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Research Paper

Integrated Membrane Processes (EDR-RO) for Water Reuse in the Petrochemical Industry

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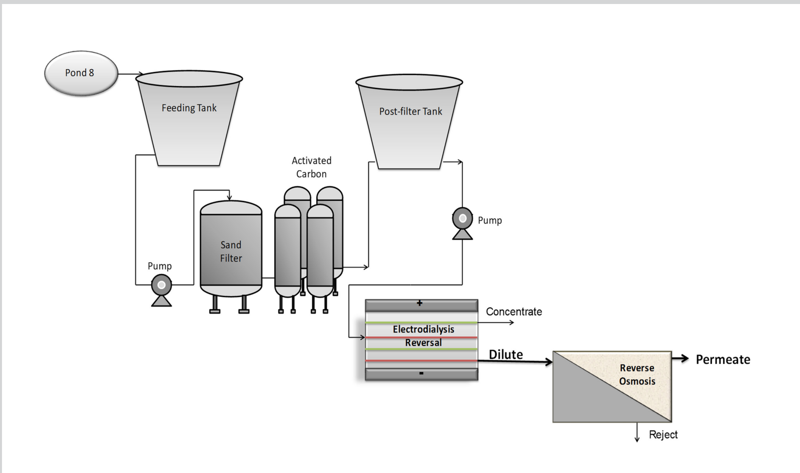
Highlights

- EDR-RO hybrid process treating petrochemical wastewater
- EDR-RO hybrid process produced high quality industrial process water
- Integrated membrane processes allowed water recovery in the industry
- Water reuse in a petrochemical industry

Graphical abstract



Abstract

The objective of this work was to apply a hybrid process, including electrodialysis reversal (EDR) and reverse osmosis (RO) to the treatment of petrochemical wastewater in order to obtain process water for reuse. A water balance was carried out to define the main water consumers and the process step that could receive the produced water. Additionally, toxicity assays were performed to evaluate the removal of toxic compounds after EDR and RO processes. Different operation parameters in the EDR and RO processes were investigated to enhance the membrane performance. The EDR assays were performed in a pilot plant, with 300 ion-selective membranes and an area of 0.096 m^2 for each membrane. The process conditions were: electrical potential of 150 V and 250 V, dilute flow rate at 600 $L.h^{-1}$ and 1,000 $L.h^{-1}$, concentrate flow rate maintained at 200 $L.h^{-1}$, with 25% recirculation and operation in series and parallel modes. The RO assays were conducted in pilot equipment, with a polyamide spiral membrane module with a membrane area of 7.2 m^2. Assays were performed at 8 bar, varying the reject flow in each experiment as follows: 150, 300, 450 and 600 $L.h^{-1}$. The EDR-RO hybrid system presented a removal rate above 90% for most physicochemical parameters from the wastewater, generating a process water without toxicity.

1. Introduction

Currently, the degradation of water quality and associated scarcity is a serious concern to the industrial sector, particularly the petrochemical sector since its production processes need high-quality water [1]. In this sense, the amount of water extracted from the environment needs to be reduced, and one solution is reusing wastewater. However, it is necessary to produce quality water from the waste that achieves the intended purposes.

According to Padaki et al. [2], the petrochemical industry consumes a huge volume of water. On average, six barrels of water are consumed for each barrel of oil produced [3]. It is used as process water, in boilers or cooling towers, as fire contention water, and so on. Among these stages, the cooling

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system is the highest water consumer [4, 5].

The petrochemical industry evaluated in the present study uses around 2,333 $m^3.h^{-1}$ of water. In addition to this large water consumption, there is a high volume of wastewater generation, nearly 700 $m^3.h^{-1}$ [6]. The wastewater has high conductivity, sulfates, chlorides, iron, calcium, hardness, chemical oxygen demand (COD), suspended solids and other pollutants. Thus, in order to produce adequate wastewater into the discharge standards, the conventional treatment is usually adopted. Nevertheless, it has been reported that conventional treatment is insufficient at removing the high salt content, thus impeding the water reuse in the production process [7]. In this sense, membrane separation processes, such as electrodialysis reversal (EDR) and reverse osmosis (RO) may be an option for water recovery. The EDR process will be used to remove the ions present in the wastewater by transport of the ions through ion-exchange membranes by means of electric current as the driving force [8]. Conversely, by using a semipermeable membrane and with the transmembrane pressure acting as the driving force, the RO will retain the contaminants from the wastewater [9].

Research about integrated processes to produce process water have been found in the literature. Koo et al. [10], aiming to produce demineralized water for boilers, applied ultrafiltration followed by reverse osmosis to the wastewater treatment from the palm oil industry. In the same way, Petrinic et al. [11] employed ultrafiltration and reverse osmosis to metal finishing wastewater treatment and reuse. Other researchers [1] studied the technical feasibility of a membrane bioreactor treating petrochemical wastewater. The treatment was very efficient, allowing the water to be reused in the production process. Furthermore, EDR was applied as a treatment process to wastewater generated in an oil refinery, intending for the water to be reused in cooling towers. This technology was able to remove dissolved solids and chlorides by around 70% [12]. Although there are studies related to the use of membrane processes for water reuse in water-intensive industries, the subject is still a matter of research and the investigation presented in this paper addresses membrane technology associated with a real water balance in the petrochemical industry.

In the light of these considerations, this research aims to investigate the EDR-RO hybrid process in the treatment of a petrochemical wastewater, in order to get process water that achieves the quality requirements for its reuse in cooling towers.

2. Materials and methods

2.1. Water balance

The first step of this work consisted of a study of the total water flow rate used in the petrochemical process. A survey of all existing flowmeters was carried out through a process data management software (Aspen Process Explorer version 8.4, 2013).

