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# The Effect of pH on Aniline Removal from Water Using Hydrophobic and Ion-Exchange Membranes

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**Abstract:** The presence of aniline, a toxic aromatic amine, has been recorded in different industrial wastewaters. This study aims to investigate the transport of charged and neutral aniline species in aqueous solutions through hydrophobic and ion-exchange membranes (IEMs). Hydrophobic polyoctylmethylsiloxane (POMS) and polydimethylsiloxane (PDMS) membranes and cationic (CEMs) and anionic (AEMs) exchange membranes were tested using diffusion cells and electrodialysis (ED). Diffusion experiments showed that neutral aniline removal reached 90% with POMS and 100% with PDMS due to the concentration gradient between feed (pH = 10) and receiving (pH = 3) solutions. For IEMs, neutral aniline exhibited a faster transport than charged species, with neutral-to-charged transport ratios of 6.6:1 for AEMs and 3.2:1 for CEMs, type I. During ED experiments, an external electric potential increased the charged aniline transport, achieving higher initial fluxes (124.7 $\text{mmol}\cdot\text{m}^2\cdot\text{h}^{-1}$ at pH 4) compared to neutral aniline (43.6 and 53.2 $\text{mmol}\cdot\text{m}^2\cdot\text{h}^{-1}$ for AEMs and CEMs, type I). ED also demonstrated that charged aniline can be removed up to 97% using IEMs. These findings demonstrate the effectiveness of hydrophobic and IEMs in removing aniline, providing insights into its transport mechanism, contributing to the optimization of membrane technologies in treating industrial wastewater effluents, and environmental sustainability.

**Keywords:** aniline; hydrophobic membranes; electrical gradient; ion-exchange membranes

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## 1. Introduction

The World Health Organization has recently acknowledged the importance of evaluating and regulating risks using combined toxicity data from organic compounds [1,2]. Aniline is one of the most toxic organic compounds widely used as an industrial chemical, being highly reactive toward electrophilic aromatic substitution [3]. Research has shown that aniline has carcinogenic, teratogenic, and mutagenic properties [4–6], impacting the skin, lungs, and stomach and changing the pathway oxygen takes when it is absorbed in blood [7].

Also known as benzene-amine, phenylamine, or aminobenzene, aniline consists of a benzene ring attached to an amino group (-$NH_2$), and it is a primary aromatic amine manufactured and used by diverse industries such as petrochemical, pharmaceutical, and agrochemical [8]. Several methods can be used for aniline production. The most common are the catalytic reduction of nitrobenzene in the presence of iron, the catalytic reaction of chlorobenzene and aqueous ammonia at elevated temperatures and pressures, and the ammonolysis of phenol [9]. The global aniline market reached 9.9 million tons in 2023 and is forecast to reach 15.2 million tons by 2032 [10].

The presence of aniline has been confirmed in wastewater from pharmaceutical and chemical industries, with concentrations reaching 2480 mg/L and 1370 mg/L, respectively [11,12]. The annual emissions of aniline into aquatic ecosystems (i.e., bioaccumulation in groundwater sediments in a half-life of approximately 1000 days and a natural photolysis in surface water of 18 days) are estimated at 30,000 tons due to the illegal dumping of municipal and industrial wastewater, excessive use of pesticides, and accidental leaks [1,13]. Different treatment processes are used to remove aniline. Recent technologies include combined microbial treatment and advanced oxidation process (AOP), which reaches a removal rate of 99.89%; AOP using activated persulfate, which achieves removals of 83%; and forward osmosis (FO), attaining 90% removals [12,14,15]. The first notable case of widespread poisoning was linked to the discharge of industrial waste containing synthetic dyes with aniline in the 1860s, where a factory operated by Müller-Pack in Basel, Switzerland, caused aniline concentrations to exceed 210 mg/L in groundwater sources used for domestic purposes [16]. More recently, China, one of the world's largest producers of textiles and dyes, has faced challenges associated with the discharge of aniline-enriched effluents. In the Guangdong province, a wool printing and dyeing company released wastewater containing aniline concentrations of up to 10 mg/L into local waterways and streams after inadequate wastewater treatment [17]. Although aniline is susceptible to photodegradation and biodegradation, it is essential to remove it from wastewater before it enters the aquatic systems [18]. Effluents containing aniline can be treated using various methods, including distillation, adsorption, ligand exchange, advanced oxidation, and biodegradation [19–21].

Briefly, the application of pseudomonas strains demonstrated the ability to degrade 1600 mg/L of aniline with high efficiency, achieving optimal growth within a pH ranging from 5 to 9. Under ideal conditions (pH 7, 25 °C), approximately 800 mg/L of aniline was almost entirely degraded within 24 h [22]. Additionally, Zhu et al. [15] evaluated the efficiency of a combined microbiological and advanced oxidation process (AOP) for aniline degradation. Using *Staphylococcus aureus* CUGB-LJL5 followed by an AOP, this method successfully removed high concentrations of aniline (1000 mg/L), achieving a degradation rate of 99.9%, leaving only 1.1 mg/L remaining. Optimal conditions for this process included the addition of 5 mM peroxymonosulfate (PMS) and 1 mM Fe (II) after inoculation with a 3% bacterial culture for 96 h at pH 7 and at 30 °C. The electrochemical oxidation of aniline in the presence of NaCl and $Na_2SO_4$, as reported by Li et al. [23], revealed that approximately 70% of aniline could be degraded within 2 h of exposure. Another alternative for wastewater management utilized dielectric barrier discharges (DBD) at atmospheric pressure, achieving an 84.3% removal of aniline after 10 min of DBD treatment with a discharge power of 21.5 W [24]. Advanced oxidation processes (AOP) show great potential for the removal of these organic pollutants [25]. Nevertheless, these above-described processes can be costly and technically challenging.

