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Special Edition

Industrial reuse of petrochemical effluents: A case study of ultrafiltration and reverse osmosis

Reúso industrial de efluentes petroquímicos: Um estudo de caso da ultrafiltração e osmose reversa

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ABSTRACT

The petrochemical industry uses high volumes of water in its production processes and generates effluents that have a great potential for reuse in production processes. The reuse of these effluents is, therefore, an alternative for the sustainable development of the sector. This study aimed at evaluating the application of ultrafiltration (UF) and reverse osmosis (RO) in the treatment of petrochemical effluents for the production of industrial reuse water, reducing environmental impacts caused by the disposal of effluents in the soil. The experiments were carried out with effluents named waste stabilization pond 1 (WSP-1), waste stabilization pond 8 (WSP-8) and an inorganic effluent (INO), which was used as feedwater in the pilot unit with a treatment capacity of 1 $m^3.h^{-1}$. The parameters chosen for evaluation in the treated effluents were calcium, magnesium, chloride, sulfate, electrical conductivity (EC), total organic carbon, color, chemical oxygen demand (COD), pH, total suspended solids and turbidity. Membrane permeate fluxes were determined to evaluate the performance of the pilot system. After treatment and characterization of each effluent, the results were compared to define the most suitable effluent to achieve the quality required for industrial reuse. The results showed that the proposed UF/RO treatment provided a stable flux for the WSP-8 effluent. Conversely, the other streams showed an accentuated decrease in flux, which indicates fouling processes of the UF and RO membranes. As for the efficiency of the treatment, the process removed compounds of interest such as COD above 90%, salts and EC above 92% for the three assessed effluents. Thus, considering all aspects evaluated in this study, WSP-8 was the most suitable to be used as feed in the pilot system with UF and RO. The permeate produced presented the necessary quality for reuse in the industries of the Southern Petrochemical Complex, presenting equivalent characteristics to those of clarified water. Thus, the reuse of treated petrochemical effluents may be an important alternative source of water resources in face of availability and scarcity restrictions in industries in southern Brazil.

Keywords: Industrial reuse; Petrochemical effluent; Reverse osmosis

RESUMO

A indústria petroquímica utiliza elevados volumes de água em seus processos produtivos e geram efluentes que apresentam grande potencial para a reutilização nos processos produtivos. Neste cenário o reúso destes efluentes é uma alternativa para o desenvolvimento sustentável do setor. Portanto, este estudo teve como objetivo avaliar a aplicação da ultrafiltração (UF) e osmose reversa (OR) no tratamento dos efluentes petroquímicos para produção de água de reúso industrial reduzindo impactos ambientais com a disposição de efluentes no solo. Os experimentos foram realizados com os efluentes da Lagoa 1 (LE-1), efluente da Lagoa 8 (LE-8) e efluente inorgânico (INO), os quais foram utilizados como água de alimentação na unidade piloto com capacidade de tratamento de 1 $m^3.h^{-1}$. Os parâmetros avaliados nos efluentes tratados foram o cálcio, magnésio, cloreto, sulfato, condutividade, carbono orgânico total, cor, demanda química de oxigênio, pH, sólidos suspensos totais e turbidez. Foram determinados os fluxos dos permeados das membranas para avaliar o desempenho do sistema piloto. Após tratamento e caracterização de cada efluente, os resultados foram comparados para a definição do efluente mais adequado para alcançar a qualidade requerida para reúso industrial. Os resultados mostraram que o tratamento UF/OR proposto forneceu um fluxo estável para o efluente da LE-8, e para as demais correntes houve queda acentuada de fluxo que indicam processos de incrustação das membranas de UF e OR. Quanto à eficiência do tratamento, o processo apresentou a remoção de compostos de interesse como a demanda química de oxigênio (DQO) acima de 90%, remoção de sais e condutividade elétrica (CE) acima de 92% para os efluentes da Lagoa 1, efluente da Lagoa 8 e efluente inorgânico. Assim, considerando todos os aspectos avaliados neste estudo, o efluente LE-8 foi o mais adequado para ser utilizado como alimentação no sistema piloto com UF e OR, de tal modo, que o permeado produzido apresentou a qualidade necessária para reúso nas indústrias do Polo Petroquímico do Sul, atingindo qualidade equivalente à água clarificada. Desta forma, o reúso de efluentes petroquímicos tratados poderá ser uma importante fonte alternativa de recursos hídricos frente às restrições de disponibilidade e escassez nas indústrias no Sul do Brasil.