Once the existing flowmeters were identified, data were compiled using the same software. With this survey, the averages for consumption flow rates, water production and wastewater generation were obtained to identify the major water consumers that could reuse the water produced in this work on a pilot scale.

2.2. Wastewater characterization

The wastewater used for the present work was collected from the petrochemical industry. The three steps of the conventional wastewater treatment plant (CWWTP) are physicochemical (primary), activated sludge in the extended aeration (secondary) and eight stabilization ponds in series (tertiary). The wastewater was collected at the end of the CWWTP, i.e. at the exit of the last pond. Figure 1 shows the CWWTP as well as the collection point of the wastewater used in this work, the output of the 8th pond.

2.3. EDR – RO hybrid system

The EDR-RO hybrid process, including the pre-treatment used to treat the petrochemical wastewater is displayed in Figure 2.

In order to avoid damages to EDR and RO equipment, a sand filter and an activated carbon column were applied as a pre-treatment, as previously described elsewhere [13, 14].

2.3.1. Tests performed in the EDR

The EDR experiments were carried out in a pilot plant manufactured by Hidrodex, Brazil. This equipment had two stacks, each one having two electrodes made of titanium coated with platinum, 75 anion-exchange membranes (Hidrodex® HDX 200) and 75 cation-exchange membranes (Hidrodex® HDX 100) alternately separated by polypropylene spacers, corresponding to 14.4 m² of membrane area per stack. Every 15 min, the electrode polarities are reversed and the concentrate and dilute channels are cleaned. This procedure was adopted in order to reduce the interruptions for maintenance, since it controls the incidence of scaling and fouling on membranes.

The EDR system can be hydraulically operated in three different configurations: single stack, two serial stacks or two parallel stacks. In order to evaluate the removal rates of the ionic species present in the wastewater, as well as the efficiency of the EDR process, the current experiments were conducted taking the two last options into account (in series and in parallel formations). As displayed in Table 1, four experiments were conducted in triplicate, changing only the flow rate and the applied potential. At the same time, the concentrate was set to 25% of recirculation at a constant flow rate of 200 $L.h^{-1}$.

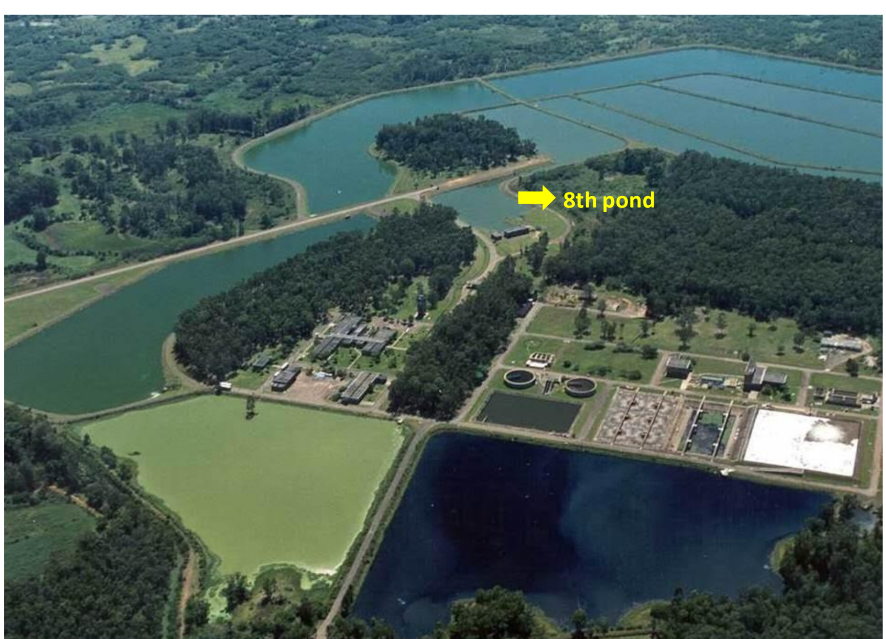


Fig. 1. Aerial view of the wastewater treatment plant showing the collection point.