Aniline removal methods based on membrane technology are also being developed. Membranes play an important role in separation processes. Briefly, direct membrane filtration (DMF) systems using ultrafiltration membranes have shown a similar recovery of organic matter and nutrients from synthetic and real wastewater [26]. Furthermore, strategies combining backwashing with mechanical methods have been developed to generate shear without promoting aerobic microbial activity. These processes can reduce membrane fouling in municipal wastewater DMF and allow for sustainable municipal wastewater treatment [27]. Also, a moving bed biofilm reactor (MBBR) has been used as a pretreatment for DMF systems. The MBBR pretreatment can considerably mitigate membrane fouling in DMF, including removing small organic molecules and degrading UV-sensitive biopolymers [28]. For instance, the membrane aromatic recovery system (MARS) and permeation and chemical desorption (PCD) methods have proved to be effective for the removal of aromatic amines (e.g., aniline) [29–31]. Nonporous polydimethylsiloxane (PDMS) or polyoctylmethylsiloxane (POMS) hydrophobic membranes have been used to selectively transport aromatic compounds in a neutral form and reject their charged forms. Remarkably, electrodialysis (ED) and ion-exchange membranes (IEMs) have been widely used for different separation processes such as the desalination of water, recovery of bases and acids from waste streams, and removal of nitrite ions from groundwater [32,33]. Also, ED is a promising method of treatment of the organic pollutants-contaminated wastewater streams and has been studied for the removal of a mix of organic compounds as a part of a desalination process [34–36]. Nevertheless, no studies have investigated the transport mechanisms of organic micropollutants in their neutral and charged form through ion-exchange membranes as a function of solution pH.

The main objective of this research is to investigate the influence of pH on the mechanisms of the transport of aniline through hydrophobic POMS and PDMS membranes and ion-exchange membranes of different characteristics (i.e., thickness, ion-exchange capacity, electrical resistance, and water permeation), focusing on the influence of pH. The transport of aniline was investigated at the single membrane level (i.e., using two-compartment diffusion cells) and using an ED membrane stack. Additionally, desorption experiments were conducted to study the adsorption of aniline in the membranes. These results emphasize both the strengths and limitations of hydrophobic and ion-exchange membranes in removing aniline from aqueous solutions.

## 2. Materials and Methods

### 2.1. Chemical Reagents and Analytical Tools

Aniline (analytical grade > 99.5%, Sigma-Aldrich, Bornem, Belgium) was prepared at a final concentration of 5 mM. The solution was heated to 45 °C and kept in an ultrasound bath (S 100 H, Elmasonic, Singen, Germany) until completely dissolved. The pH of aniline was adjusted to pH 3 and pH 10 using 0.1 M HCl and NaOH, respectively, to achieve a positive and a neutral charge. The concentration of aniline at different pH conditions was measured by UV-spectrophotometry (UV-1600 PC, VWR, Leuven, Belgium) at specific wavelengths (232 nm for pH 3 and 230 nm for pH 7 and 10, respectively).

### 2.2. Hydrophobic and Ion-Exchange Membranes

Hydrophobic polyoctylmethylsiloxane (POMS) and polydimethylsiloxane (PDMS) membranes on polyacrylonitrile support and polyester nonwoven were supplied by the Center for Membranes and Structured Materials of the Institute of Polymer Research of the Helmholtz-Zentrum, Geesthacht, Germany. The anion and cation exchange membranes selected for this study were provided by Fujifilm (FF, Tilburg, The Netherlands) and termed AEM I, CEM I, AEM II, and CEM II (Table A1).

### 2.3. Two-Compartment Diffusion Cell Experiments

Two-compartment diffusion cells separated by a flat membrane (active area: 5.9 cm$^2$) were used to investigate the transport of aniline through different types of membranes under different pH conditions. The design of the diffusion cell setup was described elsewhere [37,38], and is shown in Figure A1. Briefly, the two compartments were filled with a 150 mL feed (containing aniline) and 150 mL receiving solution (Milli-Q water) without adding extra salts to avoid osmotic pressure differences and, thus, water transport across the membrane. Water transport was continuously monitored. Feed and receiving solutions were constantly stirred to avoid the influence of concentration polarization. No external current was applied in this experimental setup. The pH of the feed and receiving solutions was adjusted to 3 or 10 using HCl and NaOH for different membranes, according to Table 1. Samples were collected on feed and receiving solutions and analyzed using UV, as described in Section 2.1. Duplicate experiments were conducted to assess the replicability of results. Only the results of one of the setups were reported in the current study, while representative results of the duplicates are illustrated in Appendix A.

**Table 1.** The selection of membranes, pH conditions of the feed and receiving solution, and operational conditions during the diffusion cell and ED experiments.

| Experimental Condition | Membrane | pH |  | Duration (h) |
|---|---|---|---|---|
|  |  | Feed | Receiving |  |
|  | Diffusion Experiments |  |  |  |
| *a* | POMS | 3 | 10 | 500 |
| *b* | PDMS | 3 | 10 | 500 |
| *c* | AEM type I | 7 | 7 | 350 |
| *d* | CEM type I | 7 | 7 | 350 |
| *e* | AEM type I | 3 | 10 | 200 |
| *f* | AEM type I | 10 | 3 | 200 |
| *g* | CEM type I | 3 | 10 | 200 |
| *h* | CEM type I | 10 | 3 | 200 |
| *i* | AEM type II | 3 | 10 | 200 |
| *j* | AEM type II | 10 | 3 | 200 |
| *k* | CEM type II | 3 | 10 | 200 |
| *l* | CEM type II | 10 | 3 | 200 |
|  | Electrodialysis Experiments |  |  |  |
| *m* | AEM/CEM type I | 4 | 4 | 3 |
| *n* | AEM/CEM type I | 4 | 10 | 3 |

### 2.4. Desorption Experiments

The aim of the desorption experiments was to study the adsorption of aniline into the membranes. After the diffusion experiments, the units were emptied, and while still clamped, both compartments were gently rinsed with demineralized water to remove any impurities that could have developed on the sides of the glass or the membranes. Then, 150 mL of Milli-Q water was poured into each compartment. The unit was placed on the magnetic stirring plate, and the desorption experiments were started immediately. Samples were collected from the feed and stripping compartment after 2, 4, 6, 8, 10,12, 24, 48, and 96 h and analyzed as described in Section 2.1.

### 2.5. Electrodialysis Experiments

The electrodialysis stack used in this study was a PCCell ED 64004 (PCA GmbH, Maintal, Germany) and is described elsewhere [39], comprising five cell pairs of 8 × 8 cm$^2$ alternating AEM I and CEM I. The membranes were pretreated in 1 M NaCl prior to assembly. Silicon spacers (thickness of 0.5 mm) were placed between the membranes to create the diluate and concentrate compartments. An external potential at 7.5 V was provided by a PS5005 DC Lab Power Supply source (Singen, Germany). The ED setup unit was flushed and stored in 1 M NaCl between the experiments. After each experiment, the electrode chamber was flushed with water to remove the electrode reaction products.