Palavras-chave: Reúso industrial; Efluente petroquímico; Osmose reversa

1 INTRODUCTION

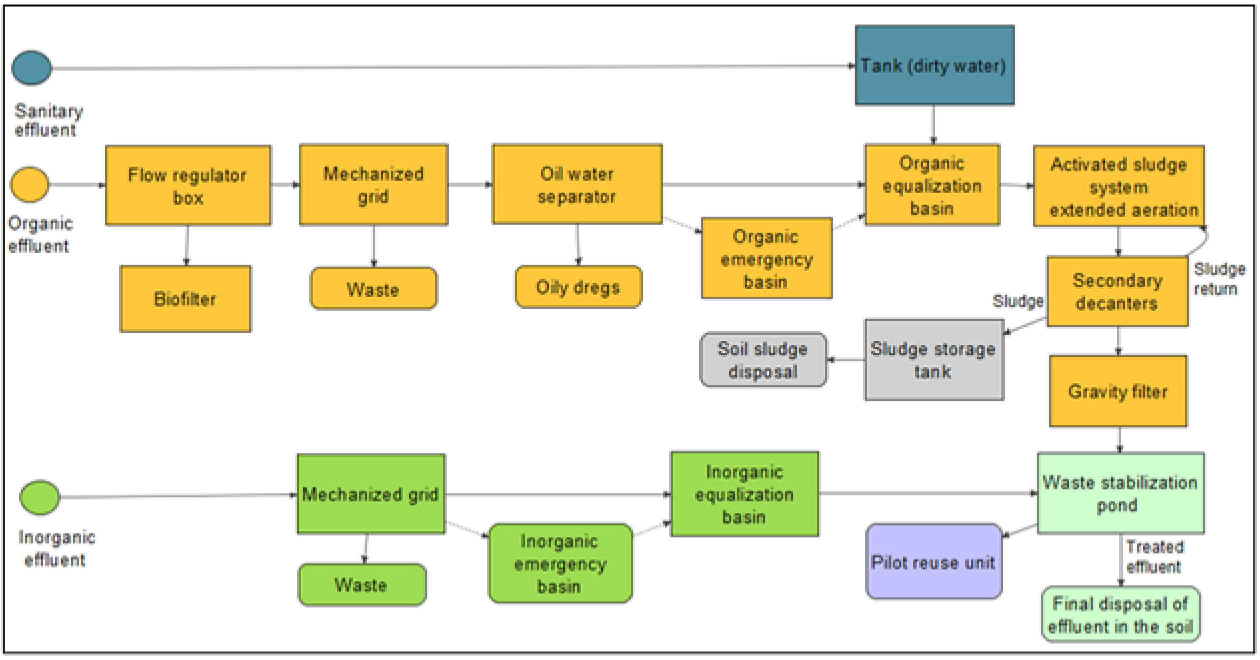
In Brazil, the industry uses 9.1% of water resources (ANA, 2018). The segment of oil derivatives and biofuels corresponds to 11% of the Brazilian industrial production (CNI, 2017). In 2016, the absolute consumption of water in one of the largest petrochemical industries in the country was approximately 66 million $m^3.year^{-1}$, with the specific consumption of water for the production of petroleum products of 4 $m^3.t^{-1}$ and generation of liquid effluents of 1.11 $m^3.t^{-1}$ (LIMA, 2018), demonstrating significant water consumption and effluent generation. In this segment, processes such as distillation, liquid-liquid extraction, washing operations and refrigeration systems are some examples that intensively use water in these industries (HANSEN, 2019). Thus, the effluents generated may contain different chemical compositions, depending on the oil refinery processes and the type of crude oil used (IEA, 2017).

The Southern Petrochemical Complex uses naphtha, condensate, gas and ethanol as basic raw materials in its production chain (COFIP, 2021). After the cracking process, basic petrochemicals such as ethylene, propene, butadiene, solvents and gasoline are obtained (SPEIGHT, 2019). These chemicals can be sold to third parties or used in the polymerization process to obtain thermoplastic resins such as polypropylene, polyethylene and polyvinyl chloride, which, in turn, become inputs for manufacturing companies to produce plastic films, packaging, cups, bottles, rubbers, and other products for sale (EPE, 2018).

The industrial water treatment unit captures around 67,000 $m^3.d^{-1}$ of raw water from the Caí River Basin and produces clarified, demineralized and potable water to supply the Southern Petrochemical Complex. The clarified water is used to replenish the cooling water system, for heavy ash treatment systems resulting from the burning of carbon, in addition to being used as firefighting water (HANSEN, 2019).

The industries of the Complex generate approximately 18,000 $m^3.d^{-1}$ of liquid inorganic and organic effluents, segregated at the source according to their composition. These effluents are received at the petrochemical wastewater treatment plant (WWTP) where the raw inorganic effluent goes through preliminary and primary treatment (VENZKE *et al*., 2018a). The raw organic affluent, on the other hand, has a treatment system composed of a swirling system and Aeroferm® biofilter where the biological degradation of volatile organic compounds occurs (SAPOTEC, 2021). The process includes a preliminary, primary and secondary treatment by activated sludge with prolonged aeration (HANSEN, 2019; SANTOS, 2020). Subsequently, the effluents are unified in the tertiary treatment. This treatment consists of eight serial stabilization ponds, for subsequent release into the soil, in which the effects of evaporation, evapotranspiration and infiltration or percolation in the soil occur (HANSEN, 2019). Figure 1 presents a flowchart of the treatments.

Figure 1 – Flowchart of the Inorganic, Organic and Sanitary Effluent Treatment Systems at the of WWTP of the Liquid Effluent Treatment Superintendence (SITEL)



Source: Authors, 2020

The tertiary effluent from the Southern Petrochemical Complex was characterized and presented potential for industrial reuse (HANSEN, 2016; VENZKE *et al*., 2017; VENZKE *et al*., 2018b; HANSEN, 2019) with the application of treatment technologies such as reverse electrodialysis and reverse osmosis (VENZKE *et al*., 2018a). Aware of the opportunity, the petrochemical industry in question invested in the implementation of a pilot unit installed at the WWTP for the continuous treatment of effluents (BARRETO, 2020; GONÇALVES, 2020; SANTOS, 2020), in order to assess the quality of reuse water and the performance of membranes.

