Submerged microfiltration membrane and activated carbon processes for recalcitrant compounds removal in oil refinery effluent as electrodialysis pre-treatment

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ABSTRACT

The combination of suspended activated carbon (AC) and submerged microfiltration (SMF) processes was applied to polish a biotreated effluent generated in a refinery industry. Preliminary results indicated that Norit 1240 W AC was more suitable than Carbomafra AC brand for total organic carbon (TOC) removal due to the highest Freundlich adsorption constant value ($1.97 \pm 0.42$ and $0.96 \pm 0.23$ (mg/g)/(L/mg)$^{1/n}$, respectively), thus the first one was used in the combined system. Among all particle sizes of AC tested (0.041–1.01 mm), AC/SMF system was better performed, according to permeation flux, when applying granular AC instead of the powder one. On the other hand, the best response regarding TOC removal and absorbance at 254 nm (ABS$_{254 \text{ nm}}$) reduction were observed when applying powder AC (89% and 97%, respectively). Statistical analysis with two-sample T-test ($p$-value, 0.05) endorsed the need of both air purge (20 L/h) and backwash strategies (8 min of permeation and 10 seconds of backwash) to diminish fouling occurrence in the SMF system. Finally, it was found that 2 g/L of Norit 1240 W PAC (0.041 mm particle size) condition fitted the effluent to further electrodialysis reversal (EDR) process (3.4 mg/L TOC) with consistent normalized permeate flux after 5 h of permeation (0.76 $\pm$ 0.1 J/J$^3$).

Key words: activated carbon, refinery effluent, reuse, submerged membranes

HIGHLIGHTS

- Air purge and backwash was ultimately important to AC/SMF system to prevent membrane fouling.
- AC/SMF system could effectively polish the biotreated refinery effluent to suit it to the EDR process.
- Higher particle size of granular activated carbon (GAC) prevented permeate flux reduction.
- AC/SMF system showed the possibility of replacing at least three consecutive processes in pilot-plant scale.
INTRODUCTION

Petroleum refinery industries are lately seeking for new approaches concerning circular economy in light of the knowledge that natural resources are ultimately finite rather than endless. In this new era of reusing natural sources, the idea of refinery effluent recyclability, for example, is a proven alternative to reduce catchment of natural water for regular purposes, such as cleaning, irrigation, makeup water, process water or boiled feed water (Domingos & Fonseca 2018; Jafarinejad & Jiang 2019; Jain et al. 2020). In addition, this approach is reported to minimize several damages to the environment caused by inappropriate effluent discharges (Jafarinejad & Jiang 2019; Jain et al. 2020; Mohammadi et al. 2020). Not only the environmental concerns lead to effluent reusage, but also the high cost of the supply and the stricter legislation, which changed the way of thinking and limited the concentration of pollutants and the volume of the discharges to the environment (Domingos & Fonseca 2018; Jafarinejad & Jiang 2019). In oil refineries, for instance, large amounts of effluents (up to 152 mbpd of wastewater generated globally in 2015) are generated due to the large consumption of water in the processes (Domingos & Fonseca 2018; Jafarinejad & Jiang 2019). Those effluents generally consist of a complex mixture of compounds mainly featured as aromatic ones, e.g., benzene, toluene, ethylbenzene, xylene – BTEX materials – that directly threaten human health, especially when there is an increasing challenge for the wastewater treatment plants to fit the discharging guidelines (Jafarinejad & Jiang 2019; Jain et al. 2020; Mohammadi et al. 2020).