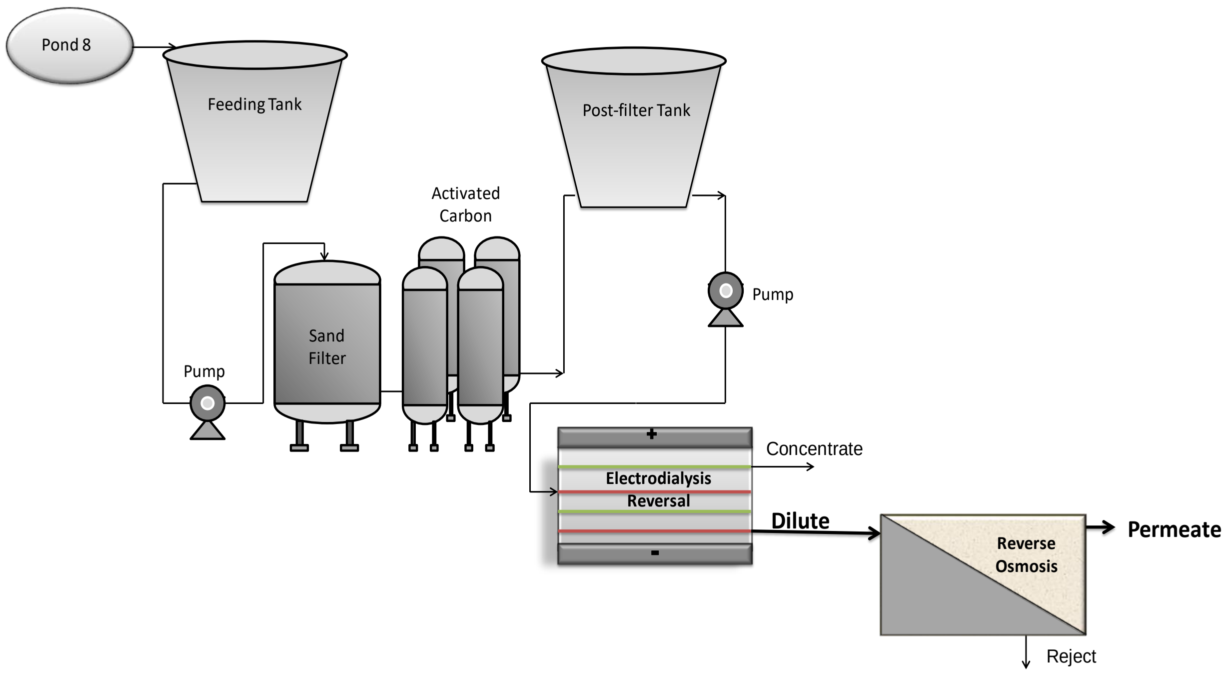


Fig. 2. Conceptual framework of the EDR-RO hybrid system treating the petrochemical wastewater [14].

Table 1
EDR tests performed with different configurations.

Experiment	Mode	Electric Potential (V)	Dilute flow ($L.h^{-1}$)	Concentrate flow ($L.h^{-1}$)	Concentrate recirculation (%)
1	In series	150	600	200	25
2	In parallel	150	1,000	200	25
3	In series	250	600	200	25
4	In parallel	250	1,000	200	25

The dilute conductivity was monitored in each cycle. Later, with the system stabilized, samples of the dilute and feeding water were collected for physicochemical analysis.

2.3.2. Tests performed in the RO

A RO pilot plant, manufactured by PAM Membranas Seletivas, with 250 $L.h^{-1}$ of treatment capacity, was used to treat the EDR dilute. This equipment had a single spiral polyamide membrane module, model BW 30-4040 (Filmtec, Dow Chemical), with 7.2 m^2 of membrane area. Based on a previous work [15] where the RO performance was evaluated in terms of the operation pressure, the assays were performed at 8 bar. The osmotic pressure of the feed solution was ~ 0.79 bar, which was calculated trough the Van't Hoff equation [16].

The reject flow was varied in each experiment to be 150, 300, 450 or 600 $L.h^{-1}$. The experiments were carried out over a period of 3 hours, and every 15 minutes conductivity and pH of the reject and permeate samples were measured. At the end of the experiments, samples were collected for physicochemical analysis.

2.4. Toxicity assay

Acute toxicity of a single contaminant and of a complex mixture can be verified through germination and root elongation evaluation [17, 18]. These assays have been proposed by government agencies as part of the evaluation of the potential for contamination of waste and wastewater disposed into the environment and to show the interaction effects from all constituents of the wastewater on the test organisms [19]. Lettuce is an important agricultural crop and is fairly sensitive to toxic chemicals [20].

Acute phytotoxicity tests were carried out with the sample from conventional treatment (feed) before and after the EDR-RO treatment (permeate) using lettuce (*Lactuca sativa*) seeds as test organisms, evaluating seed germination and root growth. The seeds were exposed at a sample concentration of 12.5%, 50% and 100%. The tests were based on the OECD test nº 208- Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test [21]. Each test was compared to a control group with deionized water. The statistical analysis was performed using ANOVA, followed by the Tukey multiple comparison test. All analyses were carried out using the Statistical Package for the Social Sciences (SPSS) 15.0 for Windows, considering a significance level of $p < 0.05$.

3. Results and discussion

3.1. Water balance

The average water consumed by the assessed industry is 2,333 $m^3.h^{-1}$, with a total annual consumption of 20,437,080 cubic meters, which corresponds to 4.5 cubic meters of water consumed per ton of petrochemical products. This specific water consumption is low in comparison to other chemical industries. Alkaya and Demirer [22] identified a specific water consumption of 7.31 $m^3.t^{-1}$ in the polyethylene terephthalate industry in Turkey. Schultz [3] identified a consumption of 6 $m^3.t^{-1}$ of processed petroleum in oil refineries. In addition, in 2015, the Brazilian Chemical Industry Association released data referring to an average consumption of water by the chemical industry of 4.75 $m^3.t^{-1}$.

The water used in this petrochemical industry is captured from the Caí River and treated at a water treatment plant for the industry. Classification is done according to the treatment level: clarified (flocculation and sedimentation), demineralized (flocculation, sedimentation, filtration, and reverse osmosis/ion exchange resin), filtered (flocculation, sedimentation and sand filter) and potable (flocculation, sedimentation, sand filter, and chlorination). Regarding the most consumed types, clarified water accounts for 55.5% of the industry's water consumption, which is the largest consumption of the unit. The consumption of demineralized water follows in second place, representing 40% of the total. Filtered water corresponds to 3%, and potable water is 1.5% of the total.

The clarified water is mainly used for replacement of the cooling water system (87%). This is due to the large volume of water that is evaporated or purged to maintain the cooling water quality standards. Cooling towers are known as major water consumers. According to da Silva and Goodman [23], the biggest cooling towers may recirculate from 45,360 to 113,400 $m^3.h^{-1}$ of water and evaporate approximately from 1,404 to 3,420 $m^3.h^{-1}$ of water.

The filtered water is used as service and replacement water for the unit's bearing water system. Potable water is used in its totality for sanitary and potable purposes. Regarding the use of demineralized water, 99% is used to produce steam, and only 1% is used for diluting chemicals in the process.

Based on the results of the water balance, it was observed that the largest volume of water consumed in the industry is for replacement of water losses in the cooling water system. Thus, the treatment processes evaluated in the present study have the objective of treating wastewater in order to reuse it for the makeup of the cooling towers from this industry. The average amount of wastewater treated by the CWWTP is 706 $m^3.h^{-1}$.