Information on the characterization of the treated effluent and the quality required for reuse is used to define the technologies to be tested. Due to the requirements of the water used in the Southern Petrochemical Complex such as the level of electrical conductivity of clarified water (165 $\mu S.cm^{-1}$) and chemical oxygen demand (3.5 $mg.L^{-1}$) reverse osmosis was selected as the most adequate method to achieve the quality required for reuse (SANTOS, 2020).

Membrane separation processes have the characteristic of enabling the treatment of effluents by providing sufficient quality to guarantee its reuse. Among these processes, reverse osmosis has been used due to its high performance in desalination and effectiveness to produce water suitable for reuse in the oil industry (TANG, 2014; JAFARINEJAD, 2019).

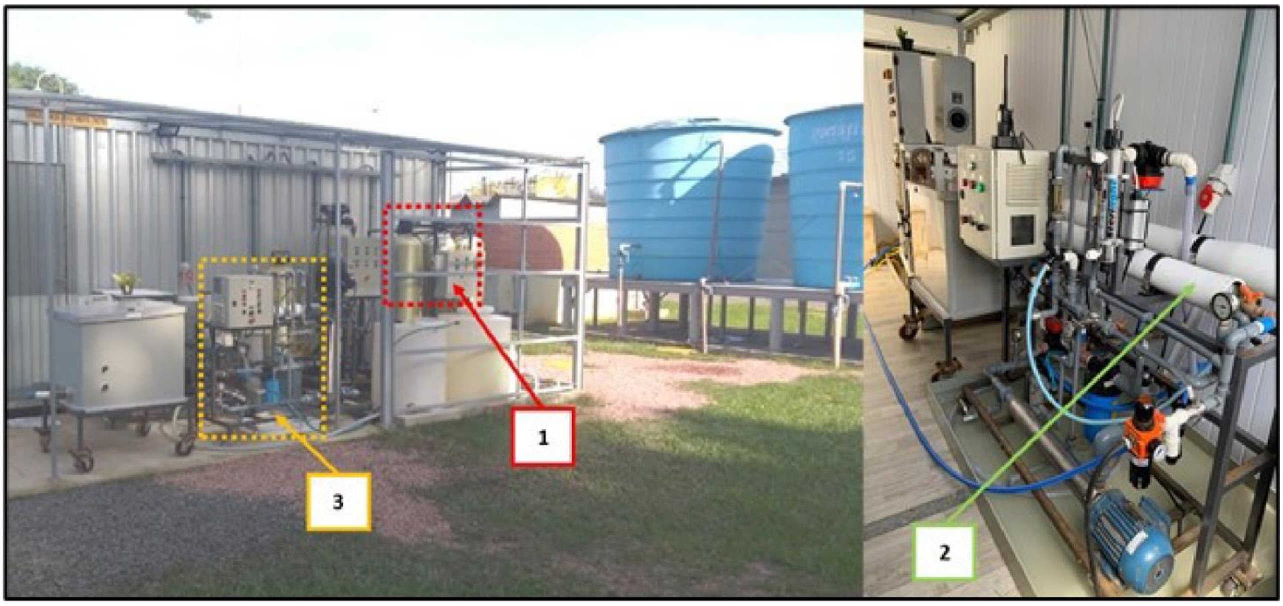
However, reverse osmosis needs control in the feedwater in order to minimize membrane fouling (VENZKE *et al*., 2018b). Feedwater turbidity must be monitored and controlled to maintain constant system performance (QASIM *et al*., 2019). Thus, processes such as microfiltration and ultrafiltration are used as RO pretreatments of feedwater in wastewater (YU, 2017). In this study, UF was used to remove colloidal matter and dissolved organic substances from the feedwater and protect RO membranes (QASIM *et al*., 2019) from fouling caused by inorganic and organic materials present in petrochemical effluents (ROMERO-DONDIZ *et al*., 2016; LUJAN-FACUNDO *et al*., 2017).

The objective of this study was to characterize three effluent streams and use them as feedwater in the pilot effluent treatment unit consisting of ultrafiltration followed by reverse osmosis and to evaluate the quality of the reuse water produced, comparing it with the threshold parameters set out by the industries of the Southern Petrochemical Complex.

2 MATERIAL AND METHODS

This study was carried out in the pilot unit installed in the WWTP of the Southern Petrochemical Complex, which has a continuous treatment capacity of 1 $m^3.h^{-1}$. In Figure 2, the overview of the reuse pilot unit is presented.

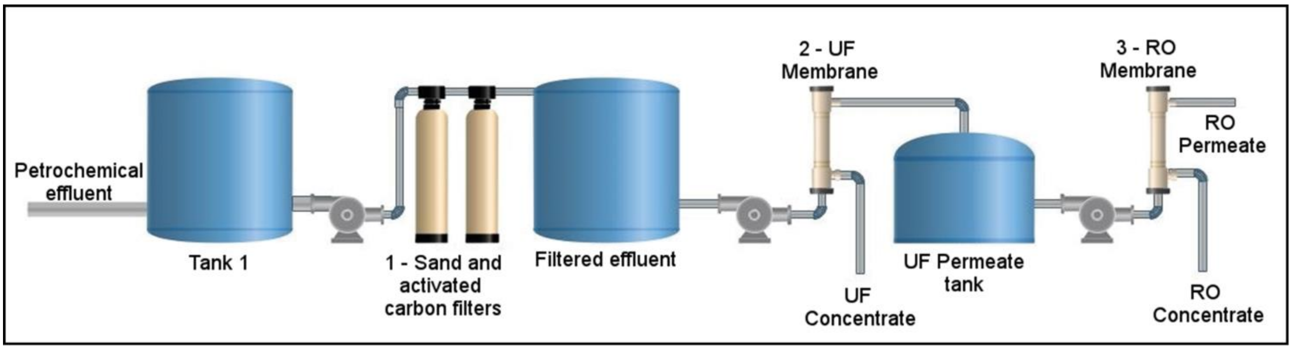
Figure 2 – Treatment equipment installed in the external and internal areas of the pilot reuse unit located in the operational area of the WWTP



Caption: 1 - Sand and activated carbon filter 2 - Ultrafiltration 3 - Reverse osmosis
Source: Authors, 2020

The treatment unit consists of 3 storage tanks with a storage capacity of 15 m³ each, sand and activated carbon filters, UF and RO. Figure 3 shows the pilot unit scheme.