The experiments were performed in batch mode at ambient temperature. The diluate, concentrate, and electrode rinsing solution (ERS) were recirculated in batch mode at a 30 L/h flow rate using a peristaltic pump (Watson-Marlow 530s, Wilmington, NC, USA). The concentration of the solutes was measured at 15 min intervals in real time. The duration of the experiments was determined by the evolution of the concentration in time. The experiments were stopped once the plateau was reached.

The diluate compartment initially contained 2 L of the aniline solution at a concentration of 5 mM, while the concentrate comprised 2 L of Milli-Q water. The pH in both compartments was adjusted to a desired value according to the selected experimental conditions (Table 1). The electrode compartment contained 2 L of $NaNO_3$ at a 5 g/L concentration. An additional 500 mL of aniline at a concentration of 5 mM was flushed through the ED prior to each condition to ensure membrane equilibrium. The ED experiments were conducted at two different pH conditions (pH 4 and 10) in the concentrate compartment (Table 1). In contrast, the pH in the diluate compartment was maintained at a constant pH of 4 (i.e., where aniline is in its charged form). Samples of 1 mL were collected at 15 min intervals.

## 3. Results and Discussion

The current section investigates the removal of aniline from an aqueous solution through the following: (i) the diffusion of neutral aniline using hydrophobic POMS and PDMS hydrophobic membranes (experimental conditions *a* and *b*) and (ii) the diffusion of charged and neutral aniline using two types of IEMs (experimental conditions *c* to *l*) in a diffusion cell setup, followed by (iii) the transport of aniline through IEMs in ED experiments (experimental conditions *m* and *n*) (Table 1).

### 3.1. The Diffusion of Aniline Through POMS and PDMS Hydrophobic Membranes

The transport of aniline from feed (pH 10) to the receiving solution (pH 3) through hydrophobic POMS and PDMS membranes (experimental conditions *a* and *b*) is shown in Figure 1. At these pH levels, 99.9% of aniline is expected in its neutral form in the feed. In comparison, 98% of aniline is expected in its positively charged form in the receiving solution. When using the POMS membrane, the concentration of aniline in the feed dropped from 4.7 to 0.5 mM after 500 h, achieving a 90% removal. Correspondingly, the concentration of aniline in the receiving solution increased from 0 mM to 3.9 mM. The mass balance showed a 6% mass loss at the end of the experiment, indicating the adsorption of aniline in the POMS membrane. The observed aniline adsorption would be induced by hydrophobic interactions with the POMS membrane. The concentration profile of aniline in PDMS was similar to that in POMS. However, the removal of aniline reached 100% at 384 h, thus showing a faster aniline transport through the PDMS membrane, while a 10% mass loss was observed at the end of the experiment. The initial fluxes of aniline from the feed (i.e., calculated from the initial linear regime) were 38.9 and 30.8 $mmol \cdot m^2 \cdot h^{-1}$ for the POMS and PDMS, respectively, thus showing similar values.

The transport of neutral aniline in a hydrophobic membrane was induced by the concentration gradient between the feed and receiving solution across the membrane. The Log D of aniline is approximately 0.9, thus describing the relative hydrophobicity of the molecule and allowing interactions with these hydrophobic membranes [40]. The transport would stop when an electrochemical potential equilibrium across the membrane was achieved. However, to increase the removal of neutral aniline from the feed, the pH of the receiving solution was adjusted to below the pKa of aniline (i.e., 4.6) to protonate this molecule into a positively charged anilinium ion. Therefore, the concentration gradient of neutral aniline was maintained throughout the experiments (i.e., driving force), thus promoting the transport of the aniline from the feed side to the stripping side. At alkaline conditions, the percentage of the neutral species of aniline is predominant, and hence the mass transfer coefficient increases [41]. Interestingly, the modification of PDMS membranes with amino groups improves the surface polarization and decreases the water contact angle [42]. This could result in an improvement in the permselectivity and transport of aniline through the membrane, as observed in the current study. Duplicate experiments showed comparable transport trends of aniline through hydrophobic membranes (Figure A2a).

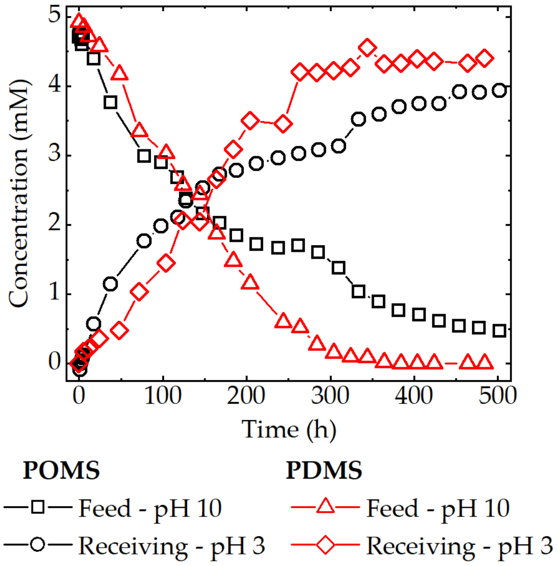

**Figure 1.** Concentration profile of the aniline in the feed (pH 10) and receiving solution (pH 3) using the POMS and PDMS membranes as a function of time.

### *3.2. The Influence of pH on the Transport of Aniline Through IEMs*

#### 3.2.1. The Diffusion of Aniline Through IEMs at Neutral pH Conditions in the Feed and Receiving Solutions

The impact of pH on the diffusion of aniline through AEM type I and CEM type I membranes was investigated. The feed and receiving compartments were adjusted to pH 7 to maintain aniline in its neutral form and thus create conditions where diffusion of aniline will be driven only by the concentration gradient (experimental conditions *c* and *d*). At pH 7, aniline is mainly present in its neutral form (99.6%). Therefore, no transport would be observed after an equilibrium concentration in the feed and receiving compartment is reached due to a lack of a driving force.