3.2. EDR test results

Table 2 shows the wastewater characteristics when treated at the CWWTP and post-filtration, along with the efficiency obtained after EDR treatments for its four different configurations (Exp. 1-4). A comparison between the water control parameters for cooling tower utilization (that were established according to the petrochemical industry activity) and the chemical characteristics of water produced by EDR in each experiment are presented. These tests allowed evaluation of the best performance of the EDR pilot unit, including the limitations of each experiment, as well as their stability and efficiency.

The filtration step (sand and activated carbon filters) was used for the removal of coarser material, thus reducing the occurrence of fouling and scaling on membranes and minimizing equipment damage [24]. As shown in Table 2, the pre-treatment (filtration step) was efficient for this purpose, removing 33% of the total suspended solids, 27% colour and 14% turbidity.

Regarding the EDR treatment results, different effects were obtained for the experiments in the serial and parallel modes, as demonstrated in Table 2. For experiments 1 and 3, where the conditions operated with the stacks in series, the highest electric potential for experiment 3 showed significant reductions for most parameters, likely because a higher potential promotes an increase in the ion migration rate [25]. As expected, this behaviour was also observed with stacks arranged in parallel for experiments 2 and 4. Experiment 4 presented removal rates around 25% higher than the ones achieved in experiment 2 for most parameters. Therefore, based on the analytical results and on the conductivity behaviour, it was possible to conclude that the increase of contact time of the fluid with the membranes favoured ion removal.

The higher removal efficiencies for experiments 1 and 3 (in series) compared to the ones in parallel (Exp. 2 and 4) can be explained by the longer residence time of the wastewater inside the system. When the stacks are arranged in series, the dilute from the 1st stack is used as feed solution to the 2nd stack. However, it is worth remembering that the experiments carried out in series produced a lower water recovery rate, inasmuch as this configuration achieved only 75% recovery (with a flow rate of 600 $L.h^{-1}$), whereas in parallel 83% was recovered (due to a higher flow rate of 1,000 $L.h^{-1}$).

Figure 3 compares the removal efficiency obtained by the EDR system under different configurations to the main parameters under evaluation. Efficiencies were calculated based on the post-filter wastewater values (feed solution on the EDR system).

According to the efficiencies shown in Figure 3(a), the experiments carried out in series (experiments 1 and 3) achieved very similar efficiencies, with electric potentials of 150 V and 250 V. It should be noted that EDR demonstrated good performance for ion removal, with a removal higher than 90% for all parameters under research. Referring to anions, the Cl^- was the one that presented the greatest efficiency in relation to the others. In their respective studies, Goodman et al. [26] and Valero et al. [25] applied ED and EDR to treat wastewater, and they also observed that chloride had a higher mobility when compared to sulfate, considering that ion removal efficiency by an EDR treatment can be influenced by ionic radius and charge.

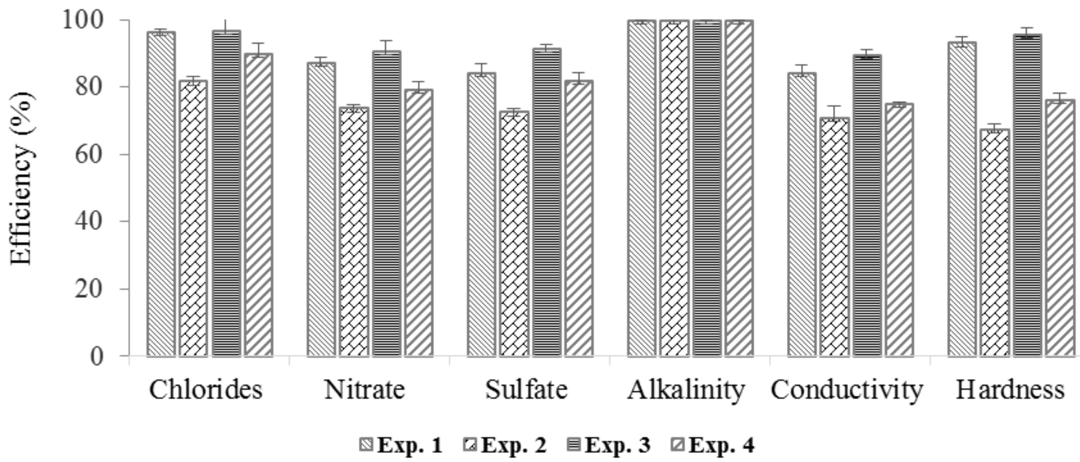
On the other hand, the efficiencies for experiments in parallel (experiments 2 and 4) were lower than for the serial system tests. The parameters of conductivity, sulfate, nitrate and chloride showed efficiency above 70%, and when a 250 V potential was applied, the removals were higher. At the end, only alkalinity presented removal efficiency above 98% for all of the experiments.

The removal efficiencies obtained in the present research (in series with 300 membranes, flow rate of 600 $L.h^{-1}$ and electric potential of 250 V) were higher than those reached by de Barros Machado and Santiago [12]. They also applied a pilot EDR unit with two stacks, composed of 360 membranes, with a diluted flow rate of 1,100 $L.h^{-1}$ and an electric potential of 275 V, to treat the wastewater from Gabriel Passos Refinery, located in the State of Minas Gerais, Brazil. There, the removal efficiencies were 76% for chlorides, 68% for TDS, 87% for conductivity, 83% for alkalinity and 85% for sulfate, with 82% of treated water recovery.