Figure 3 – Scheme of treatment technologies used in the pilot unit for reuse of WWTP petrochemical effluent - 2020



Source: Authors, 2020

2.1 Treated petrochemical effluent streams

In this study, the effluents used as feedwater for the pilot unit were collected in different stages of treatment, as shown in Figure 4.

Figure 4 – Effluent collection sites tested at the WWTP: inorganic (INO), waste stabilization pond 1 (WSP-1) and waste stabilization pond 8 (WSP-8)

Source: Authors, 2020

The sites were defined according to the type of effluent, origin and treatment process. The information relating to these items is described in table 1.

Table 1 – Types of feedwater (influent) used in the pilot reuse unit during the period of testing – 2020

Type	Origin	Treatment
Inorganic effluent	Inorganic treated effluent	Preliminary and Primary
Waste stabilization pond 1	Unification of secondary effluent and treated inorganic effluent	Preliminary, Primary and Secondary by activated sludge
Waste stabilization pond 8	Tertiary effluent from the last WWTP stabilization pond	Preliminary, Primary, Secondary, and Tertiary

Source: The Authors, 2020

2.2 Ultrafiltration

The experiments with the UF system were carried out for 45 days, for 6 hours a day with each of the tested effluents. The pilot system operated with a pressure of 2.5 bar in the UF and temperatures in the range of 18 to 22°C, being composed of a 20 μm wound filter and two polyethersulfone UF membranes with a molecular weight cutoff of 10,000 Da, model PW4040F30. An automatic membrane cleaning system was installed, which injects 10 liters of drinking water into the system for 6 minutes at intervals of 30 minutes to prevent incrustations. The dosage of 1 $mg.L^{-1}$ of biocide Acticide DB 20 supplied by the company Thor Brasil LTDA was dosed in the influent and 3.2 $L.h^{-1}$ of 4% sodium hypochlorite after the sand filter. To evaluate the ultrafiltration performance, the cleaning frequency and the stability of the UF permeate flux were considered. When a 10% flux reduction was observed, chemical cleaning was performed to reestablish the UF permeate flux.

2.3 Reverse osmosis

The RO pilot system consists of an electrical panel, a high-pressure pump, flow meters, pressure gauges, a 5 μm cartridge filter, a heat exchanger, an hour meter and a BW30 polyamide membrane (4040). This system operated at a pressure of 4 bar for 45 days, for 4 hours a day, using the ultrafiltration permeate as feedwater, for each of the effluent streams tested. Daily cleaning for 20 minutes was performed during the experiments. For the performance of the RO pilot system, the cleaning frequency and stability of the RO permeate flux were considered. The quality of the reuse water produced was evaluated by comparing the permeate quality of the RO with the threshold parameters stipulated by the Southern Petrochemical Complex industries. In this study, the reuse water produced with the 3 effluent streams was compared with the threshold parameters for reuse as clarified water, as shown in Table 2.

Table 3 describes the data from the ultrafiltration and reverse osmosis membranes used in the experiments. To assess the tendency for particulate clogging of reverse osmosis membranes an empirical test known as the silt density index (SDI). The SDI indicates the amount of submicron particles present in the feedwater, while turbidity is a measure of water transparency (GOH, 2018).

Table 2 – Parameters of the clarified water required for use in production processes in the Southern Petrochemical Complex, RS - 2020

Parameter	**Clarified water**	**Parameter**	**Clarified water**
Calcium (mg.L^{-1})	30	Magnesium (mg.L^{-1})	0.5
Chloride (mg.L^{-1})	22	pH	7 - 8
Electrical Conductivity (μS.cm^{-1})	165	Total Suspended Solids (TSS)(mg.L^{-1})	2.0
Color (mg. Pt-Co. L^{-1})	<10	Sulfate (mg.L^{-1})	22
Chemical Oxygen Demand (mg.L^{-1})	3.5	Turbidity (NTU)	1
Iron (mg.L^{-1})	0.1		

Source: HANSEN, 2019; SANTOS 2020

Table 3 – Characteristics of ultrafiltration and reverse osmosis membranes used in the WWTP pilot unit during the 2020 testing period

Model	**PW4040F30 GE[a] UF**	**BW 30 (4040) FILMTEC[b] RO**
Membrane Material	Polyethersulfone	Polyamide
Settings	Spiral	Spiral
Membrane area (m^2)	7.3	7.2
Feed pH	4 - 11	2 - 11
Temperature (°C)	50	45
Pressure (bar)	5 - 9.5	15.5
Chlorine tolerance limit (mg.L^{-1})	5	< 0.1
Maximum SDI (15 minutes)		5
Salt rejection average (%)		99.5

Source: [a] GE Lenntech 2015; [b] FILMTEC™ 2018

2.4 Analytical Methods

The characterization of feed streams and permeates was performed according to the methodology described in the Standard Methods for Examination of Water and Wastewater 22 ed., listed in table 4.

