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Electrodeionization for Wastewater Reuse in Petrochemical Plants

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Abstract: This study investigated a hybrid membrane and electro-membrane separation process for producing demineralized water from tertiary petrochemical effluent, reusing it as feeding water for high-pressure boilers for steam generation. The effluents were treated in a pilot plant with a 1 $m^3\ h^{-1}$ capacity by using a hybrid process of ultrafiltration (UF), reverse osmosis (RO), and electrodeionization (EDI). The physicochemical parameters of interest and maximum limits in industrial water were pre-determined by the industries. Operating parameters such as flow rate, pressure, percentage of recovery, and electric current were monitored, along with the frequency of chemical cleaning. The UF and RO systems operated with average permeate fluxes of 17 ± 4.06 L $h^{-1}\ m^{-2}$ and 20.1 ± 1.9 L $h^{-1}\ m^{-2}$, respectively. Under optimal operating conditions (flow rate of 600 L h^{-1}, voltage of 22.2 ± 0.7 V, and electric current of 1.3 A), EDI produced high-quality water with an average electrical conductivity of 0.22 µS cm^{-1}. Thus, the industrial water produced reached the quality required for reuse as make-up water for high-pressure boilers in the petrochemical industry. In addition, the specific energy consumption; the use of chemicals, spare materials, equipment; and labor costs were determined to support the technical feasibility study for implementing an industrial plant with a 90 $m^3\ h^{-1}$ producing capacity. This resulted in a cost of USD 0.64 per cubic meter of demineralized water produced, a cost similar to values reported in the literature.

Keywords: circular economy; ultrafiltration; reverse osmosis; electrodeionization; electro-membrane process; petrochemical wastewater

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1. Introduction

The growing scarcity of water resources, worsened by climate change, highlights the pressing need to explore non-conventional water sources, such as wastewater. Considering the high volumes of water used in petrochemical plants [1] and the increased demand for petroleum derivatives worldwide, the reuse of treated wastewater in the petrochemical industry is relevant from an environmental and economic point of view [2–4]. In addition, selecting the most appropriate and sustainable technologies to deal with organic and inorganic contaminants in these industrial effluents to meet stringent environmental standards is a complex task [5]. Therefore, implementing water reuse systems faces significant obstacles, including high costs and a lack of familiarity with advanced treatment technologies usually required to achieve high-purity water.

In fact, high-purity water with an electrical conductivity lower than 0.06 µS cm^{-1} is a critical factor for several industrial applications, such as semiconductor manufacturing and pharmaceutical formulations [6], as well as for steam generation in high-pressure boilers in the petrochemical industry [7]. These boilers require high-quality water to protect equipment and to prevent scaling and corrosive processes [8], in addition to avoiding other undesirable problems, such as a reduced heat exchange rate and increased fuel consumption, reduced steam production, the overheating and rupture of pipes, and the fouling of instruments and control devices [9].

In this context, boiler feed water requires a very refined treatment, which generally employs conventional treatment systems (coagulation/flocculation plus sedimentation or flotation) together with one or more advanced ones [10], such as ion exchange resin [1,11], reverse osmosis (RO) [8], electrodialysis reversal (EDR) [12], and electrodeionization (EDI) [13,14].

Previous studies, carried out to characterize tertiary petrochemical wastewater and to evaluate advanced technologies, allowed us to propose a hybrid treatment system comprising ultrafiltration (UF), RO, and EDI to produce high-purity demineralized water (conductivity < 0.17 $\mu S\ cm^{-1}$) [15]. This hybrid system takes advantage of tertiary petrochemical wastewater, and operates at low pressures, reducing energy consumption. The benefits of this approach include not only the energy savings associated with wastewater disposal, but also reduced maintenance costs of current sprinkler and wastewater drip networks, as well as savings in monitoring efforts in these sprinkler areas [2,16]. Furthermore, the implementation of the reuse system offers additional advantages, such as interrupting the degradation process of the soil currently used for wastewater disposal.

On the other hand, implementing treatment systems on an industrial scale involves a technical assessment of economic and management factors, with a special focus on water quality, and capital and operational costs, in addition to the energy consumption [5], scalability, and long-term stability of treatment plant components (e.g., membranes lifetime) [17]. The energy consumption to produce water in the industry using conventional treatment methods is between 2.5 and 4 kWh m^{-3}, depending on several factors such as the type of abstraction and pre-treatment, as well as the turbidity of the raw feed water [18]. Nevertheless, for low-pressure and brackish water reverse osmosis (3–15 bar applied pressure and 500–2000 ppm feed water), energy consumption is less than 1 kWh m^{-3} [19].

The costs of treating and producing water from wastewater generally range between USD 0.40 and 1.26 per cubic meter [20], depending on the level of conventional treatment adopted (i.e., primary, secondary, or tertiary wastewater) and the specific quality requirements of treated water for its reuse, as well as the size and capacity of the plant [21]. This combination of factors makes the hybrid UF/RO/EDI process a promising solution for the treatment and reuse of industrial wastewater. However, the final cost of the produced water can differ significantly due to inaccuracies in calculation methods, such as whether the costs of conventional treatment, that are already being used, are taken or not into account.

In light of these considerations, the present study aims to (i) optimize a hybrid UF/RO/EDI system on a pilot scale for the production of demineralized water from tertiary petrochemical wastewater; (ii) based on this optimization, present a technical and economic feasibility study to implement a demineralized water production plant (DWPP) with a production capacity of 90 $m^3\ h^{-1}$; and (iii) evaluate the quality and treatment cost of demineralized water produced from tertiary petrochemical wastewater.