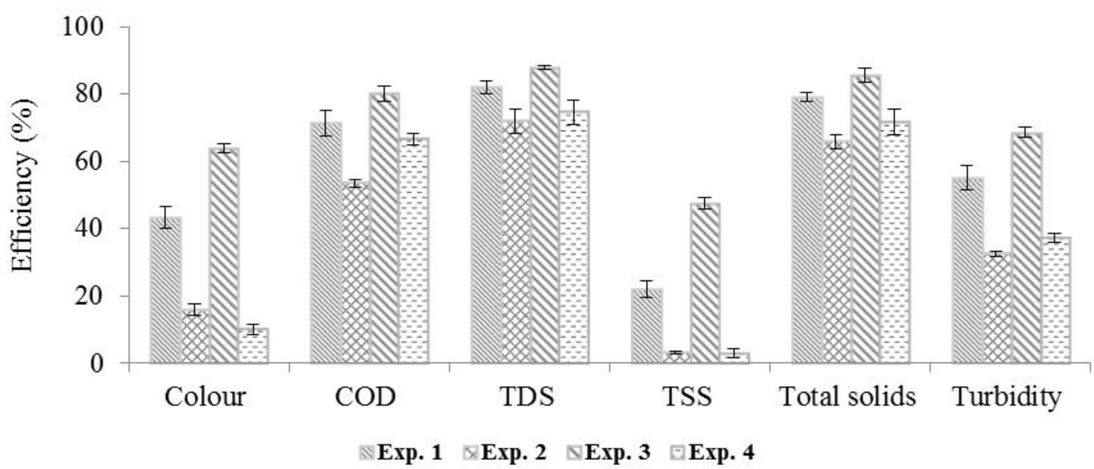
Table 2
Wastewater physicochemical characterization after CWWTP and filtration, efficiency of the water produced by the EDR system at different configurations and the limits for water reuse in cooling towers.

Parameter	After CWWTP	Post-filter	EDR treatment				Limit for Cooling towers *
			Experiment 1 (150 V – Series)	Experiment 2 (150 V– Parallel)	Experiment 3 (250 V – Series)	Experiment 4 (250 V – Parallel)	
Chlorides ($mg.L^{-1}$)	108.7 ± 4.86	100.9 ± 6.35	3.76 ± 0.72	18.58 ±1.53	3.32 ±3.84	10.18 ±3.18	22.00
Nitrate ($mg.L^{-1}$)	0.56 ± 0.08	0.53 ± 0.03	0.07 ± 1.78	0.14 ±1.15	0.05 ±3.30	0.11 ±2.36	-
Sulfate ($mg.L^{-1}$)	430.7 ± 8.63	395.0 ± 6.95	62.14 ± 2.73	108.8 ±1.14	**34.19 ±1.34**	71.72 ±2.26	22.00
Alkalinity ($mg.L^{-1}$)	127.6 ± 5.66	125.7 ± 4.16	0.67 ± 0.28	2.60 ±0.33	0.50 ±0.28	0.50 ±0.18	26.00
Conductivity ($\mu S.cm^{-1}$)	1,575 ± 6.83	1,495 ± 5.60	237.9 ± 2.68	436.1 ±3.47	156.6 ±1.68	374.0 ±0.51	165.0
Hardness ($mg.L^{-1}$)	130.6 ± 4.20	129.9 ± 4.98	9.57 ± 1.78	42.50 ±1.72	5.95 ±2.53	31.23 ±2.37	30.00
Colour ($mg.L^{-1}$ Pt-Co)	110.9 ± 4.92	**80.57 ± 4.73**	43.30 ± 3.11	67.66 ±1.77	29.00 ±1.36	84.66 ±1.36	-
COD ($mg.L^{-1}$)	38.48 ± 3.05	37.67 ± 2.39	10.90 ± 3.89	17.54 ±1.15	**7.48 ±2.18**	12.60 ±1.54	3.50
pH	7.57 ± 0.10	7.47 ± 0.11	3.59 ± 0.18	3.78 ±0.36	**3.61 ±0.32**	3.37 ±0.92	7.0 – 8.00
TDS ($mg.L^{-1}$)	1,157 ± 19.10	1,147 ± 11.1	209.6 ± 1.86	322.6 ±3.66	141.0 ±0.60	292.6 ±3.75	-
TSS ($mg.L^{-1}$)	36.17 ± 1.29	**23.94 ± 2.89**	18.60 ±2.36	23.73 ±0.40	**12.60 ±1.67**	23.23 ±1.38	2.00
Total solids ($mg.L^{-1}$)	1,165 ± 6.83	1,152 ± 7.50	242.3 ±1.36	395.3 ±2.01	166.7 ±2.19	328.0 ±3.80	-
Turbidity (NTU)	34.63 ± 1.55	**29.57 ± 2.48**	13.17 ± 3.61	19.96 ±0.90	**9.30 ±1.44**	18.56 ±1.27	1.00
Calcium ($mg.L^{-1}$)	36.55 ± 6.24	35.48 ± 4.29	7.08 ± 2.25	13.99 ±2.69	6.50 ±1.63	14.34 ±2.69	30.00
Iron ($mg.L^{-1}$)	0.93 ± 0.33	0.64 ± 0.07	0.40 ±1.12	0.79 ±1.36	**0.34 ±1.41**	0.83 ±2.25	0.10
Magnesium ($mg.L^{-1}$)	7.30 ± 0.76	7.28 ± 1.36	1.27 ±1.29	4.18 ±1.42	**1.03 ±2.39**	4.30 ±1.89	0.50
Sodium ($mg.L^{-1}$)	338.0 ± 5.75	333.9 ± 6.30	16.25 ±1.30	64.63 ±2.54	11.60 ±2.92	42.86 ±1.80	-

*Restrictions established by industry for wastewater appropriate reuse in that industrial structure.