Table 4 – List of parameters and respective analytical methods used in the characterization of feedwater and permeates – 2020

Parameter	**Metodology** [a]	**Parameter**	**Metodology** [a]
Calcium	SM 3111 D	pH	SM 4500 H+
Color	SM 2120 B	Total Dissolved Solids	SM 2540 C
Chemical Oxygen Demand	SM 5220 C	Total Organic Carbon (TOC)	SM 5310 B
Electrical Conductivity	SM 2510 B	Total Suspended Solids	SM 2540 D
Chloride	SM 4110 B	Sulfate	SM 4110 B
Iron	SM 3111 B	Turbidity	SM 2130 B
Magnesium	SM 3111 B		

Caption: [a] *Standard Methods for Examination of Water and Wastewater, 22nd edition*
Source: APHA, 2012

3 RESULTS AND DISCUSSION

3.1 Characterization of streams used in the reuse pilot system

During the operation of the WWTP, the concentration of pollutants in the petrochemical effluents presented variations inherent to the production processes, due to the season, climate and plant maintenance. These variations can affect the performance of the treatment processes and the quality of the effluents used as feedwater in the reuse pilot system. The variation of the physicochemical parameters of interest for reuse in the feed water of the 3 tested effluents are presented in table 5.

The color present in the tested effluents results from the decomposition of natural humic substances, the presence of conjugated organic compounds

(STEVENSON, 1982) and algae. Thus, WSP-8 presents significantly higher values resulting from the effluent retention time in the WWTP's tertiary system. Furthermore, it is noteworthy that the color present in the INO is associated with the proliferation of algae in the inorganic effluent treatment system during the experiment.

Table 5 – Characterization of treated effluent streams used as feedwater in the pilot unit – 2020

Parameter	**Unit**	**WSP-1**	**WSP-8**	**INO**	**QL**
Calcium	($mg.L^{-1}$)	25.2 ± 2.75	16.2 ± 0.79	49.6 ± 4.13	0.021
TOC	($mg.L^{-1}$)	17.1 ± 1.55	8.45 ± 0.21	24.8 ± 5.55	-
Chloride	($mg.L^{-1}$)	110 ± 25.3	43 ± 0.96	98 ± 37.46	1.297
EC	($\mu S.cm^{-1}$)	1065 ± 84.7	869 ± 35.0	1917 ± 210	1 - 5000
Color	($mg.\ Pt\text{-}Co.\ L^{-1}$)	14.8 ± 3.04	57.4 ± 9.97	40.1 ± 36.2	6.4
COD	($mg.L^{-1}$)	50.7 ± 13.1	35.2 ± 13.9	47.4 ± 4.55	45.07
Iron	($mg.L^{-1}$)	0.204 ± 0.05	0.37 ± 0.07	0.14 ± 0.02	0.02
Magnesium	($mg.L^{-1}$)	9.66 ± 1.48	5.21 ± 0.20	13.3 ± 1.97	0.003
pH	-	7.40 ± 0.30	7.63 ± 0.01	8.48 ± 0.49	1-14
TSS	($mg.\ L^{-1}$)	6.70 ± 5.23	2.55 ± 0.63	12.5 ± 6.53	2.1
Sulfate	($mg.L^{-1}$)	202 ± 19.9	220 ± 23.6	658 ± 46.8	1.139
Turbidity	(NTU)	5.15 ± 0.14	23.2 ± 6.10	11.0 ± 4.71	0.15

Caption: QL – Quantification Limit
Source: The Authors, 2020

The total organic carbon present in the 3 streams studied is highly dependent on the molar mass of the organic compounds. The rejection of these compounds in the UF system can be reduced if they present a molar mass lower than the molecular mass of the UF membrane, causing incrustations on the RO membrane (WANG, 2011). Thus, pre-treatment with sand and activated carbon filter before UF, dosage of Acticide DB 20 and 4% sodium hypochlorite (ANIS, 2019) were used as alternatives to increase the lifetime of UF elements and prevent incrustations in the RO. These dosages were previously defined during the operation of the pilot unit.

Higher concentrations of calcium, chloride, magnesium and sulfate were found in the INO effluent which, together with the basic pH of the effluent, caused inorganic incrustation in the ultrafiltration and reverse osmosis membranes, reducing the permeate fluxes. This effluent showed greater variability in the load of pollutants in relation to the other streams tested. These variations in feedwater contribute to the formation of fouling and biofouling in the UF and RO membranes, thus increasing the frequency of cleaning in the system to keep permeate fluxes constant.

The effluent from WSP-8, on the other hand, presented greater turbidity among the streams studied due to the presence of algae, colloidal and biological material in suspension in the tertiary system of the WWTP, being controlled by the dosage of Acticide DB 20 and sodium hypochlorite in the pilot unit.