Considering that the economic evaluation is key to the industrial scaling up of a process, in this paper, technical and practical information are used, based on data collected directly on a pilot plant set at a petrochemical industry, and treating a real petrochemical effluent. The technical challenges of using this real effluent in a pilot plant are presented as important practical information to industries in need of high-purity water.

2. Materials and Methods

2.1. Description of the Wastewater under Study

The industries of the Southern Brazil Petrochemical Complex (SBPC) generate heterogeneous wastewaters, which are therefore segregated at the source as inorganic or organic. The inorganic wastewater undergoes preliminary and primary treatment, while the organic one also undergoes secondary treatment (activated sludge with extended aeration). Subsequently, these wastewaters are combined, treated in eight stabilization ponds in series, and sprayed on soil. A more detailed description of the wastewater treatment systems used in the SBPC can be found in previous studies [16,22,23].

2.2. Hybrid UF/RO/EDI Treatment System

A hybrid system comprising UF, RO, and EDI was evaluated in treating tertiary petrochemical wastewater, aiming to produce demineralized water with conductivity lower than 0.3 μS cm^{-1}. This system was operated on a pilot scale to treat the tertiary petrochemical wastewater, which was collected at the outlet of the last stabilization pond of the SBPC wastewater treatment plant. The pilot plant is equipped with flow, pressure, and current meters, which allow the continuous monitoring of the operating parameters. A schematic flowchart of the hybrid treatment system is presented in Figure 1.

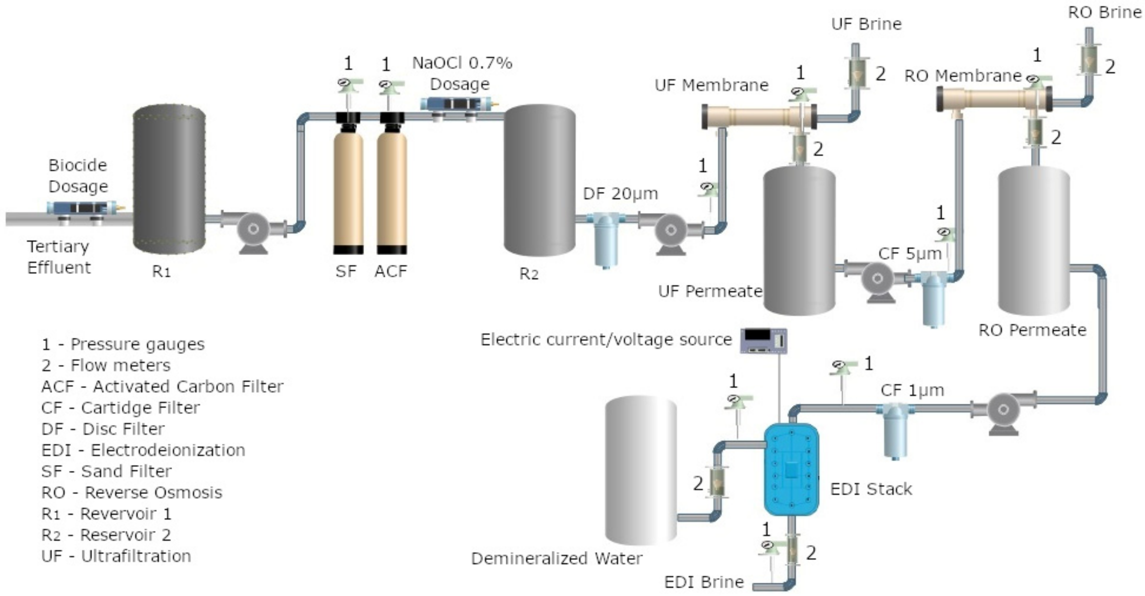

Figure 1. Schematic diagram of the hybrid demineralized water production system in pilot scale. Adapted from [15].

The effluent from the last stabilization pond, namely stabilization pond 8 (SP8), is pumped to a 15 m^3 reservoir (R_1), where 1 mg L^{-1} of ACTICIDE® DB 20—biocidal agent supplied by Thor (São Paulo, SP, Brazil)—is dosed to inhibit the growth of microorganisms. This wastewater is subjected to a system of sand and activated carbon filters, followed by in-line dosing of 3.2 L h^{-1} of 0.7% sodium hypochlorite. The up-flow sand filter has a 1 m thick bed divided into three layers, each composed of sand with a particle size of 1.4, 0.9, or 0.4 mm. The activated carbon bed (Alphacarbo brand, Guarapuava, PR, Brazil) is 1 m thick, with an average particle size of 1 mm and a filtration rate of 15.15 m^3 m^{-2} h^{-1}. When the pressure exceeds 2.1 bar, the filters are backwashed for 30 min and then rinsed with drinking water for 10 min. After the filtration stage, the wastewater is stored in another 15 m^3 reservoir (R_2).

The wastewater from R_2 passes through a 20 μm disc filter to minimize possible damage to the membrane and is then sent to the UF. A commercial PVDF hollow-fiber UF membrane (model SFX-2860, supplied by DOW Water & Process Solutions, Minneapolis, MN, USA) with a 51 m^2 membrane area and 0.03 μm average pore size was used. The UF system was operated for 130 days, 8 h per day, with temperature in the range of 20.3 ± 1.6 °C, average pressures at the module inlet and outlet of 1.9 ± 0.4 bar and 1.6 ± 0.42 bar, respectively, and 90% of water recovery. The UF has an automatic cleaning system to prevent fouling, which consists of backwashing with air, backwashing with UF permeate, and cleaning with 0.7% sodium hypochlorite every 30 min.