(a)



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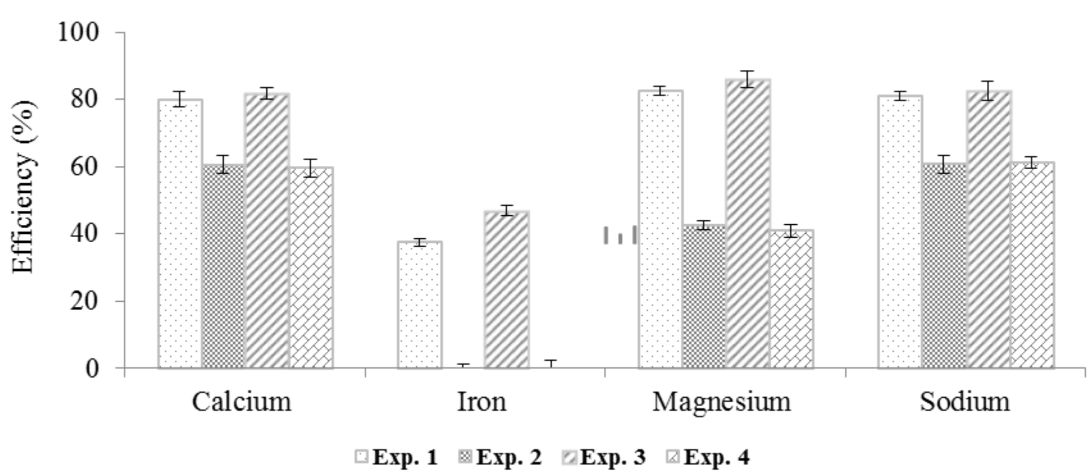

(c)

Fig. 3. Removal efficiency of the main physicochemical parameters after EDR treatment in different configurations. Operating conditions displayed in Table 1.

In Figure 3(b), one can observe that removal efficiency was superior for serial system experiments (experiments 1 and 3). The parameters that reached the greatest efficiencies were total solids and total dissolved solids, both higher than 85%. Colour, COD, suspended solids and turbidity presented lower efficiencies as expected, since the EDR process does not remove non-charged compounds, such as organic and nonpolar ones.

Regarding the cations removal, in the serial stack experiments (experiments 1 and 3) it can be observed in Figure 3(c) that their concentrations showed a very significant reduction. In this context, for each cation, different removal rates were obtained. Considering the ionic radii (IR) and the ion charges of Mg^{2+} (IR = 0.71 Å), Ca^{2+} (IR = 0.99 Å) and Na^{+} (IR = 1.13 Å), it is clear that Mg^{2+} has the smallest ionic radius that allows more mobility, as well as the greatest charge that enables a wide action on the electric field, therefore providing a higher migration [12, 25, 27].

On the other hand, iron was the one with the lowest efficiency. Previous studies reported some difficulty in transporting Fe ions at a pH higher than 0.4 because there may be crystalline complexes that prevent the transport of iron through membranes [28].

As observed in Table 2, the results for experiment 3 (carried out in series with a 250 V potential) present values closer to the standards set by the industry. Some parameters, such as turbidity, pH, magnesium, sulfate, iron, COD, and suspended solids, overstepped the tolerated recommended values.

Thus, by analysing the experimental results as well as the options for wastewater reuse, it was decided to perform the EDR-OR hybrid test with the best operating conditions determined in the EDR experiments: in series, 250 V, and 600 $L.h^{-1}$ dilute flow rate.

3.3. Water recovery as RO permeate

Figure 4 shows the results of the water recovered (RO permeate) in different reject flows that were assessed.

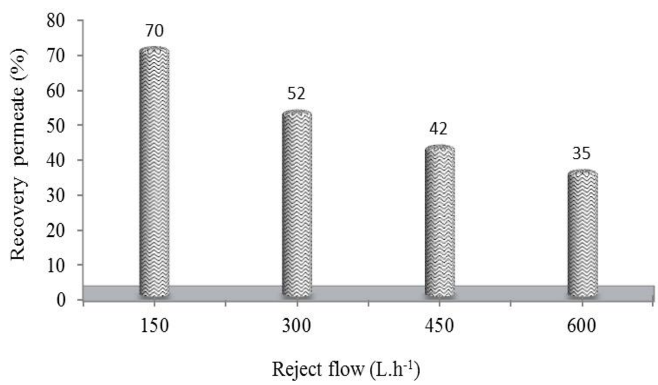

Fig. 4. Water recovery percentage as a function of the RO reject flow (150, 300, 450, and 600 $L.h^{-1}$). Operating conditions included a constant pressure of 8 bar during 3 h for each reject flow.

As can be seen in Figure 4, the reject flow is directly related to the recovery of water obtained in the permeate, i.e. the lower the reject flow, the greater the water recovery. However, lower reject flow rates tend to increase the concentration of solutes near the membrane surface, increasing the possibility of concentration polarization, fouling, scaling and biofouling to occur, which in turn reduce the lifespan of the membrane. This factor is conditioned by the increase in the frequency of cleanings [10]. Furthermore, Bhattacharya et al. [29] observed that by keeping the recovery of the permeate within the appropriate range, its performance will be ensured, and the formation of scales due to precipitations on its surface will be minimized.

Another important aspect to be considered is the decrease of the permeate flux, which becomes higher with the increase in the solute concentration in the membrane/feed solution interface, reducing the driving force for the separation. In this case, a drop in the permeate flux was observed, from 45 $L.h^{-1}.m^{-2}$ to 40 $L.h^{-1}.m^{-2}$ working at 150 $L.h^{-1}$ of the reject flow rate. In contrast, no decrease in the flux was observed for 300, 450, and 600 $L.h^{-1}$ reject flow rates during the period of 3 hours.

3.4. Analytical monitoring of the RO permeate in different reject flows

Figure 5 shows the monitoring of the analytical results of the RO permeate, as a function of the reject flow variation, considering that assays were performed at the following flows: 150, 300, 450 and 600 $L.h^{-1}$.