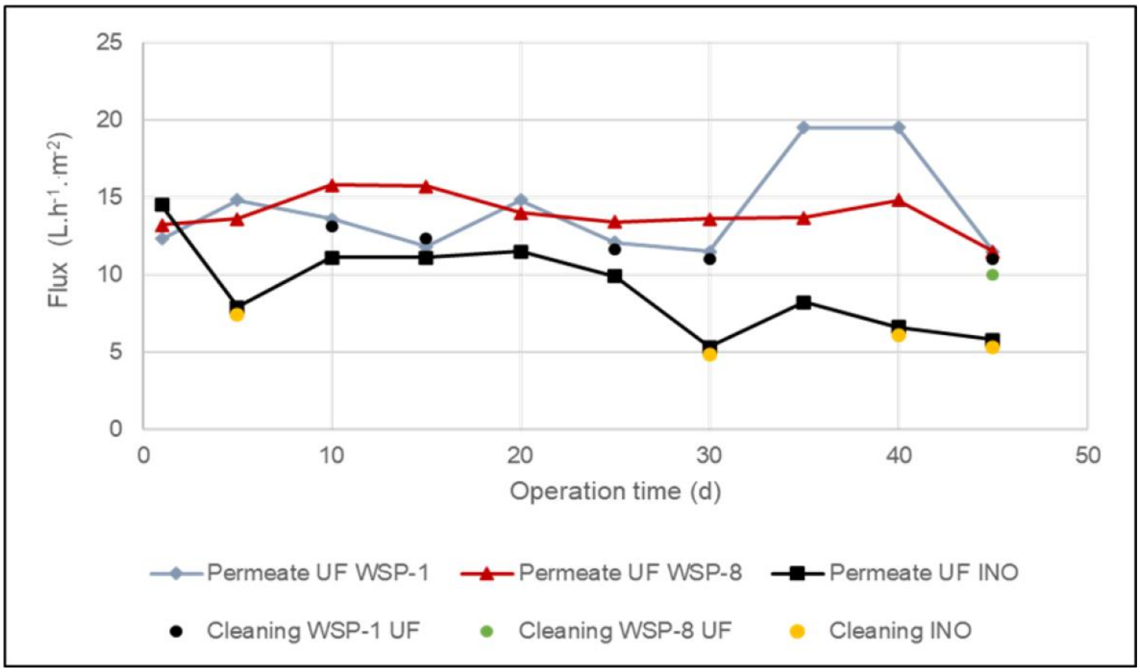
The characterization and results of color, TOC and turbidity in the 3 effluents were evaluated as potential fouling of the RO membrane. Thus, ultrafiltration was used as a pre-treatment to reduce these parameters in the RO feedwater.

3.2 Effects of effluent composition on ultrafiltration permeate fluxes

During the application of ultrafiltration, permeate flux is a critical factor with regard to treatment efficiency, operating stability and membrane fouling (LI, 2017; TIN *et al*., 2017). In order to define the most suitable stream as feedwater for the pilot unit, the three effluents were treated in the ultrafiltration system to evaluate the removal efficiency and membrane fouling. The cleaning frequency for each tested effluent was recorded and used as a membrane fouling indication, as shown in figure 5.

The UF operated with the WPS-1 effluent as feedwater and presented an average flux of 14.1 ± 3.2 $L.h^{-1}.m^{-2}$. During the testing period, chemical cleaning with 0.01 M sodium hydroxide, 0.01 M hydrochloric acid and 0.2% sodium hypochlorite was performed five times due to the decrease in flux. The effluent had a significant amount of biological material, so a daily cleaning of 20 minutes with 0.2% sodium hypochlorite was adopted for the operation of the UF.

Figure 5 – Ultrafiltration permeate flux with WPS-1, WPS-8 and INO effluents throughout the testing period



Source: Authors, 2020

As to the WPS-8 effluent as feedwater, the UF presented an average flux of 14.3 ± 1.79 $L.h^{-1}.m^{-2}$. Daily cleaning with 0.2% sodium hypochlorite was performed to keep the operating flux stable during the experiment. Only one chemical cleaning with 0.01 M sodium hydroxide, 0.01 M hydrochloric acid and 0.2% sodium hypochlorite was performed during the testing period.

During the ultrafiltration operation using INO effluent as feed water, an average flux of 9.1 ± 3.5 $L.h^{-1}.m^{-2}$ was verified. After 40 days of operation, it was necessary to replace the cartridge filter, which filled up due to the accumulation of biological material such as algae, larvae and formation of gelatinous material on the surface. During this period, the greatest reduction in UF flux was observed.

Chemical cleaning with 0.01 M sodium hydroxide, 0.01 M hydrochloric acid and 0.2% sodium hypochlorite was performed 4 times. However, the flux was not recovered. In addition to daily cleaning for 20 minutes with 0.2% sodium hypochlorite, a chemical cleaning with 0.1% sodium metabisulfite was necessary to reestablish the membrane flux.

The UF flux was, then, one of the criteria used to define the most adequate stream to feed the pilot system. Therefore, analyzing the results obtained in this study, it was found that the ultrafiltration fluxes for the WPS-1 and INO effluents were reduced by more than 10%. Consequently, frequent stops for chemical cleaning were required, which caused interruptions in the permeate production process to feed the RO system. This reduction may be associated with a higher concentration of total suspended solids and total organic carbon in the WPS-1 and INO effluents. Furthermore, these streams presented higher concentrations of calcium and magnesium than the effluents from WPS-8. Thus, for the WPS-8 effluent, only one chemical cleaning at the UF was performed during the testing period.

Considering the results of fluxes and cleaning frequency, the WPS-8 effluent proved to be the effluent with the least tendency to foul the UF membrane, after the dosage of Acticide DB 20 and 4% sodium hypochlorite.

3.2 Characterization of Ultrafiltration Permeates

The UF permeates with each of the effluents were analyzed to investigate the contributions of each process unit to the removal of pollutants. Table 6 describes the results of the UF.