The UF permeate is subjected to the RO stage, which contains a polyamide thin-film composite membrane (FilmTec Fortilife CR100 Element, DuPont, São Paulo, SP, Brazil) with an area of 7.2 m^2, and is preceded by a 5 µm cartridge prefilter. The RO was operated for 113 days and 8 h per day, with an average pressure of 5.4 ± 0.1 bar, a temperature of 19.6 ± 2.5 °C, and approximately 50% permeate recovery. Table 1 describes the characteristics of the membranes used in UF and RO systems.

Table 1. Characteristics of the membranes used in UF and RO systems.

Characteristic	UF Membrane [a]	RO Membrane [b]
Membrane Type	PVDF	Polyamide Thin-Film Composite
Product Type	Hollow fiber	Spiral-wound element
Active Area (m^2)	51	7.2
pH Range Continuous Operation	4–11	2–11
Maximum Operating Temperature (°C)	50	45
Maximum Operating Pressure (bar)	5–9.5	15.5
Free Chlorine Tolerance (mg L^{-1})	5	<0.1
Maximum Feed Silt Density Index (SDI)		5
Minimum Salt Rejection (%)		99.5

Note(s): [a] ref. [24], [b] ref. [25].

The EDI system (Ion Tech® ITDS 10, Bergen op Zoom, The Netherlands) has ten cells filled with mixed ion-exchange resins and two electrodes, a stainless-steel cathode, and a titanium anode coated with titanium oxide. This system was operated for 24 h, with average pressures of 2.0 ± 0.1 bar, 0.97 ± 0.03 bar, and 1.8 ± 0.02 bar in the feed water, treated water, and brine streams, respectively. The treated water flow rate was 600 L h^{-1} under a voltage of 22.2 ± 0.7 V, an electric current of 1.3 A, a temperature of 17.9 ± 0.8 °C, and 95.2% of water recovery. Water recovery at each treatment stage was calculated as the ratio between the permeate and the feed flow rates in each stage (UF, RO, or EDI).

2.3. Analytical Methods

Samples of the tertiary petrochemical effluent, UF and RO permeates, and EDI-treated water, as well as brine streams from UF, RO, and EDI systems, were collected and analyzed according to the methodology described in the Standard Methods for Examination of Water and Wastewater [26]. The monitored parameters and their respective analytical methods are listed in Table 2.

Table 2. List of parameters and respective analytical methods used.

Parameter	Method	Parameter	Method
Aluminum	SM 3111D	pH	SM 4500H+
Calcium	SM 3111D	Potassium	SM 3500KB
Chloride	SM 4110B	Silica	SM 4500-SiO_2C
Color	SM 2120B	Sodium	SM 3500NaB
Electrical Conductivity	SM 2510B	Sulfate	SM 4110B
Iron	SM 3111B	Total Organic Carbon	SM 5310B
Magnesium	SM 3111B	Total Phosphorus	SM 4500PD
Nitrate	SM 4110B	Turbidity	SM 2130B

Note(s): SM: Standard Methods for Examination of Water and Wastewater [26].

2.4. Technical and Economic Feasibility Analysis

A technical feasibility analysis (TFA) was carried out using the Portfolio and Project Management Methodology [27], which is currently used by the industries from the Southern Petrochemical Complex. This methodology is divided into five stages, where the first three are part of the project definition phase and are classified as Front-End Loading (FEL). In FEL 1 (investment assessment), the project team evaluates the company’s investment capacity and approves the start of the next stage. In FEL 2, the conceptual project is carried out with a technical feasibility analysis, which is used to support approval for implementing the basic engineering. In FEL 3, the basic project is prepared, and, after approval, the project execution stage proceeds. In stage 4, the project is executed, while in stage 5, the plant starts up, as illustrated in Figure 2. This study presents the results corresponding to FEL 1 and FEL 2.

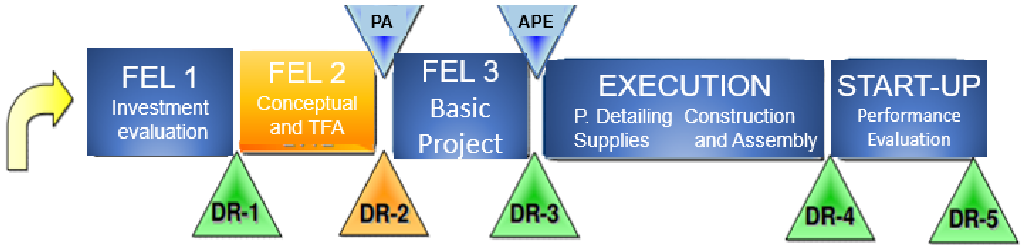

Figure 2. Portfolio and Project Management Methodology used by industries in the South Petrochemical Complex. PA: project authorization, approval to carry out basic engineering. APE: authorization for execution, approval for project execution. FEL: Front-End Loading, project definition phase. DR: design review, assessment gates with the project team. Adapted from [27].

An economic assessment containing data on capital and operational expedition, CapEx and OpEx, respectively, was carried out based on the results generated in the TFA. The total cost of the demineralized water production plant (DWPP) was defined based on a production capacity of 90 m^3 h^{-1}, evaluating the total cost of water per cubic meter. A sensitivity analysis was carried out taking into account system productivity (treatment capacity), costs of equipment, inputs, maintenance, and operation, in addition to evaluating the balance point between CapEx and OpEx.