Based on the results shown in Figure 5, the quality of the obtained permeate at the lowest reject flow (150 $L.h^{-1}$) is better. Déon et al. [30] reported in their studies that by reducing the tangential velocity at the membrane surface, the phenomena of concentration polarization might be increased as, in those cases, a concentration profile is formed in the membrane/feed solution interface. Thus, the lower the flow velocity, the more evident the increase in the solute concentration near the membrane surface. This gives rise to concentration polarization, which in turn can act as a more selective barrier, increasing the rejection to solutes. Mulder [31] states that the polarized layer causes a reduction in the permeate flow. This phenomenon can be minimized by increasing the flow velocity of the fluid.

3.5. EDR – RO hybrid system

The results of the hybrid system EDR-RO are presented in Table 3, where one can observe the removal rate higher than 98% for most of the parameters. Furthermore, these values were compared to the established limits for water reuse in cooling systems.

The efficiency in removing suspended solids and reducing turbidity was of 95.82% and 99.66%, respectively, being these parameters related to the presence of clay, silt, colloids, silica, and inorganic and organic matter [32].

The removal rates of iron and magnesium were 98.44% and 93.82%, respectively. Furthermore, these parameters reached the strict limits set by the petrochemical industry for water reuse in cooling towers, achieving concentration values as low as 0.01 $mg.L^{-1}$ and 0.45 $mg.L^{-1}$ for iron and magnesium, respectively (see Table 3). According to Malakootian et al. [33] and Panigrahi et al. [34], iron, magnesium and calcium have to be judiciously controlled, because when these ions are in excess, scale build-up can occur into the pipes, damaging the system.

Considering hardness and alkalinity, the removal rates were 99.62% and 100%, respectively. According to Suárez et al. [35], these specific parameters must be very well controlled, since they can lead to an incrustation increase in the system. The obtained results meet the quality specifications for reuse in cooling towers.

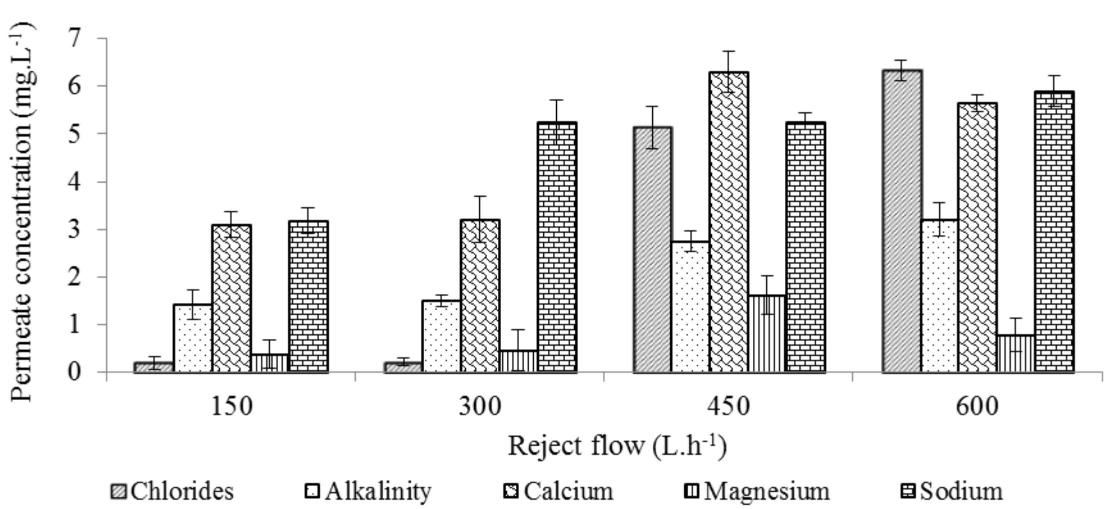

Fig. 5. Monitoring of the quality of the RO permeate in different reject flows: 150, 300, 450, and 600 $L.h^{-1}$. Operating conditions: constant pressure of 8 bar during 3 h for each reject flow.

Table 3
Physicochemical characterization and efficiency of EDR/RO system. The EDR operating conditions were: two stacks in series, electric potential of 250 V, concentrate and dilute flow rates of 200 and 600 L.h^{-1}, respectively. The RO operating conditions were: 8 bar, reject and permeate flow rates of 300 and 348 L.h^{-1}, respectively.

Parameter	EDR Dilute (RO feed)	RO permeate	RO Efficiency (%)	EDR-RO Efficiency (%)	Limit for Cooling towers*
Turbidity (NTU)	9.30 ±0.52	0.10 ± 0.05	98.92	99.66	1.00
pH	3.61 ±0.24	**5.55 ±0.09**	-	-	7.0 - 8.0
Conductivity (µS.cm^{-1})	156.6 ±1.74	6.08 ±0.50	96.12	99.59	165.0
Hardness (mg.L^{-1})	5.95 ±0.92	<0.5	91.60	99.62	30.00
Colour (mg.L^{-1} Pt-Co)	29.00 ± 1.36	0	100	100	-
Calcium (mg.L^{-1})	6.50 ±0.95	3.20 ±0.09	51.00	90.98	30.00
Magnesium (mg.L^{-1})	1.03 ±1.02	0.45 ±0.01	56.31	93.82	0.50
Chlorides (mg.L^{-1})	3.32 ±0.76	0.21 ±0.04	93.67	99.79	22.00
Alkalinity (mg.L^{-1})	0.50 ±0.18	0	100	100	26.00
Sulfate (mg.L^{-1})	34.19 ±2.30	<0.07	100	100	22.00
Iron (mg.L^{-1})	0.34 ±0.12	0.01 ±0.00	97.06	98.44	0.10
COD (mg.L^{-1})	7.48 ±1.19	<0.5	93.32	98.67	3.50
TSS (mg.L^{-1})	12.60 ±1.08	<1.0	92.06	95.82	2.00

(<) limit of detection
*Limit for the cooling towers set by the assessed industry

The COD, an indirect parameter to quantify the organic matter, was reduced by 98.67%. This parameter needs to be controlled because the presence of organic matter can promote the proliferation of micro-organisms, forming biofilms that can restrict the flow into the pipes as well as increase the system corrosion rate [14, 34].