Among several technologies that are effective for treating refinery effluent and adequate for proper disposal, just a few can efficiently suit it to reuse purposes, e.g., adsorption process (AP), and membrane separation processes (MSP) (Jafarinejad & Jiang 2019; Jain et al. 2020). Nonetheless, a combination of multifaced processes must be planned in order to treat refinery effluent from its generation until the reuse (IPIECA 2010; Jafarinejad & Jiang 2019). It is reported that a usual refinery effluent treatment plant comprises of physical-chemical processes (for suspended solids and oil droplets removal) followed by biological treatment (for dissolved organic compounds biodegradation) (Jafarinejad & Jiang 2019; Jain et al. 2020). Yet, for reuse purposes, tertiary treatment in industrial scale usually relies on ultrafiltration and reverse osmosis (RO); and, at small industrial scale, in ion exchange resins, electrodialysis (ED) and electrodialysis reversal (EDR) (Domingos & Fonseca 2018; Jafarinejad & Jiang 2019; Jain et al. 2020). Although the high efficiency of those tertiary treatments, their operation requires specific influent characteristics (e.g., total organic carbon (TOC) in EDR and RO inlet should be as minimum as 10 and 3 mg/L, respectively (Domingos & Fonseca 2018)), being a challenge to the previous biological treatment
(Shanmuganathan et al. 2015). Thus, as recalcitrant compounds might still be present after secondary process, an intermediate one should be planned before the tertiary treatment (IPIECA 2010; Shanmuganathan et al. 2015).

Activated carbon (AC) is normally used as a final polishing step in wastewater treatment plants, which the main goal is to adsorb recalcitrant contaminants that remain in the water after biological treatment (IPIECA 2010; Domingos & Fonseca 2018; Jafarinejad & Jiang 2019). Specifically in oil refinery, AC is used for dissolved recalcitrant organic compounds removal (IPIECA 2010; Mohammadi et al. 2020). The efficiency of AC relies on the adsorption capacity of the adsorbent, which depends on the intraparticle size, surface area, surface-active sites, and contact time (Mohammadi et al. 2020). Likewise, MSP have been widely used in wastewater treatment plants, including the refinery ones, and, as a result, nowadays MSP is an economical competitive process that can achieve high quality treated effluents, along with relatively simple operation (IPIECA 2010; Jafarinejad & Jiang 2019). Membrane is a selective barrier that, depending on the morphology, will retain different compounds. Among all membranes that can be applied in MSP, Microfiltration (MF) is featured to be effective to suspended solids and turbidity removal, with low operational costs (Shanmuganathan et al. 2015; Nunes et al. 2020). As its pores are in a range of microsize, MF is not suitable to remove soluble materials, such as low molecular weight hydrocarbons and BTEX present in refinery effluents (IPIECA 2010; Shanmuganathan et al. 2015; Nunes et al. 2020). Instead, MF can achieve high performance towards such soluble compounds when applied alongside adsorbents, e.g., AC has been reported to remove organic matter from effluents, while MF separate them from the treated stream (Tomaszewska & Mozia 2002; Kim et al. 2005; Kim et al. 2009; IPIECA 2010; Zhao et al. 2013; Amaral et al. 2014; Shanmuganathan et al. 2015; Liu et al. 2017; Wang et al. 2017; Mohammadi et al. 2020). On the other hand, MSP presents some limitations, such as irreversible deposition of solid materials and further pores clogging, i.e., fouling, which decreases the permeation flow (Jafarinejad & Jiang 2019; Nunes et al. 2020).

Therefore, in order to avoid several steps on wastewater treatment plants and suit the biologically treated refinery effluent to tertiary treatment, microfiltration membranes with submerged modules in the effluent tank feature several advantages, including reduced area needed and increased contact time of the effluent with the adsorbent. However, intrinsic operation issues, such as fouling, rises as one of the biggest concerns since it can directly affect the membrane lifespan as well as the permeation flux (Shanmuganathan et al. 2015). Therefore, several studies have focused on applying aeration at the inlet stream, which could increase the turbulence on the effluent/membrane interface, resulting in less deposition effects of particulate materials (Kim et al. 2009; Mororó et al. 2018). Likewise, backwash application is reported as one of the interesting approaches to detach them from the pores of the membranes (Vigneswaran et al. 2007; Mororó et al. 2018).

Considering that previous studies have reported that combined submerged microfiltration (SMF, membranes immersed on the reaction media) and AC process can achieve both high removal of organic compounds and high permeation flux, the hypothesis of using it for refinery effluent is thus noteworthy and, until now, not assessed. Therefore, in order to verify such hypothesis, this work aimed to evaluate the efficiency of AC/SMF system for polishing biotreated refinery effluent and remove recalcitrant matter to adequate it to EDR process.