A calculation spreadsheet was generated based on the methodology described below and the data from the TFA. Version 1.75.753 of the DuPont company's Water Application Value Engine (WAVE) software was used to simulate the UF and RO systems, while the values for the EDI system were calculated based on results obtained and budgets from the equipment manufacturer. So, the calculations were based on the following assumptions: (i) plant with 90 m^3 h^{-1} demineralized water production capacity; (ii) the values referred to commercial proposals (budgets) prepared in 2022 or 2023; (iii) electricity costs were set at USD 0.08 per kW h^{-1} (BRL 0.39 per kW h^{-1}), the amount contracted with the electricity concessionaire; (iv) UF system with 2448 m^2 of hollow fiber membranes, permeate flux of 39 L h^{-1} m^{-2}, and 90% water recovery; (v) RO system with 6466 m^2 of membranes, pressure vessels to accommodate 174 spiral-wound membrane elements, permeate flux of 15.5 L h^{-1} m^{-2}, and 75% water recovery; (vi) 5 years of useful life for the membranes; (vii) plant lifespan established at 30 years; (viii) EDI system with 20 modules, each with the capacity to treat 5 m^3 h^{-1}, and 90% water recovery; (ix) energy consumption of 0.60 kWh m^{-3} for the pre-treatment/UF/RO system, obtained in a commercial proposal; (x) energy consumption for EDI (E_{EDI}) was calculated based on the parameters optimized in the pilot plant, using Equation (1). It consists of the sum between the energy consumed in the stack ($E_{\text{EDI-stack}}$) and that spent in the EDI pumping system ($E_{\text{EDI-pump}}$), which were determined using Equations (2) and (3), respectively [28,29].

$$E_{\text{EDI}} = E_{\text{EDI-stack}} + E_{\text{EDI-pump}} \tag{1}$$

$$E_{\text{EDI-stack}} = \frac{VIt}{L} \tag{2}$$

$$E_{\text{EDI-pump}} = \frac{\dot{W}}{Q} \tag{3}$$

where V is the applied voltage (22.2 V), I is the electric current (1.3 A), t is the time used (1 h), L is the volume of water treated (0.6 m^3), $\dot{W}$ is the rate of work done by the pump (kW), and Q is the pumping flow rate in the EDI system (0.6 $m^3\ h^{-1}$). A Power Quality Analyzer PQA 824 m (HT Instruments, Faenza, Italy) was used to measure the power pump. Therefore, the total energy consumption of the DWPP comprises the energy costs of the pretreatment/UF/RO system plus the E_{EDI}.

The conceptual framework of the demineralized water production plant (DWPP) is illustrated in Figure 3.

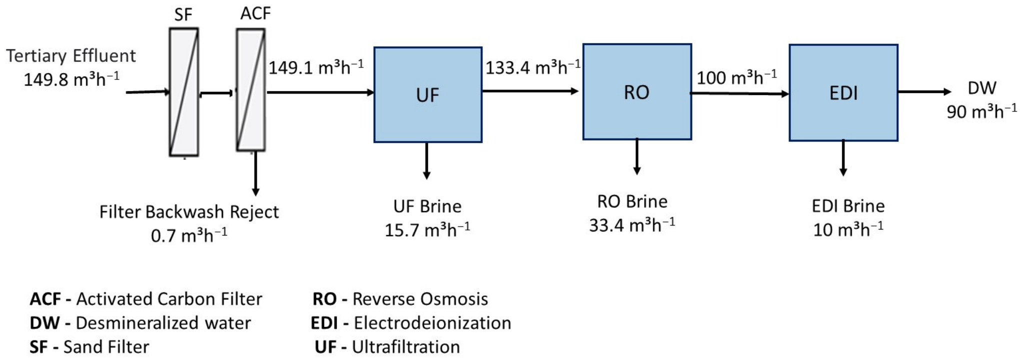

Figure 3. Conceptual framework of the demineralized water production plant in industrial scale.

3. Results and Discussion

3.1. Characterization of the Tertiary Petrochemical Effluent

Table 3 shows the physicochemical characterization of the tertiary petrochemical effluent used as feed water for the pilot plant, as well as the standard for demineralized water required in the petrochemical complex. This water-quality standard was defined by the petrochemical industry under study, whose objective is to use high-quality water to maximize heat-exchange efficiency and protect boilers and pipelines against corrosion, scaling, and other damages, as discussed in a previous work [2].

Table 3. Physicochemical characteristics of tertiary petrochemical effluent and the standard for demineralized water (DW) required in the petrochemical complex.

Parameter	Tertiary Effluent	Standard for DW [a]
Aluminum (mg L^{-1})	<2.50	ns
Calcium (mg L^{-1})	23.2	0.12
Chloride (mg L^{-1})	103	ns
Color (mg Pt-Co L^{-1})	31.6	ns
Electrical Conductivity (µS cm^{-1})	1222	<0.30
Iron (mg L^{-1})	0.51	<0.01
Magnesium (mg L^{-1})	5.27	0.25
Nitrate	2.12	ns
pH	7.77	6–7
Potassium (mg L^{-1})	64.0	ns
Silica (mg L^{-1})	25.0	0.02
Sodium (mg L^{-1})	170	ns
Sulfate (mg L^{-1})	272	ns
Total Organic Carbon—TOC (mg L^{-1})	10.0	ns
Total Phosphorus (mg L^{-1})	1.38	ns
Turbidity (NTU)	13.7	ns

Note(s): ns: not specified. [a] ref. [2].

The effluent has a neutral to slightly basic characteristic (pH 7.77), low levels of organic matter (10 mg L^{-1} TOC) and turbidity (13.7 NTU), and moderate color (31.6 mg Pt-Co L^{-1}), in addition to an electrical conductivity of 1222 µS cm^{-1} which is mainly attributed to sodium, chloride, and sulfate. Silica, magnesium, nitrate, iron, and other contaminants are present in lower concentrations, but well above the values required for high-purity water as those used in high-pressure boilers. Both contaminants and concentrations detected are in line with studies previously carried out with the aforementioned tertiary petrochemical effluent [15,16,22,23,30].