After filtering the effluents, the UF process decreased turbidity and removed total suspended solids. The increase in chloride concentration and EC of ultrafiltration permeates occurred due to the dosage of sodium hypochlorite to reduce biofouling (JIANG, 2017) caused by biological material (organic matter, microorganisms and algae) in the effluent.

The removal percentages of TOC, TSS and turbidity were evaluated in regards to UF performance. The removal percentages were 19.3%, 68.6% and 96.4% for WPS-1, 40.8%, 17.6% and 98.1% for WPS-8 and 32.8 %, 83.2% and 98.4% for INO. The results indicate that the UF system showed removal of total suspended solids and turbidity for all streams tested. However, TOC concentrations in the UF permeate can cause flux drop in the RO system. According to Malaeb and Ayoub (2011), organic membrane fouling occurs due to high concentrations of TOC in wastewater, in the range of 10 to 20 $mg.L^{-1}$. Among the tested streams, only the permeate of the UF of WPS-8 presented total organic carbon equal to 5 $mg.L^{-1}$, below that range, which is an adequate value to feed the RO pilot system.

Table 6 – Characterization of UF permeates with INO, WPS-1 and WPS-8 effluents

Parameter	**Permeate UF WPS-1**	**Permeate UF WPS-8**	**Permeate UF INO**
Calcium ($mg.L^{-1}$)	20.9 ± 4.40	13.5 ± 1.17	38.8 ± 9.52
TOC ($mg.L^{-1}$)	13.8 ± 3.53	5.0 ± 1.13	16.7 ± 7.55
Chloride ($mg. L^{-1}$)	118 ± 35.3	71 ± 5.70	153 ± 53.2
Color (mg. Pt-Co. $L^{-1)}$	9.75 ± 4.73	<6.4	<6.4
COD ($mg.L^{-1}$)	21.5 ± 1.27	22.3 ± 1.34	22.7 ± 1.27
EC ($\mu S.cm^{-1}$)	1033 ± 122.7	878 ± 51.4	2081 ± 482
Iron ($mg.L^{-1}$)	0.159 ± 0.016	0.02 ± 0.01	0.06 ± 0.02
Magnesium ($mg.L^{-1}$)	9.49 ± 1.04	5.16 ± 0.07	10.8 ± 3.01
pH	7.01 ± 0.04	7.44 ± 0.27	8.00 ± 0.42
TSS ($mg.L^{-1}$)	<2.1	<2.1	<2.1
Sulfate ($mg. L^{-1}$)	186 ± 10.7	186 ± 21.1	648 ± 104
Turbidity (NTU)	0.18 ± 0.05	0.45 ± 0.46	0.18 ± 0.06

Source: Authors, 2020

3.4 Characterization of reverse osmosis permeates and comparison with standards for reuse

To evaluate the performance of the RO, the quality of permeates generated in the pilot reuse system was compared to the parameters established for clarified water in the studied industry. These parameters are relevant to ensure the reliability of industry production processes (HANSEN, 2019). The characterization of the RO permeates indicates that the compounds of interest were removed efficiently. Values are shown in table 7.

Table 7 – Characterization of permeates from the WPS-1 and WPS-8 and INO effluents after reverse osmosis and threshold standards for reuse as clarified water in the Southern Petrochemical Complex – 2020

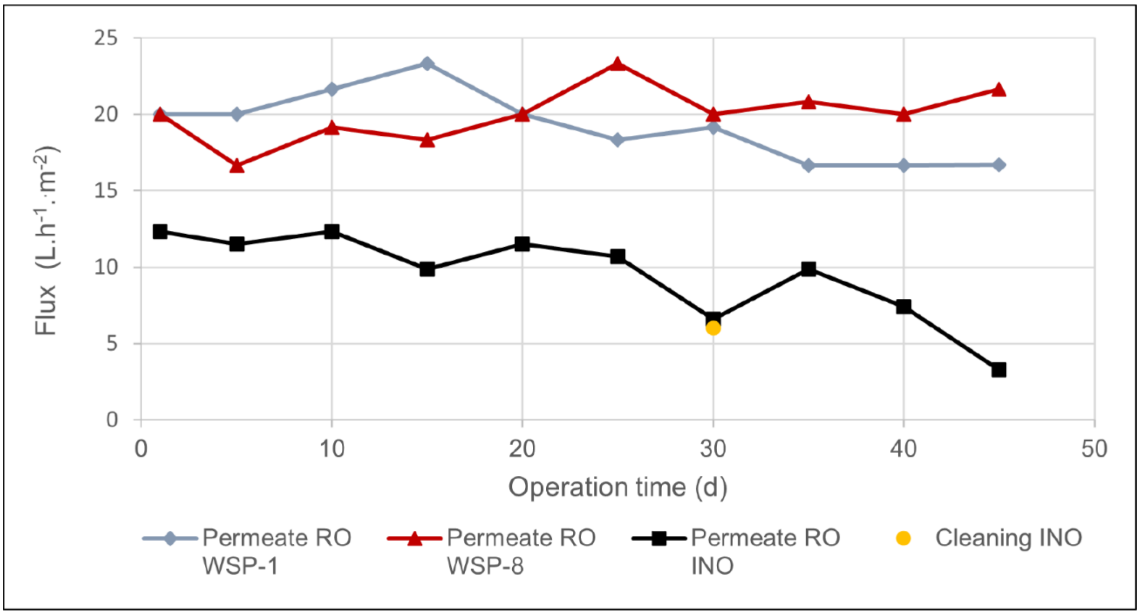
Parameter	**Permeate RO WPS-1**	**Permeate RO WPS-8**	**Permeate RO INO**	**Clarified Water Standard**
Calcium ($mg.L^{-1}$)	0.43 ± 0.32	0.10 ± 0.01	0.21 ± 0.12	30
Chloride ($mg.L^{-1}$)	3.77 ± 0.78	3.23 ± 0.16	4.25 ± 3.77	22
EC ($\mu S.cm^{-1}$)	44.0 ± 1.53	23.2 ± 1.51	40.5 ± 30.9	165
Color (mg. Pt-Co. L^{-1})	< 6.4	< 6.4	< 6.4	<10
TOC ($mg.L^{-1}$)	1.3 ± 0.85	2.0 ± 0.4	8.07 ± 6.96	-
COD ($mg.L^{-1}$)	< 2.85	< 2.85	3.76 ± 1.29	3.5
Iron ($mg.L^{-1}$)	0.024 ± 0.004	0.02 ± 0.003	0.030 ± 0.01	0.1
Magnesium ($mg.L^{-1}$)	0.06 ± 0.018	0.05 ± 0.001	0.06 ± 0.03	0.5
pH	6.25 ± 0.26	6.81 ± 0.17	8.21 ± 1.18	7.0 - 8.0
TSS ($mg.L^{-1}$)	< 2.1	< 2.1	< 2.1	2
Sulfate (mg. L^{-1})	<1.139	<1.139	1.18 ± 0.07	22
Turbidity (NTU)	<0.15	0.2 ± 0.06	0.11 ± 0.01	1