After 220 h, the equilibrium was reached in AEM type I, and no further transport was observed (Figure 2a). The diffusion of aniline through the CEM type I membrane showed slightly faster (Figure 2b), where the equilibrium was reached after 124 h. A previous study similarly observed a faster transport of phenol through CEMs [43]. The difference in transport kinetics between AEM and CEM would be due to their different characteristics. Although thinner, AEM type I shows a lower water permeation than CEM type I, suggesting a denser structure of the former. Interestingly, a previous investigation has recorded a higher intensity of free-volume elements in CEM compared to AEM, as well as a higher density (g/mL) of AEM [38,44]. Nevertheless, the faster diffusion of aniline through CEM type I would also be induced by membrane–aniline interactions, as previously reported [38]. Thus, the physicochemical properties of IEMs (i.e., functional groups and backbone polymers) and aniline (i.e., structure, Log D, and MW) would play a key role during transport. Remarkably, the initial fluxes of aniline from the feed were 43.6 and 53.2 mmol·m$^2$·h$^{-1}$ for the AEM type I and CEM type I, respectively, and were slightly higher than those of the POMS and PDMS membranes. However, this result indicates similar transport kinetics between IEMs type I and the hydrophobic membranes. Duplicate experiments confirmed these reported trends (Figure A2b).

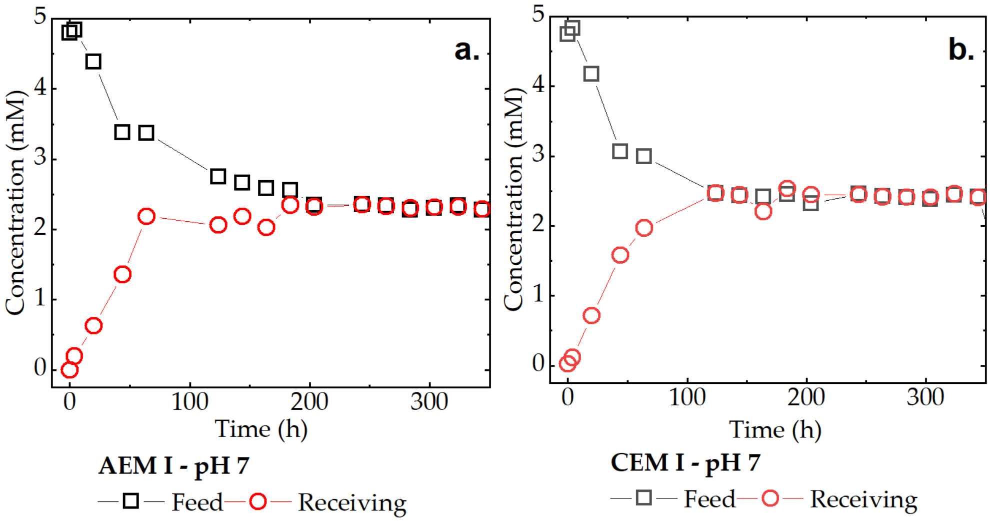

**Figure 2.** The concentration profiles of aniline using (**a**) AEM and (**b**) CEM type I and at a feed pH 7 and receiving solution pH 7, as a function of time.

### 3.2.2. The Impact of Varying pH at the Feed and Receiving Solutions on Aniline Transport

The main characteristic of ion-exchange membranes is their preferential permeability to counter-ions. However, co-ions can also be transported through the membrane due to a difference in the chemical potential of the solution and membrane [45]. The transport of neutral aniline in IEMs of different characteristics as a function of pH has received little attention and, hence, needs further investigation. Based on the different properties of the membranes (Table A1), the current experiments compared the transport of neutral and positively charged aniline ions using AEM type I, CEM type I, AEM type II, and CEM type II (experimental conditions *e* to *l*) (Table 1).

The transport of charged aniline from the feed (pH 3) through AEM type I and II toward the receiving solution (pH 10, where the aniline is expected to turn neutral) was studied (Figure 3a). AEM types I and II allowed the transport of the co-ion (positively charged) aniline despite electrostatic repulsion forces. However, the transport kinetics was slow in both AEMs, resulting in initial fluxes of 3.4 and 2.4 mmol·m$^2$·h$^{-1}$ for AEM type I and II, respectively. For example, after 200 h, 89% and 96% of the aniline were retained in the feed compartment for AEM types I and II, respectively. These values are close to the permselectivity reported by the manufacturer (i.e., 92% and 95% for AEM types I and II, respectively). In addition, this trend is also consistent with that reported by the manufacturer (Table A1); specifically, AEM type II showed a higher permselectivity. As discussed in the previous section, IEMs show a permselectivity value below 100%, thus allowing the transport of co-ions (Figure 4) [46].

A significant difference in transport between neutral and charged aniline through AEM types I and II was observed. The diffusion of neutral aniline from the feed (pH 10) through AEM type I and II toward the receiving solution (pH 3, where the aniline is expected to gain a positive charge) showed considerably faster due to the absence of electrostatic repulsion

(Figure 3b). For instance, approximately 50% and 72% of neutral aniline transport through AEM type I was achieved after 92 h and 200 h, respectively (Figure 4). Although slower, neutral aniline also showed diffusion through AEM type II. After 200 h, approximately 45% of aniline was transported through AEM type II (Figure 4). Remarkably, aniline transport through AEM type I was faster than AEM type II, regardless of its neutral or charged form, thus indicating the higher permeability of the former membrane to this organic micropollutant and resulting in initial fluxes of 38.4 and 19.0 mmol·m$^2$·h$^{-1}$ for AEM type I and II, respectively. The former flux value was similar to the flux of neutral aniline through AEM type I at pH 7 in both the feed and receiving solution. Mass balances indicated negligible aniline adsorption on both AEM type I and II (i.e., below 3%).