Considering the characteristics presented in Table 3, in this study, UF was applied as a pretreatment of RO, and especially to remove turbidity and color. After that, RO was responsible for removing TOC, iron, calcium, magnesium, monovalent ions, and other contaminants. As a final treatment, EDI was assessed for producing high-purity water.

3.2. Performance of the UF/RO/EDI Hybrid Treatment System

Figure 4 shows the behavior of pH, turbidity, and flux of the UF permeate over the 130 operating days, obtaining the following average values: 7.9 ± 0.33, 0.37 ± 0.2 NTU, and 17 ± 4.06 L h^{-1} m^{-2}, respectively. The mean pressures at the UF module inlet and retentate stream were 1.9 ± 0.43 and 1.6 ± 0.42 bar, respectively. In the first eleven operating days, the UF permeate flux remained above 20 L h^{-1} m^{-2}. After that, a permeate flux reduction was observed, resulting from membrane fouling caused by organic matter and microorganisms (mainly algae) remaining in the tertiary effluent, as already demonstrated in previous studies [15]. From the twelfth operating day, two flux bands were observed. Between the 41st and 60th day and from the 92nd day onwards, higher fluxes were observed, with an average value of 18 L h^{-1} m^{-2}, while from the 12th to the 40th day and from the 61st to the 91st day, the average flux was 14 L h^{-1} m^{-2}. These periods with higher and lower fluxes were related to a smaller and larger proliferation of algae in the stabilization ponds, respectively, whose occurrence was influenced by climatic conditions. A greater algal bloom was observed in the driest and hottest periods, which coincided with periods of lower permeate fluxes, that is, between the 12th and 40th operating day and between the 61st and 91st day. In fact, the UF membrane systems require strict control, such as oxidant dosages, to mitigate fouling and maintain constant permeate flux [5,31].

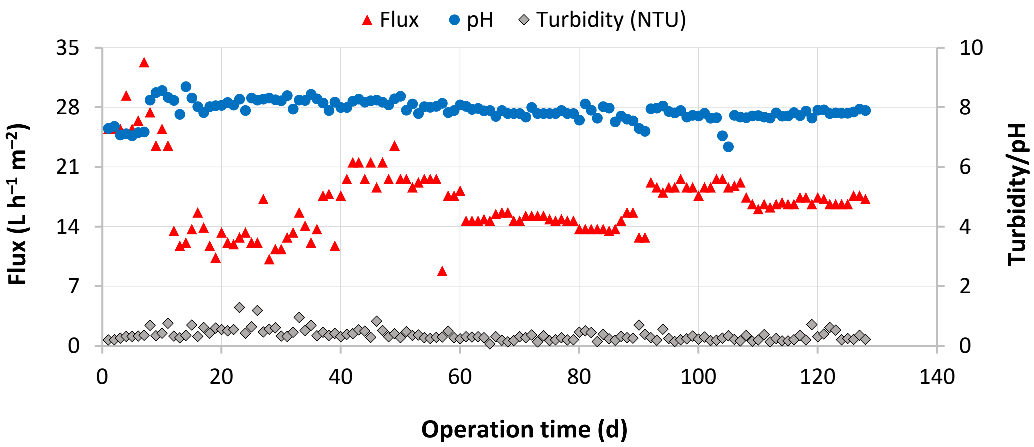

Figure 4. Behavior of the flux, turbidity, and pH of the UF permeate over the operating time.

The UF permeate was then treated by RO to produce water with enough quality to feed the EDI process. Figure 5 shows the behavior of the main parameters monitored over the 113 days of RO operation. During this period, the RO presented average permeate flux values of 20.1 ± 1.9 L h^{-1} m^{-2}, with a turbidity of 0.25 ± 0.1 NTU, EC of 17.1 ± 4.9 μS cm^{-1}, and neutral pH (7.1 ± 0.4).

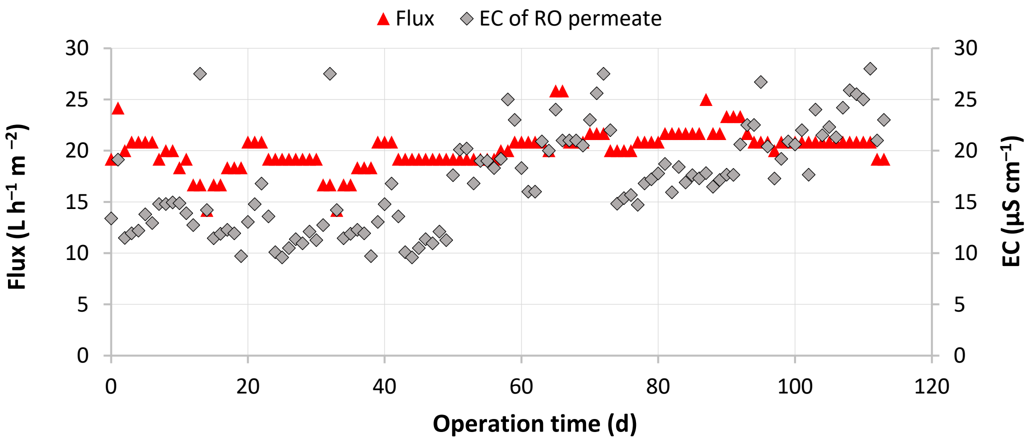

Figure 5. Flux and electrical conductivity of the RO permeate over the operating time.