MATERIALS AND METHODS

Characterization of the effluent from refinery wastewater treatment plant

The effluent used in this work was obtained from a prototype unit set in the petroleum refinery. The unit carries tertiary treatment studies aimed at the reuse of the effluent. The processes involved in this unit are: advanced high-rate clarification, sand filter, granular AC (GAC) filter, and reverse electrodialysis. For instance, GAC filters aim at removing TOC in order to protect the EDR membranes, which eliminates the salinity of the effluent to generate water for reuse purposes. However, the pretreatment of EDR is seldom reliable since the adsorbent material can release from the filter and reach the EDR membranes. Therefore, in this current work, experiments were carried out by catching effluent from the rotating biological contactor outlet in order to study a substitute system, i.e., AC/SMF, for the pre-treatment of EDR process.

The biotreated effluent was stored at 4 °C, and its characterization was performed according to chemical oxygen demand (COD), TOC, ABS254 nm (10-cm path-length quartz cuvette), ammoniacal nitrogen, turbidity, chlorides, and pH, following the standard analysis (SMWW 2012).

Organic matter adsorption in activated carbon (AC) – batch experiments

Batch experiments were conducted in order to select the more suitable AC for recalcitrant organic matter removal. Two different commercial powder activated carbon (PAC) – Carbomafra and Norit 1240 W – were evaluated according to
adsorption isotherms. First, the adsorbents with particle size of 0.045–0.037 mm were treated at 100 ± 5 °C for 24 hours to properly dry it, then specific amounts (5–300 mg) were immersed in flasks containing 100 mL of the effluent (Campos et al. 2014). Control experiments, i.e., without the addition of PAC, was planned to each isotherm test and no volatilization of the organic compounds was observed (TOC results remained the same). The adsorption assays were carried out in shaker under 25 °C for 2 h and filtered, afterwards, with 0.45 µm membranes to remove the AC and stop the adsorption reaction.

Adsorption capacity of TOC on both PAC, Norit and Carbomafra brands, was evaluated by means of isotherms according to Langmuir (Equation (1)) and Freundlich (Equation (2)) adsorption models.

\[
q_e = \frac{q_m \times k_L \times C_e}{1 + k \times C_e} \quad (1)
\]

\[
q_e = K_F \times C_e^{1/n} \quad (2)
\]

where \(q_e\) (mg/g) is the mass of the adsorbed compound per unit mass of adsorbent; \(q_m\) (mg/g) is the maximum adsorption capacity; \(k_L\) (L/mg) and \(k_F ((\text{mg/g})(\text{L/mg})^{1/n})\) is the Langmuir and Freundlich constants that indicates free interaction binding energies and the adsorptive capacity bond, respectively; \(n\) is the adsorption intensity of Freundlich model, which measures the deviation degree from linearity; and \(C_e\) (mg/L) is the equilibrium concentration of solute in the bulk solution (Nworie et al. 2019).

**AC/submerged microfiltration (SMF) system**

The MSP used in this work relied on MF membranes with the configuration of submerged modules, in which the membrane is immersed in the feed tank with the effluent for proper separation of AC. In order to keep the AC suspended in the feed tank and to diminish fouling on the surface of the membrane (Pradhan et al. 2012; Mororó et al. 2018), aeration (20 L/h) was settled at the bottom of the feed tank. The system also has the possibility to operate in backwashing mode, in order to promote cleaning cycles in the membrane (Abadi et al. 2011). Figure 1(a) and 1(b) show the flowchart of the bench scale system during filtration and backwash operating modes, respectively, as well as presence of an automated solenoid valves which allowed the maneuver, at pre-set times, between the two operations. Table 1 describes the equipment with their respective flowchart acronyms and specifications.

The filtration was operated with recirculation of the effluent from feed tank (T-1) towards tank T-2 (permeate of treated effluent) by the suction of pump B. When T-2 is filled, it overflows to tank T-1 to increase the contact time of the AC (placed in T-1) with the effluent, and thus the system operates in batch convective mode. The backwash was operated with an electrical signal sent by the timer, which changes the position of the valves, i.e., the open valves close and the close valves open, allowing the reversing of the flow. In backwash mode, the permeate returns from T-2 to the feed tank (T-1) through the membrane while removing solids deposited on membrane.