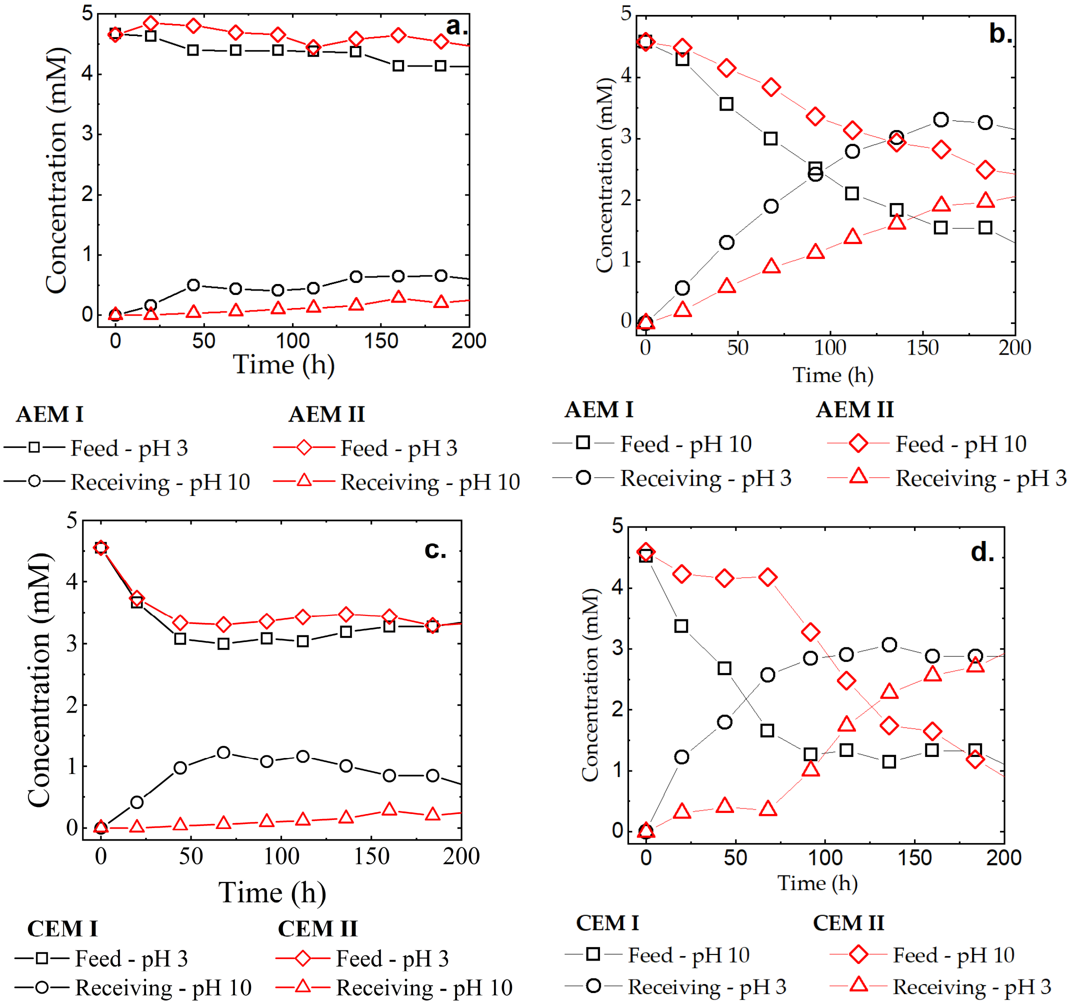

**Figure 3.** The concentration profiles of aniline using AEM type I and II at (**a**) feed pH 3 and receiving solution pH 10, (**b**) feed pH 10 and receiving solution pH 3, and using CEM I and II at (**c**) feed pH 3 and receiving solution pH 10, and (**d**) feed pH 10 and receiving solution pH 3.

Conversely, the transport of charged aniline from the feed (pH 3) through CEM type I and II toward the receiving solution (pH 10, where the aniline is expected to turn neutral) showed different mechanisms compared to that of AEMs (as depicted in Figure 3a,c). In this case, CEM types I and II allowed the transport of the counter-ion (positively charged) aniline (i.e., not displaying electrostatic repulsion forces). Although initially fast (initial flux of 56.1 mmol·m$^2$·h$^{-1}$), the transport of charged aniline through CEM type I reached a plateau at approximately 50 h of the experiments. Then, the aniline concentration in the feed and receiving solutions slowly increased and decreased with time, respectively. This occurrence can be attributed to a back-diffusion phenomenon, where neutral aniline in the receiving solution (pH 10) compartment diffuses back to the feed compartment (pH 3) based on a concentration gradient mechanism. No further transport was recorded, and no equilibrium was reached (Figure 3c). After 200 h, approximately 23% of the aniline was transported from the feed (Figure 4), while the mass balances indicated a possible 12% of aniline adsorption in the membrane (CEM type I). The adsorption of positively charged organics on negatively charged CEMs has been previously reported by Roman et al. [47], and could be attributed to electrostatic interactions. Similarly, the concentration of charged aniline in the feed also showed a stepped decrease during the initial diffusion through CEM type II (initial flux of 46.0 mmol·$m^2$·$h^{-1}$) and a plateau at around 50 h of the experiments (Figure 3c). Also, a slow back-diffusion phenomenon in the feed solution was observed during the rest of the diffusion experiment. Nevertheless, the concentration profile of aniline in the receiving solution slightly increased with time and did not show any evidence of back-diffusion as in the case of the CEM type I experiment. The mass balance showed a possible 22% aniline adsorption in the CEM type II membrane, which was considerably higher than its type I counterpart. The higher aniline adsorption on CEM type II would suggest stronger interactions between the functional groups or backbone polymers of the membrane with the aniline molecule.

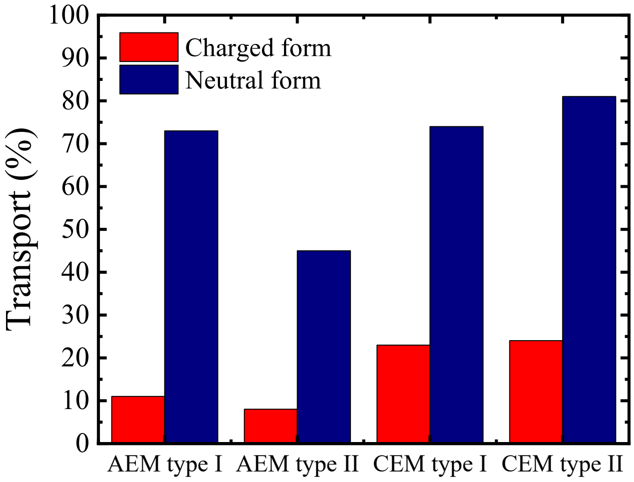

**Figure 4.** The transport of charged and neutral aniline through AEM type I, CEM type I, AEM type II, and CEM type II after 200 h.