On only two events (days 14 and 33) was a more significant decrease (ca., 20%) in RO permeate flux observed, probably caused by membrane fouling. This may have been related to the increase in biological material in the UF permeate, resulting from variations in influent quality. Nevertheless, the RO permeate flux was restored to its average value after a simple cleaning procedure consisting of rinsing for 5 min with the RO permeate. This behavior with a low variation indicates that the pre-treatment with UF allows water production with sufficient quality to feed the RO, minimizing fouling on the RO membrane, as recommended by Jafarinejad [31]. Furthermore, adding biocides also contributed to the maintenance of the stability of the RO permeate flux [16]. Moreover, the EC of the RO permeate remained below 30 µS cm^{-1} throughout the evaluated period, classifying this stream as suitable for feeding EDI, which requires feed water with an EC lower than 40 µS cm^{-1}. The small variation observed in EC values of the RO permeate is associated with the natural variability of the feed water composition, a typical behavior for real samples such as the tertiary petrochemical wastewater used in this study.

Subsequently, the EDI system was operated with a flow rate of 600 L h^{-1}, electrical current of 1.3 A, and feed water EC of 11.4 µS cm^{-1}, reaching an average water recovery of 95.2%. During the operation of the EDI system with the RO permeate as feed water, stability was observed in both the flow rate and the EC of the EDI product, which remained at around 0.22 µS cm^{-1}. This is a valuable result, as it meets the parameter required for demineralized water from the Petrochemical Complex, i.e., EC < 0.3 µS cm^{-1}.

Figure 6 shows the concentrations of the major ions monitored in this study after each treatment step, namely stabilization pond 8 (SP8), ultrafiltration, reverse osmosis, and EDI. The tertiary effluent from SP8 contains 23.2, 5.27, 0.51, and 1.38 mg L^{-1} of calcium, magnesium, iron, and total phosphorus, respectively, with these values being kept practically constant also in the UF permeate and then diminished drastically after RO treatment. Despite not producing a permeate complying with demineralized water standards (<0.3 µS cm^{-1}), RO acted as an excellent pre-treatment for EDI. RO removed more than 90% of the ions and organic compounds remaining from the UF step, which could cause fouling in the EDI system, as pointed out by Hernon et al. [32]. EDI, in turn, removed the ions that had prevailed in the RO permeate, producing water within the quality standards required for the demineralized water currently used in the Southern Petrochemical Complex [2]. Among these ions, calcium was about 0.32 mg L^{-1} in the RO permeate; however, as it is considered a cation that can be easily removed via EDI due to its ease of adsorption by resins, a reduction of 98% was achieved.

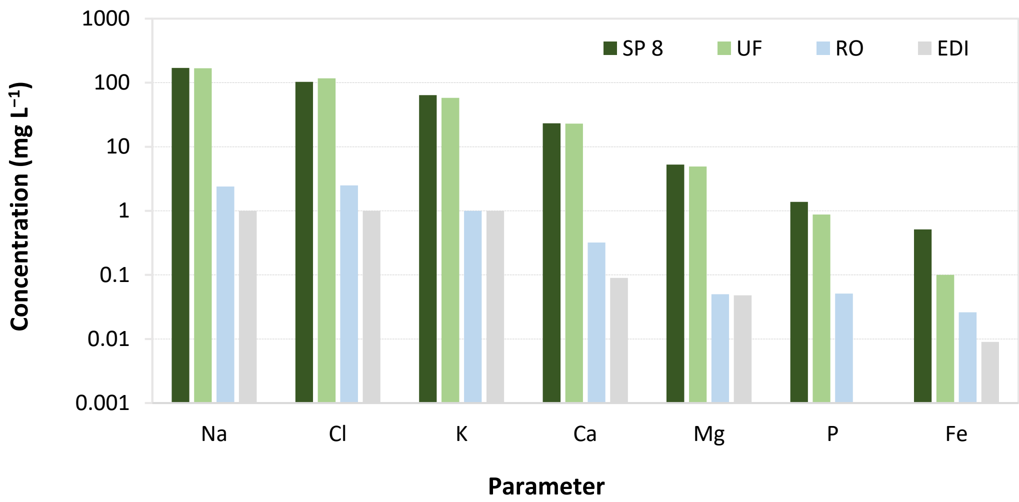

Figure 6. Concentration values (in logarithmic scale) of the major ions monitored throughout this study after each treatment stage: stabilization pond 8 (SP8), ultrafiltration (UF), reverse osmosis (RO), and electrodeionization (EDI).

The iron from the tertiary effluent (0.51 mg L^{-1}) was removed by 80% in the UF stage, which is in agreement with the study by Chaturvedi and Dave [33], who also reported the effective use of ultrafiltration for removing this contaminant. In turn, the remaining iron was removed by RO and EDI. Indeed, the iron concentration after RO treatment was 0.026 mg L^{-1}, above the standard required for demineralized water (<0.01 mg L^{-1}, Table 3). After being processed by EDI, it was reduced to 0.009 mg L^{-1}, equivalent to 61% of the concentration found in the RO permeate. Conversely, the magnesium concentration in the RO permeate was already within the recommended values for demineralized water (0.25 mg L^{-1}).

The tertiary effluent also presented, ca., 170, 103, and 64 mg L^{-1} for sodium, chloride, and potassium, respectively, with a significant decrease achieved after RO treatment. The demineralized water produced in the pilot unit presented concentrations of 0.14, 0.05, and <1 mg L^{-1} for potassium, sodium, and chloride, respectively. These ions should also be monitored as they have a major influence on the electrical conductivity of water. A 98% sodium removal was achieved after EDI. Analogous results were obtained by Wenten et al. [14] when producing demineralized water by EDI for steam generation, where the sodium concentration reached about 0.003 mg L^{-1}. In another study [11] for producing demineralized water from secondary wastewater, using ion exchange resins in a separated and mixed-bed configuration, removals of chloride, sodium, potassium, magnesium, and calcium of 98, 99, 65, 100, and 89% were achieved, respectively. However, EDI has advantages over the ion exchange process, as it does not require chemicals to regenerate the resins, being a continuous and environmentally cleaner process.

