Finally, the CEM that separates the diluted and the cathodic concentrate used in the continuous experiments was subjected to scanning electron microscopy analysis, to characterize its morphology and identify possible changes during the process. The heterogeneity of the membrane can be visualized by the random distribution of functional groups (lighter spots) fixed in the polymer matrix in the original membrane (Fig. 6a) (Rotta et al., 2021). However, when analyzing the images obtained from the membranes after use (Fig. 6b), cavities in the polymer structure were observed (black dots). Pismenskaya et al. (2012) explain that these cavities may be the result of the electrochemical degradation of the polymer matrix, which has its chains ruptured by the action of a high electric field and by the presence of H⁺ and OH⁻ ions generated at the membrane/solution interface in overlimiting conditions. The flow of the bulk solution ends up washing the surface of

the membrane and removing the products of its degradation, and then there is the appearance of the cavities.

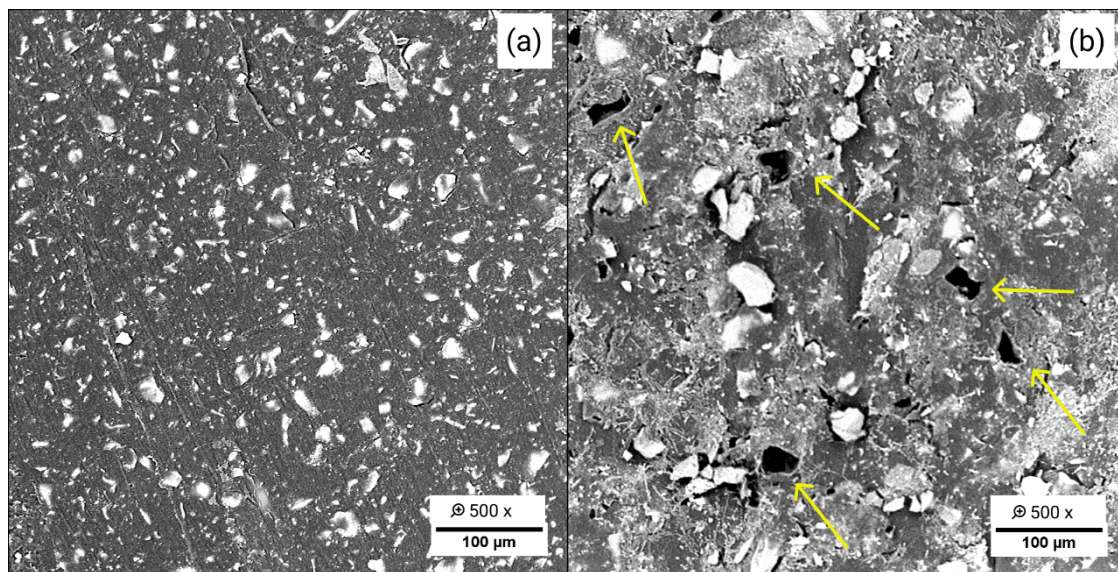


Fig. 6. Scanning electron microscopy images of the CEM (500 \times magnification): (a) original and (b) after the continuous experiments. The yellow arrows indicate the cavities.

Conclusions

Underlimiting and overlimiting conditions were evaluated towards the ATL transport through a CEM. The decrease of ATL concentration in the diluted compartment and its increase in the cathodic concentrate presents a direct relation with the applied current density, confirmed by the ionic flux values. It indicates that for charged ATL, the transport through the membrane will be mostly driven by the current density. An experiment with inverse polarity revealed that ATL-membrane adsorption interactions are reversible and can be modulated by the imposition of an electric field. It probably occurs as a result of weak electrostatic interactions between ATL and the functional groups on the membrane matrix.

At overlimiting condition the ATL removal in the diluted compartment was almost complete, while at underlimiting conditions the removals were 7% and 84%, by applying 5 mA/cm² and 10 mA/cm², respectively. Finally, a difference in the mass balance between the compartments was identified during the individual experiments and in the continuous ones, indicating that part of the

ATL sorbed on the membrane permeates in subsequent experiments with a new application of an electric field.

Considering the data obtained in this study, it is possible to state that overlimiting current condition provides better results towards ATL transport through CEM. Besides that, the results obtained in this study indicates that the pharmaceuticals low concentration would no longer be an issue in the electrooxidation process and that the hybrid process would be a feasible strategy to treat solutions containing ATL or even other pharmaceutical compounds.

Acknowledgments

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