Source: Authors, 2020

The INO effluent presented COD above the established threshold for reuse, and all streams tested require pH adjustment to meet industry reuse standards, which can be easily adjusted with the distribution of reuse water together with the clarified water produced in the Petrochemical Complex. The assessment of the EC required for reuse (165 μS.cm^{-1}), showed that after treatment with the RO all permeates reached the established reuse standards. The concentrations of TOC (mg.L^{-1}) in the permeates were of 1.3 ± 0.85; 2.0 ± 0.4 and 8.07 ± 6.96, respectively for WPS-1, WPS-8 and INO, demonstrating lower removal efficiency in the INO permeate due to the characteristics of this effluent. Studies have shown that organics can pass through the RO membrane (DRAŽEVIĆ *et al*., 2017).

The combined process of ultrafiltration and reverse osmosis has received increasing attention in the treatment of petrochemical wastewater, due to its high efficiency in removing organic compounds and salts present in secondary and tertiary industrial effluents (HAIDARI, 2018; KAMALI, 2019). Figure 6 presents the variations in the reverse osmosis permeate fluxes in the testing period.

Figure 6 – Reverse osmosis permeate fluxes with WPS-1, WPS-8 and INO effluents throughout the testing period



Source: Authors, 2020

During the RO operation with the WPS-1 UF permeate as feedwater, a stability of the flux in the first 15 days was observed. After this period, there was a drop in flux due to biofouling, caused by biological materials present in the WPS-1

UF permeate, causing the proliferation of microorganisms on the RO membrane surface due to adsorbed organic compounds and soluble nutrients in the feedwater (JIANG, 2017). The average RO flux during the testing period for the WPS-1 effluent was 19.6 ± 2.1 $L.h^{-1}.m^{-2}$.

The WPS-8 permeate presented a stable flux in the testing period with a mean of 20.8 ± 2.5 $L.h^{-1}.m^{-2}$. As it presented the lowest concentration of total organic carbon in the permeate, this stream presented a lower tendency to fouling and kept the flux stable throughout the testing period.

Finally, the INO presented an average flux of 9.14 ± 3.8 $L.h^{-1}.m^{-2}$ and a sharp drop in flux during the experiment. For this stream, a chemical cleaning with 0.01 M sodium hydroxide and 0.01 M hydrochloric acid was necessary after 30 days of operation, which increased the flux, but a new reduction was observed. The performance of these RO treatment systems depends on a number of factors, including operating parameters such as feed flowrate, pressure, pH, temperature and feedwater characteristics. The results of the INO UF permeate characterization, with higher concentrations of salts, metals and pH than the other streams tested, lead us to consider that it may have caused the concentration polarization phenomenon during the RO operation (QASIM *et al*., 2019).

Thus, the WPS-8 effluent presented a stable flux during the evaluated period and proves to be the most suitable stream for reuse.

3.5 Final Considerations

This study used a combined process of ultrafiltration and reverse osmosis for the treatment of petrochemical effluents. Ultrafiltration proved to be able to minimize incrustations, deposits and membrane degradation, optimizing permeate production, in addition to guaranteeing the minimum requirements for feeding the RO.

The results showed that the proposed process provided a stable flux for the WPS-8 effluent, but for the other streams there was an accentuated drop in flux, which indicates fouling processes in the UF and RO membranes. As for the treatment efficiency, the process showed performance for the removal of compounds of interest such as COD above 90%, salt removal and electrical conductivity above 92% for the WPS-1, WPS-8 and INO effluents.

Considering the characterization of the permeates, the efficiency of RO in removing the compounds of interest for reuse was observed. Thus, considering all aspects evaluated in this study, the WPS-8 effluent was the most suitable to be used as feedwater in the pilot system with UF and RO, in such a way that the permeate produced presented the necessary quality for reuse in industries of the Southern Petrochemical Complex, reaching quality equivalent to clarified water.

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