In the same field of water reuse, the East River Generating Station in Manhattan uses an RO/EDI system with a production capacity of 1500 m^3 h^{-1} of demineralized water for the make-up water in steam generators of the largest urban heating system in the world [34,35]. Other researchers have also investigated reclaimed water as an alternative source to produce ultrapure water. They considered a viable solution for the more sustainable use of water resources, but emphasized that the main challenge in this practice is related to the higher content of low-molecular-weight organic pollutants in reclaimed water, which is difficult to remove through traditional ultrapure water production processes [36].

3.3. Technical and Economic Feasibility Analysis of the UF/RO/EDI Hybrid Treatment System

The UF/RO/EDI hybrid system was analyzed considering the installation of a plant with the capacity to produce 90 m^3 h^{-1} of demineralized water for reuse in high-pressure boilers at the Southern Brazil Petrochemical Complex. The data collected in the technical feasibility study were used to calculate CapEx, OpEx, and the total cost per cubic meter of demineralized-reuse water produced (see Table 4).

Table 4. Economic analysis and comparison of the cost of producing demineralized water by UF/RO/EDI from petrochemical tertiary wastewater with a study producing demineralized water from drinking water by RO/EDI.

Parameter	Value	
	UF/RO/EDI (This Study)	**RO/EDI (Wenten et al. [14])**
CapEx in USD		
Equipment and materials		
Pre-treatment	93,617.02	
UF	672,340.43	
RO	704,255.32	
EDI	308,510.64	
Taxes and other fees (20% on equipment value)	355,744.68	
Construction	115,114.21	
Total CapEx	**2,249,582.30**	
OpEx in USD		
Feed water cost	-----	106,275.84
Energy consumption	89,262.54	97,240.07
Membranes' replacement	91,323.83	170,048.00
Maintenance	56,239.56	11,473.12
Labor		
Plant operation (3 technicians)	80,074.47	-----
Chemicals		
For Pre-treatment	10,026.49	
For UF	32,122.20	
For RO	41,582.04	4724.00
For EDI	24,546.80	-----
Other consumables	4427.23	
Total OPEX	**429,605.16**	**389,761.03**
Production capacity (m^3 $year^{-1}$)	788,400	950,000
Specific water production cost (USD m^{-3})	**0.54**	**0.42**
Depreciation of DWPP (USD m^{-3}) [a]	0.10	0.11
Total specific water production cost (USD m^{-3})	**0.64**	**0.53**

Note(s): [a] A depreciation time of 30 years was considered for the present study and 10 years for Wenten et al. [14].

CapEx corresponds to the DWPP's installation cost, which includes the values of equipment and materials, taxes and fees (ca., 20% over the equipment values), and other construction costs. OpEX represents the annual operating costs, including energy consumption, membranes' replacement, maintenance, labor (three technicians for plant operation), chemical products, and other consumables. Then, the specific cost was obtained from the ratio between the total OpEx and the plant's production capacity (788,400 m^3 $year^{-1}$ demineralized water). Adding the annual depreciation cost of the plant to this value, the total specific cost for producing one cubic meter of demineralized water was determined: USD 0.64 per cubic meter. Depreciation, in turn, corresponds to the total CapEx divided by the plant's operating period (30 years) and its annual production capacity. The CapEx and OpEx values were estimated based on a basic/preliminary engineering technical study, which could result in a variation of up to 15% in the values reported in Table 4.

Comparing the costs for producing demineralized water in this study with those obtained by Wenten et al. [14]—which was carried out in Indonesia using drinking water as feed with the cost of electricity being less than half that practiced in Brazil—slightly higher values were observed. This is intrinsically related to the characteristics of the feed water, since the feed water of our UF/RO/EDI system contains microorganisms (mainly algae, see ref. [15]), in addition to organic matter, requiring greater control and a higher dosage of chemicals to mitigate membrane fouling, which leads to higher chemical and operating costs. Furthermore, the ultrafiltration additional to the RO/EDI process increases the system's operation and maintenance costs, CapEx, and electrical energy consumption. It is worth highlighting that energy continues as a preponderant factor in these systems [37], especially in Brazil, where electrical energy costs USD 0.08 per kWh, while in other countries such as Indonesia [14], it is only USD 0.038 per kWh. While the total energy consumption in the DWPP was estimated at 0.938 kWh m^{-3}, the EDI system was responsible for only 0.328 kWh m^{-3}, a value similar to those found in other studies. For instance, by using an EDI system to treat feed water with 50 μS cm^{-1}, for obtaining demineralized water with 0.1 μS cm^{-1}, Wood and Gifford [38] reported a consumption of approximately 0.3 kWh m^{-3}.

The values we found (USD 0.64 per cubic meter) also comply with those reported by Pérez et al. [39], who investigated a UF/RO system treating a secondary sanitary effluent to produce water to feed low- and medium-pressure boilers. Considering a plant treating 2.5 m^3 h^{-1}, specific costs of EUR 1.096 per cubic meter were obtained, but this value would be reduced to EUR 0.57 per cubic meter for a plant treating 20 m^3 h^{-1}. Katsoyiannis et al. [11] reported a cost in the range of 1.5 to 2.5 EUR per cubic meter of water produced. The slightly higher costs are associated with the fact that, in addition to a conventional system with coagulation/flocculation/sedimentation/filtration followed by UF/RO/ion exchange resins, the authors also used evaporators and crystallizers to treat the waste generated in UF, RO, and ion exchange resins, aiming at the concept of Zero Liquid Discharge (ZLD).