Similar to their AEM counterparts, a significant difference in transport between neutral and charged aniline through CEM types I and II was recorded. The diffusion of neutral aniline from the feed (pH 10) through CEM type I and II toward the receiving solution (pH 3, where the aniline is expected to gain a positive charge) showed considerably faster because of the absence of electrostatic repulsion (Figure 3d). Remarkably, 50% of the aniline transport was observed at approximately 52 h and 127 h for CEM types I and II, respectively, thus resulting in initial fluxes of 68.4 and 33.7 mmol·$m^2$·$h^{-1}$ for CEM type I and II, respectively. Therefore, the diffusion of neutral aniline was faster in CEMs compared to AEMs of the same types, as observed in Figure 3b. After 200 h, approximately 74% and 81% of the aniline was transported from the feed. Similar to the previous experimental condition, an approximate 12% and 22% aniline adsorption on CEM types I and II was also observed, respectively. This result confirmed the affinity of the CEM polymers for aniline.

When comparing the transport of neutral vs. charged aniline through the varied IEMs, a neutral-to-charged form of aniline ratio of transport was extracted after 200 h of experiments. For AEMs type I and II, a 6.6:1 and 5.6:1 neutral–charge ratio was recorded, while for CEMs type I and II, a 3.2:1 and 3.3:1 neutral–charge ratio was calculated, respectively. These ratios, along with the transport (% and kinetics) of aniline (Figure 4), suggest AEM and CEM type I as the most suitable membranes for the following ED experiments (Section 3.4).

### *3.3. The Desorption of Aniline from IEMs and Hydrophobic POMS and PDMS Membranes*

POMS and PDMS are hydrophobic membranes; thus, the adsorption of protonated compounds is not expected. These desorption experiments aimed to investigate the difference in the desorption rate from both sides of these hydrophobic membranes, one facing the feed side (99.9% of aniline was neutral) and the other facing the permeate side (98% of aniline was charged). Despite the 6% and 10% adsorption in POMS and PDMS membranes discussed in Section 3.1, no desorption was detected after the analysis of the samples. This result suggests the irreversible organic adsorption of these hydrophobic membranes and, thus, strong interactions between the polymers of the membranes and aniline.

Similar to the hydrophobic membranes, no desorption was observed on either side of AEM type I and type II despite the negligible adsorption observed. This indicates minimal interactions between the AEM polymers and aniline structure. Nevertheless, aniline was observed to desorb from both sides of the CEM types I and II, even when the membrane surfaces were exposed to different pH conditions (Figure 5). More aniline was desorbed from CEM type II membranes compared to CEM type I. CEM type II membranes are approximately 20% thicker compared to CEM type I membranes, which would contribute to more available sites available for sorption. Also, no significant difference was observed between the aniline concentration desorbed from the feed and receiving sides. Nevertheless, the desorbed amount of aniline was small compared to the above-reported adsorbed values. These results indicate that the aniline adsorption on CEM could be reversible, unlike those occurring on hydrophobic membranes.

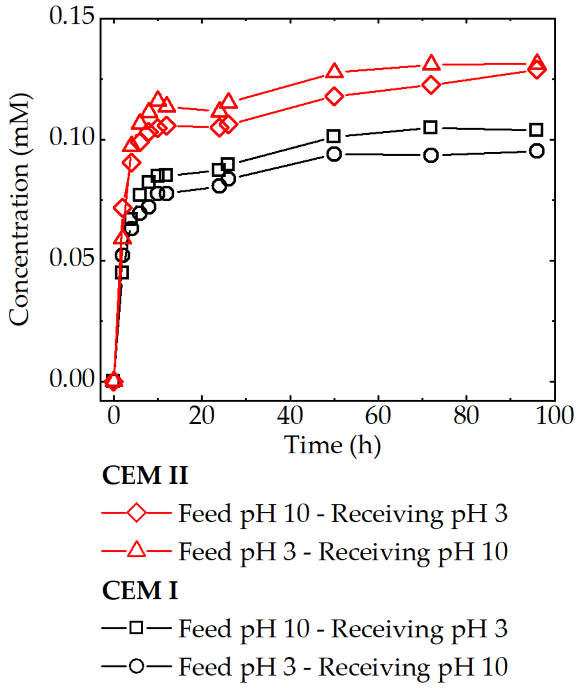

**Figure 5.** The desorption of aniline from CEM type I and type II.

### *3.4. The Removal of Aniline Using Electrodialysis*

The influence of pH on the transport of charged aniline by ED was studied under pH 4 at the diluate compartment and under pH 4 and pH 10 at the concentrate compartment (experimental conditions *m* and *n*). The pH was adjusted in real-time during the experiment to maintain the desired experimental conditions. A constant electrical potential of 7.5 V was applied. Both experiments showed a similar removal profile: an initial fast decrease in the aniline concentration in the diluate compartment (i.e., resulting in similar initial fluxes of 124.7 and 135.4 mmol·m$^2$·h$^{-1}$ for pH 4 and 10 at the concentrate compartment, respectively, due to electromigration) and a slower increase in the aniline concentration in the concentrate compartment (Figure 6a). After 3 h of experiments, a similar aniline transport (97% and 96%) was recorded for experimental conditions m and n (i.e., pH 4 and 10 at the concentrate compartment), respectively. Therefore, the pH of the concentrate compartment did not significantly influence the removal efficiency of charged aniline in the diluate compartment by ED. Nevertheless, the decrease in the aniline concentration in the diluate compartment did not translate into a corresponding increase in the concentrate compartment. Approximately 30% of the aniline was not accounted for in the mass balance for both experiments. Therefore, the transport of aniline to the electrode solution was investigated. The concentration of aniline in the electrode solution was measured. The obtained results confirmed the presence of aniline in the electrode solution. The aniline concentration gradually increased with time during the experiment. The aniline in the ERS compartment was added to the mass balances (Figure 6b), after which aniline adsorption was detected in the system. Specifically, 13% and 11% aniline adsorption were recorded for experimental conditions m and n (i.e., pH 4 and pH 10 at the concentrate compartment), respectively. As evidenced in the previous results, the adsorption of aniline would have preferentially occurred in the CEM type I membranes.