Hollow fibers module of microfiltration (MF) membrane (PAM – Membranas Seletivas Ltda., 0.1 m², 0.3 µm pore size, 182.75 L/h·m²·bar water hydraulic permeability, polyethersulfone) were used in this work. The permeate flow measurements were performed by considering the permeate volume for 1 min. The ratio between the permeate flow and the membrane area

**Figure 1** | Flowchart of the system during (a) filtration and (b) backwash operating modes. For acronyms, see Table 1.
results in the flow value. Before all experiments, the membrane was compacted and washed with deionized water at 0.3 bar until the flow rate remained constant.

**Operational parameters of SMF system**

In order to evaluate the effects caused by backwash and aeration on the permeate flow, experiments without AC were conducted. To simplify the understanding of the terms presented in the results section, the following terminology $x/y$ is hereby agreed upon $x$ representing minutes of permeation and $y$ seconds of backwash. Lower permeate flow intervals with a 3/6 backwash cycle is reported to increase the flow rate of the process rather than 15/15 cycle (Mororó et al. 2018), thus the minimum 8/10 backwash cycle was performed considering the limitations of the current system. Also, the normalized permeate flow ($J/J_0$) was calculated to represent permeate flow measurements over time ($J$) and the first flow measurement ($J_0$). The permeate flow measurements were always performed before and after backwashing. All tests were carried out at 0.3 bar of transmembrane pressure. Samples were withdrawn from T-2 at 1 h time intervals for TOC analysis.

**Performance of the AC/SMF system for organic matter removal**

The effects of particle size and concentration of each AC (added in T-1), towards COD, TOC, and $\text{ABS}_{254\text{ nm}}$ analysis, as well as to permeate flow fluctuations, were evaluated according to the experimental conditions described on Table 2.

Samples were collected at 1 h time intervals from T-2 to evaluate TOC and $\text{ABS}_{254\text{ nm}}$ until the first parameter remained constant. COD was measured at the beginning and at the end of the process. The permeate flow measurements were always performed before and after backwashing. After each experiment, the membrane was immersed in 1% sodium azide aqueous solution to avoid biofilm formation.

**Statistic evaluation**

Data acquired from permeation experiments were statistically analyzed in order to verify the correlation between the applied conditions and the measured parameters. For that, the two-sample t-test (OriginLab® 2019b) was used with stipulation that the null hypothesis corresponds to the non-existence of a relationship between the mean values of the measured parameters within the conditions used in the process. The alternative hypothesis corresponds to the influence of the conditions on the

### Table 1 | Acronyms and specifications of each equipment used in the bench-scale membrane separation system

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Acronym</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed tank</td>
<td>T-1</td>
<td>5 L</td>
</tr>
<tr>
<td>Permeate tank</td>
<td>T-2</td>
<td>500 mL</td>
</tr>
<tr>
<td>Air compressor</td>
<td>C</td>
<td>Biomec; 1/4” NPT</td>
</tr>
<tr>
<td>Pump</td>
<td>B</td>
<td>Flojet (LF112421F)</td>
</tr>
<tr>
<td>Solenoid valves</td>
<td>VS-1, VS-2, VS-3, VS-4</td>
<td>Danfoss; 1/2” NPT</td>
</tr>
<tr>
<td>Flowmeter</td>
<td>R</td>
<td>6–22 L/h</td>
</tr>
<tr>
<td>Pressure gauge</td>
<td>MV</td>
<td>Famabrás; –1 to 5 bar</td>
</tr>
</tbody>
</table>

### Table 2 | Experimental conditions of AC/SMF system regarding particle size and concentration of AC (Norit 1240 W) in the feed tank.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Particle size (mm)*</th>
<th>Concentration in the feed tank (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 g/L GAC 1.01 mm</td>
<td>1.18–0.84</td>
<td>1</td>
</tr>
<tr>
<td>1 g/L GAC 0.50 mm</td>
<td>0.59–0.42</td>
<td>1</td>
</tr>
<tr>
<td>2 g/L GAC 0.50 mm</td>
<td>0.59–0.42</td>
<td>2</td>
</tr>
<tr>
<td>2 g/L PAC 0.137 mm</td>
<td>0.149–0.125</td>
<td>2</td>
</tr>
<tr>
<td>1 g/L PAC 0.041 mm</td>
<td>0.045–0.037</td>
<td>1</td>
</tr>
<tr>
<td>2 g/L PAC 0.041 mm</td>
<td>0.045–0.037</td>
<td>2</td>
</tr>
</tbody>
</table>

*Fresh AC was carefully crushed with a mortar and pestle and separated on a sieve shaker. The crushed GAC fractions were washed, dried, and stored in a desiccator until use.
average values of the measured parameters. If the test result was of a \( p \)-value < 0.05, the null hypothesis was rejected, and the alternative hypothesis was accepted.