Indeed, it is worth noting that, although the costs of producing demineralized-reuse water from wastewater are higher than those of producing DW from fresh water, this practice has a direct influence on the wastewater treatment plant, reducing environmental impacts by decreasing the wastewater volume currently disposed on soil, and costs related to monitoring and maintenance in effluent sprinkler areas and networks. Furthermore, the reuse of wastewater reduces the intake of raw water from the environment, leaving this valuable resource available for other noble uses, such as drinking water, for example. These actions are particularly aligned with the sustainable development goals (SDG) of the 2030 Agenda [40] since reusing wastewater provides more sustainable water management (SDG 6), promotes sustained economic growth (SDG 8) and sustained industrialization (SDG 9), and ensures sustainable production patterns (SDG 12) and contributes to combating climate change (SDG 13). Moreover, our particular case study would also contribute to the sustainable use of terrestrial ecosystems, as it would avoid or at least minimize the disposal of effluents in the soil, whose action is related to SDG 15, resulting in soil protection and combating desertification, in addition to contributing for advancing the protection of terrestrial biodiversity.

The investment displayed above refers to the solution that allows the use of the EDI product as demineralized water in boilers for steam generation. When considering typical resources allocated to sanitation projects, the wastewater treatment plant for producing demineralized water stands out for presenting a moderate investment value. This is associated with the adoption of modular systems and highly energy-efficient equipment, as well as the reduced area required for their installation, compared to conventional treatment systems. An outstanding characteristic of this type of plant is the demand for low-complexity civil construction, which contributes significantly to saving resources. Furthermore, the plant installation can be completed in a relatively short period, comprising 3 to 6 months. These characteristics make the DWPP an attractive and viable option for companies seeking to implement effective, energy-efficient, and quickly implemented sanitation solutions, while ensuring sustainable management of water resources. Furthermore, considering the project's particularities, the UF/RO/EDI plant for treating tertiary petrochemical wastewater presents a certain equilibrium between the components of the total cost of producing demineralized water.

As depicted in Figure 7, the main cost components of producing demineralized water are chemical products, energy consumption, and the replacement of membranes, representing 21%, 18%, and 18%, respectively. As mentioned previously, the presence of algae in tertiary effluent raises the costs of chemical products used in cleaning procedures. Though the costs of electrical energy and membrane replacement are representative, they comply with the literature data. Valizadeh et al. [21] attributed 18.7% of the total cost for an MF/RO plant, with a capacity of 80 $m^3\ h^{-1}$, to membranes' replacement. Nevertheless, as we use conservative values for the useful life of the membranes, the cost for membranes' replacement may be overestimated. With an adequate plant operation, these values may be reduced by 17–50%, since a study [41] reported 6 years as the mean lifespan of 8″ membrane modules. But there are also studies reporting full-scale plants running well with membranes that have been in use for eight [42,43] and even more than ten [44] years. In addition, expanding the plant capacity has the potential to decrease the specific cost associated with producing reused water. This is because the relationship between the costs associated with wastewater treatment plants and their capacity is typically expressed through exponential equations [45,46]. Valizadeh et al. [21] performed the economic assessment of MF/RO integrated systems for treating oily wastewater for reuse application. By increasing the plant's capacity from 40 to 80 $m^3\ h^{-1}$, the total production cost slowed down from 0.82 to 0.61 USD m^{-3}, and for a 2000 $m^3\ h^{-1}$ plant, the total cost would be just, ca., 0.40 USD m^{-3}.

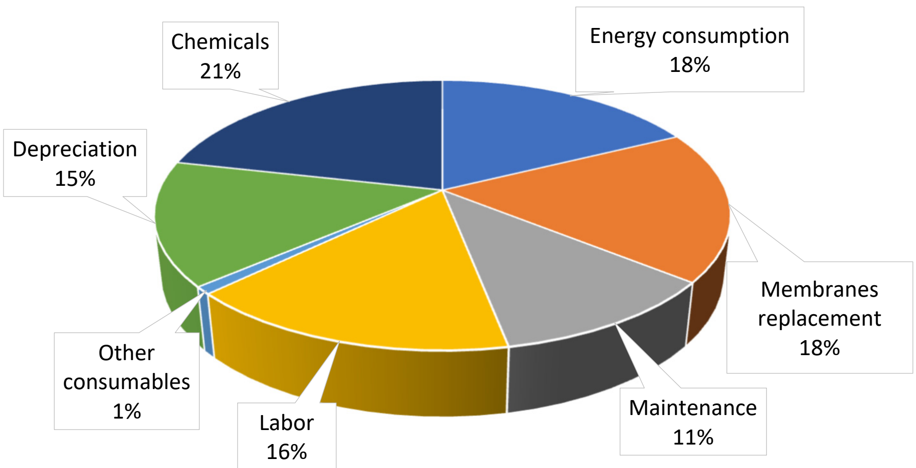

Figure 7. Percentages of the total annual cost of a UF/RO/EDI plant for tertiary petrochemical wastewater treatment with a capacity of 90 $m^3\ h^{-1}$.

4. Conclusions

The UF/RO/EDI hybrid system stood out as a promising alternative for treating tertiary petrochemical effluents to produce demineralized water. Thus, demineralized water produced from tertiary wastewater can be used as the make-up water in high-pressure boilers for steam generation in the petrochemical industry.

The economic analysis of the plant designed in this study showed a slightly higher cost estimate than those found in studies that produce demineralized water from fresh water, which is associated with the characteristics of the feed water, since tertiary petrochemical wastewater has a greater load of contaminants than fresh water.

The sensitivity analysis showed that the most critical aspect regarding the economic viability of these systems is the cost of equipment and materials. Conversely, additional advantages of hybrid wastewater treatment systems for industrial reuse include greater water security and the diversification of water sources, in addition to promoting sustainability, which is in line with the global demands for environmental conservation and protection.

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