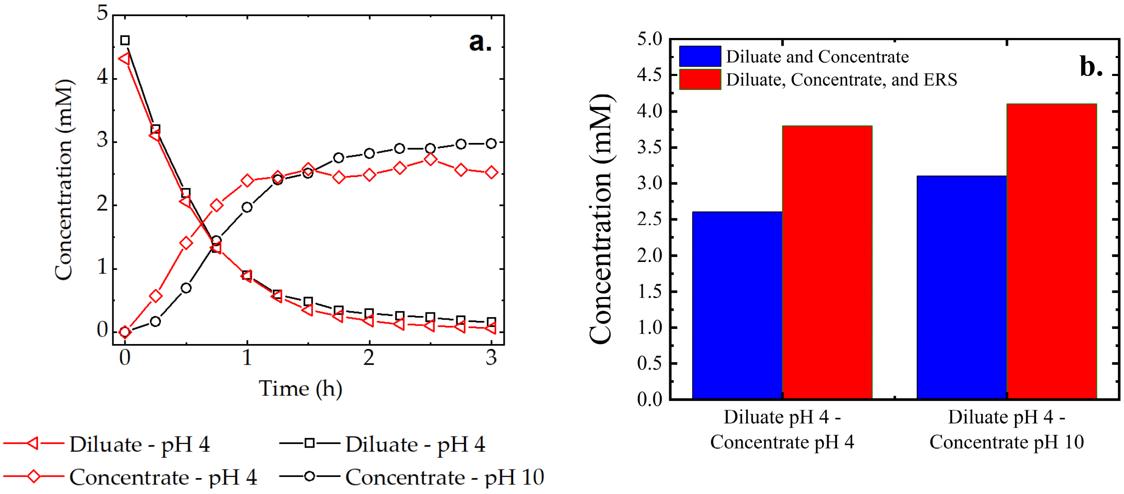

**Figure 6.** (**a**) Aniline concentration profiles in the diluate and concentrate channels during ED experiments. (**b**) Mass balances of aniline concentration in the diluate, doncentrate, and ERS channels.

### 3.4.1. Current-Voltage Curve

A decrease in electrical current was observed during ED experiments and would be attributed to the system becoming less conductive. The current–voltage curve generally represents the electric properties of the membranes and conductivity of the solution and provides information on the mechanism of ion transport, including concentration polarization [48]. While the electrical potential remained constant (7.5 V), the electrical current decreased over time during each experimental condition as the aniline was transported from the diluate solution to the concentrate (Figure 7). As a result, the resistance of the membranes increased. The concentration polarization phenomenon can generate an additional resistance for ion transport across the membrane.

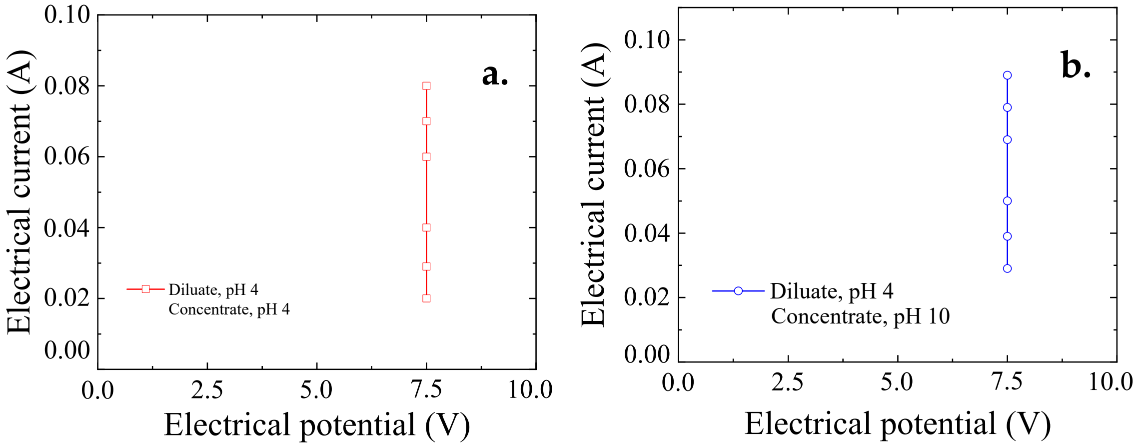

**Figure 7.** The current/voltage curve for (**a**) pH4 and (**b**) pH 10 conditions in the concentrate compartment.

A decrease in the current can be induced by the development of fouling in the membranes [45]. Specifically, organic fouling on the surface and inside IEMs can originate from electrostatic and hydrophobic interactions (i.e., charged and uncharged forms, respectively) [49,50]. This film increases the resistance of membranes and, thus, decreases the current density (mA/cm$^2$). The desorption test results also confirmed the aniline adsorption in the CEMs. Hence, a membrane-poisoning process took place.

#### 3.4.2. Water Transfer

The volumes of the solutions of the diluate, concentrate, and ERS compartments were monitored, where a gradual volume change was recorded during all experiments. On average, a 200 mL decrease in the diluate and the corresponding increase in concentrate and ERS solutions was observed. The water transfer can be explained by electro-osmosis. The first hydration shell of aniline comprises 26 molecules of water, with 6.7 being around the -NH$_2$ group [51]. Due to polar interactions, water molecules bond to the ion and move with it through the membrane. This phenomenon can also explain the presence of aniline in the ERS solution.

### *3.5. Conclusions*

This study aimed to investigate the influence of pH on the transport of aniline through hydrophobic and ion-exchange membranes in aqueous solutions. An experimental study was conducted using diffusion cells and ED. Different pH conditions were used to investigate the effect of pH on the transport of charged and neutral forms of aniline.