**RESULTS AND DISCUSSION**

**Effluent characterization**

Physical-chemical characterization of the effluent is shown in Table 3, which is in accordance with what is described elsewhere (Domingos & Fonseca 2018). The low values of all parameters were already expected since the effluent was acquired after biological treatment in the prototype unit. In fact, this effluent is usually discharged directly in the environment since it properly fits to the local legislation (CONAMA 2005). Nevertheless, the high value of TOC (>15 mg/L) demands further treatment to adequately it to reuse standards, e.g., EDR requires a TOC lower than 15 mg/L so the water can be returned to the industrial process (Domingos & Fonseca 2018).

**Isotherms of organic matter adsorption on powder activated carbon (PAC) in solution**

Figure 2 shows the experimental data of TOC (after contact of the refinery effluent with Norit and Carbomafra PAC) adjusted to Langmuir and Freundlich models, and Table 4 depicts the respective parameters.

As expected, Freundlich isotherm model better represented the experimental data (\( R^2 = 0.984 \)) than Langmuir (\( R^2 = 0.971 \)), which agrees with other works (Kim et al. 2009; Zhao et al. 2013; Domingos & Fonseca 2018). Langmuir isotherm

**Table 3 | Characterization of the biological treated effluent from refinery industry**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)(^a)</td>
<td>72</td>
<td>52</td>
<td>95</td>
</tr>
<tr>
<td>TOC (mg/L)(^a)</td>
<td>23.3</td>
<td>13.0</td>
<td>34.8</td>
</tr>
<tr>
<td>ABS(_{254\text{nm}}) (1/cm)(^a)</td>
<td>0.44</td>
<td>0.30</td>
<td>0.69</td>
</tr>
<tr>
<td>N-NH(_3) (mg/L)(^b)</td>
<td>2.44</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>pH(^b)</td>
<td>7.18</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Turbidity (NTU)(^b)</td>
<td>5.91</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Total suspended solids (mg/L)(^b)</td>
<td>22</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

\(^a\) Number of replicates: \( n = 7 \); \(^b\) \( n = 1 \).

**Figure 2 | Adsorption isotherms from organic matter removal by Norit and Carbomafra AC according to Langmuir and Freundlich models. Reaction equilibrium time: 2 h.**
model describes that the bounding of compounds to the surface of the material occurs at specific sites with only one molecule, assuming, therefore, that the surface is perfectly smooth and homogeneous, as well as that the side interactions between the adsorbed molecules are negligible, and the adsorption is reversible. Freundlich isotherm model, on the other hand, describes the possibility of forming many layers on the adsorbent, and assumes that the adsorption sites have different energies. As a result, the experimental data, regarding AC applications, usually fits better to Freundlich isotherm model than the Langmuir one (Zhao et al. 2012; Wang et al. 2013; Domingos & Fonseca 2018).

Although n constant was not substantially different between the two PAC (0.60 ± 0.04 and 0.59 ± 0.04, Norit and Carbomafra, respectively), Norit PAC favored the removal of organic matter according to the highest kF (1.97 ± 0.42 (mg/g)/(L/(mg)^1/n)) value, which led to intense adsorption in the studied concentration range. Similar results were observed by Zhao et al. (2012) and Wang et al. (2013) when applying commercial PAC for organic matter removal present in refinery effluent. Both works showed a removal efficiency of organic matter around 70%, while in this current work, TOC removal reached up to 83%. In addition, because of its bituminous source (Campos et al. 2014), Norit AC have higher surface area than Carbomafra AC (BET area ∼958 and 727 m²/g, respectively), thus presenting the best performance. Therefore, Norit PAC commercial brand was chosen to be evaluated hereafter.