In regards to the conductivity and sulfate parameters, the removal rates were 99.59% and 100%, respectively, reaching the limits established by the industry. As displayed in Table 3, the pH values are below the threshold. Hence, prior to reusing the treated wastewater, a pH adjustment is necessary. High pH values can increase the scaling formation, while a pH lower than the recommended one may cause corrosion in the pipelines [10].

In summary, the results presented here comply with the standard established by the petrochemical industry for water reuse in cooling systems and demonstrate the technical feasibility of the EDR-RO hybrid process. In fact, prior to reuse, the treated wastewater needs a pH adjustment. These findings are consistent with the ones presented by other researchers [36], who have reported that the integration of EDR with RO produces high-quality water. It is important to point out that there is a dearth of literature on EDR-OR hybrid processes, and the results displayed here highlight that the integration of membrane processes is a prominent solution for water reuse.

3.6. Phytotoxicity

The water produced by EDR-RO should be used in the cooling towers of the petrochemical industry. Since cooling tower operation involves purge systems, toxicity tests were carried out to evaluate potential risks associated with the discharge of this water in the environment.

Plants absorb essential nutrients in the form of soluble salts, but excessive accumulation strongly suppresses the plant growth [37]. Studies have found that lettuce seeds are very sensitive to the presence of metals and organic compounds, which makes them suitable for testing the toxicity of wastewaters [38, 39]. Although there is no evidence of acute toxicity in the wastewater treated by the conventional system, considering the current form of disposal of this treated wastewater in the petrochemical complex by sprinkling on vegetation and landfarming processes, the cumulative effect caused by this practice can present a potential risk to the environment. In fact, previous studies conducted by Da Silva Júnior [40] with the landfarming soil collected from this petrochemical industrial complex area demonstrated a toxic effect at the highest exposure concentration in lettuce seeds and other two species of terrestrial isopods (*Armadillidium vulgare* and *Porcellio dilatatus*).

The results of seed germination in *Lactuca sativa* are shown in Figure 6. The exposure of *L. sativa* seeds to the samples before (feed) and after the EDR-RO (permeate) treatment did not cause a significant reduction in the germination rate when compared to the control group. Indeed, root growth is known to be more sensitive than germination in lettuce toxicity tests. This is supported by Bagur-González et al. [41] and Chapman et al. [42], who found that lettuce root elongation is a more sensitive end-point than emergence or shoot length.

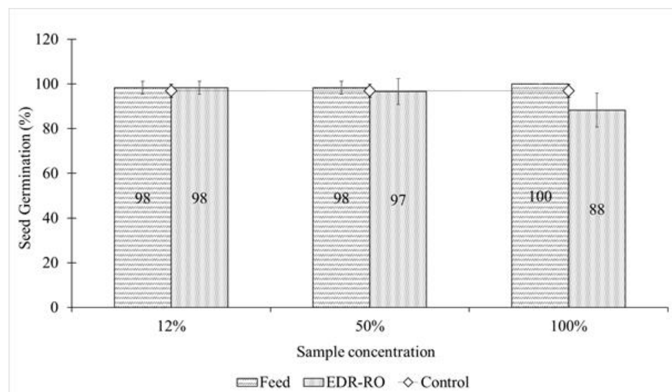

Fig. 6. Percentage of seed germination at different exposure concentrations to the samples Feed and EDR-RO and germination of the control group (dotted line).

The assessment of lettuce root elongation showed no toxicity in the samples (Figure 7), both before and after the EDR-RO treatment. In contrast, the exposure of the seeds to the feed sample at a concentration of 100%, which used the conventional wastewater treatment, shows an increase in the root elongation ($p<0.01$) in comparison to the control group. The availability of plant nutrients is essential for plant growth [43, 44]. In this case, the presence of macro and micronutrients in the wastewater may have influenced the root growth. According to Henze et al. [45], wastewater can be a source of other macro and micronutrients such as Ca, Mg, B, Mg, Fe, Mn or Zn.

The results of the toxicity tests before (feed) and after EDR-RO (permeate) treatment showed no toxicity, and thus the discharge of the purge of the cooling towers will not harm the environment.

4. Conclusions

The high efficiency in the removal of the evaluated parameters shows that the EDR-RO hybrid process is a promising solution for the production of process water, especially for the petrochemical industry. The integrated process achieved the industry requirements in a study for the reuse of wastewater from the petrochemical process in cooling systems, which according to the water balance, represents the highest consumption of water in the assessed unit. By EDR, 75% of water recovery was achieved, while 50% was recovered by RO, such that the hybrid process provided a total water recovery of 41%. Further studies will be performed in order to improve the water recovery.

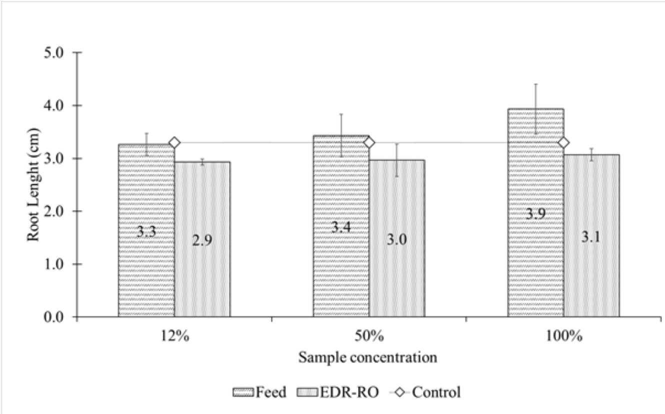

Fig. 7. Root length at different exposure concentrations to the samples before (Feed) and after (EDR-RO) hybrid process and root length of the control group (dotted line). Values marked with * show statistical differences (p<0.01) compared to the control group.

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