During diffusion cell experiments, the aniline transport through hydrophobic POMS and PDMS membranes showed very similar results, achieving 90% and 100% aniline removal, respectively. The main contribution to the transfer of neutral aniline was diffusion, which was caused by a concentration gradient across the membrane. Furthermore, the transport through ion-exchange membranes was investigated. Diffusion cell experiments confirmed that a complete exclusion of co-ions with IEM was not possible, where the selectivity of the IEMS was close to those reported by the manufacturer. Positively charged aniline was transported through the AEM from the feed to the receiving solution compartment, demonstrating co-ion transport. The overall comparison of diffusion of aniline through IEMs under the same pH conditions at the feed and receiving solution compartments demonstrated a trend: slower transport when the aniline was charged and faster transport in its neutral form. Type II IEMs showed slower transport compared to type I IEMs, probably due to the denser nature of type II membranes. The charge of the membranes did not play a significant role in transport. The transport was non-specific and was driven by a chemical gradient rather than electrochemical interactions.

On the other hand, the experiments performed with ED enabled the study of the influence of the external electric potential and pH on the transport of charged species. Varying the pH conditions of the concentrate compartment (i.e., pH 4 and 10) did not significantly influence the transport of charged aniline in ED. All pH conditions demonstrated a fast transport and aniline removal from the feed: 96–97%. Remarkably, the aniline fluxes during ED experiments were significantly higher than those observed in diffusion cell experiments. However, approximately 30% of the aniline was transported to the ERS, and an approximately 10% water flux decreased in the dilute and increased in the ERS solution and concentrate compartment. This water transport was caused due to electro-osmosis. The initial aniline concentration in the feed and flow rates (i.e., in particular, cross-flow velocities) are recommended as crucial variables for future studies. Chemical and electrical gradients were key contributing factors to the transport of charged species of aniline.

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## Abbreviations

The following abbreviations are used in this manuscript:

| | |
|---|---|
| AEM | Anion-exchange membrane |
| AOP | Advanced oxidation process |
| CEM | Cation-exchange membrane |
| DBD | Dielectric barrier discharges |
| ED | Electrodialysis |
| IEM | Ion-exchange membrane |
| MARS | Membrane aromatic recovery system |
| PDMS | Polydimethylsiloxane |
| PMS | Peroxymonosulfate |
| POMS | Polyoctylmethylsiloxane |

## Appendix A

**Table A1.** Physical–chemical properties of the selected membranes.

| Properties | AEM I | CEM I | AEM II | CEM II |
|---|---|---|---|---|
| Thickness (μm) | 75.9 | 97.7 | 129.4 | 121.1 |
| Permselectivity (%) | 92 | 95 | 95 | 96 |
| Water permeation (mL·bar$^{-1}$·m$^{-2}$·h$^{-1}$) | 6 | 10 | 3 | 3.5 |
| Burst strength wet (k·Pa) | 2.4 | 2.7 | 5 | 4.7 |
| Electrical resistance in 2 M NaCl (Ω·cm$^2$) | 0.8 | 1.3 | 3.5 | 6.1 |
| Ion-exchange capacity (meq/g) | 1.5 | 1.4 | 0.9 | 1.1 |
| pH stability | 2–10 | 4–12 | 2–10 | 4–12 |

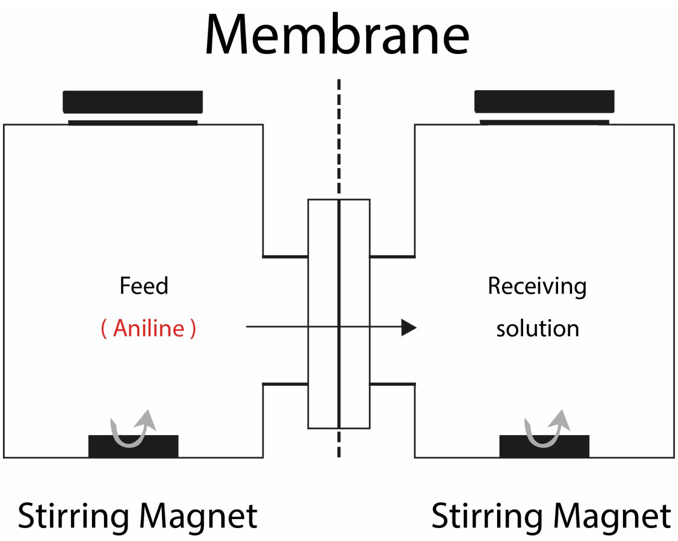

**Figure A1.** Schematic of the two-compartment diffusion cells.

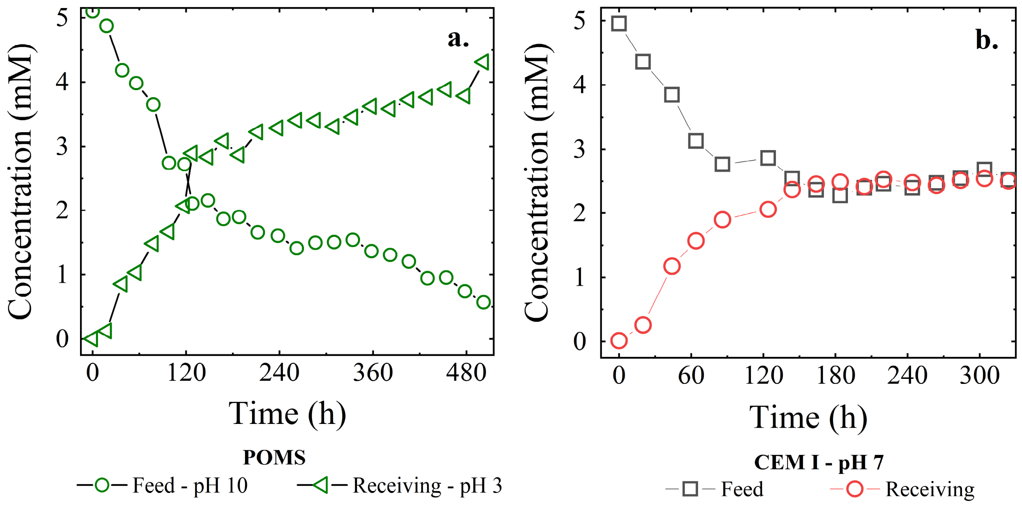

**Figure A2.** Representative duplicate experiments of the following: (**a**) a concentration profile of aniline in the feed (pH 10) and receiving solution (pH 3) using the POMS membrane as a function of time, and (**b**) concentration profiles of aniline using CEM type I and at a feed pH 7 and receiving solution pH 7, as a function of time.

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