**Optimization of SMF system**

To optimize the operation of the current SMF system, the effect on permeation flow with 8/10 backwash cycle and presence of air purge (20 L/h) in the feed tank (T-1), without adding AC, is shown in Figure 3(a).

It can be inferred that the permeation flow is ultimately dependent on backwashing operation. For instance, when the system is operated without backwashing and with air purge, a sharp decrease, i.e., 40%, on the permeate flux occurs over the first 2 h of operation. When the permeation is instead conducted without air purge and with backwashing, fouling on the membrane is reduced, and a systematic maintenance of 8/10 backwash cycle could prevent further pores blocking over 5 h of permeation. Still, the best performance of SMF system, with no significant changes on the permeation flux, was verified when both procedures were applied, 8/10 backwash and 20 L/h air purge. It should be highlighted that the turbulence generated in the bulk solution by air purge prevented larger particles from depositing on the membrane surface, while

### Table 4 | Langmuir and Freundlich adsorption isotherms model constants and errors from organic matter removal by Norit and Carbomafra AC.

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k_L</td>
<td>q_m</td>
</tr>
<tr>
<td>Norit</td>
<td>3.68 ± 0.44</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Carbomafra</td>
<td>2.29 ± 0.39</td>
<td>0.05 ± 0.01</td>
</tr>
</tbody>
</table>

**Figure 3** | SMF system performance towards biotreated refinery effluent according to (a) permeation flux and (b) TOC removal, with different operating conditions: presence of 20 g/L air purge and/or 8/10 backwash cycle. TOC₀ = 15.0 ± 1.1 mg/L.
backwash maneuver detached particulate material from the pores. Two-sample t-Test statistical analysis further confirmed that the backwash mode had higher influence on the permeate flow than air purge (Figure 4).

Smith & Vigneswaran (2009) also describes the high input on permeate flow by applying backwash cycles with 2 min duration in a side stream membrane filtration system to permeate biological treated wastewater. Abadi et al. (2011) verifies that, although membrane backwashing is highly effective on fouling avoidance during the first hour on permeating oil wastewater, after long-term operation the membrane required chemical cleaning as more severe fouling occurred. In this current work, severe fouling was instead avoided by setting air purge on the feed tank, which could increase the turbulence on the membrane surface and prevent depositions, as also demonstrated by Pradhan et al. (2012) and Shanmuganathan et al. (2017). One should note that none of those previous works have applied both backwash and air purge at once.

TOC removal mainly occurred in the first hour of operation for all conditions tested, without any significant changes afterwards (Figure 3(b)), which is attributed to the suspended matter separation from the permeate stream. Presence of air purge in the feed tank had an interesting effect towards TOC, which the removal increased around 13% when comparing the processes with 8/10 backwash cycle (~50% TOC removal) after 4 h. This observation might be due to the selective oxidation of some organic compounds in the effluent as a result of the increase in dissolved O₂ in the feed tank (Jafarinejad & Jiang 2019).

**AC/SMF system for adequation of biotreated refinery effluent to reuse features**

Different size of Norit AC was evaluated in AC/SMF system in order to achieve the best performance of permeation flux and organic matter removal. As discussed before, experiments carried out with the addition of AC in the feed tank rely on

![Figure 4](http://iwaponline.com/wst/article-pdf/84/6/1403/939934/wst084061403.pdf)

*Figure 4* | Box plot graphs related to two-sample t-test (p-value <0.05) of the data acquired from permeate flux experiments, with backwash, air purge, and air purge/backwash.
sufficient aeration to maintain particles suspended in the bulk solution, therefore, maximum aeration of the AC/SMF system was used (20 g/L) for all tests performed.

Figure 5 shows the normalized flow over time of different AC particle sizes and concentrations (1 and 2 g/L) used in the AC/SMF system. Note that some normalized flow values are higher than 1, which is a result of the first flow measurement ($J_0$) after an indefinite filtration time, as explained before, and it does not represent the initial flow. The addition of 1 g/L of GAC, with particle size of 1.01 mm, as well as the experiment without AC (Figure 3) were able to maintain the normalized flows over time. This tendency differs from experiments carried out with the same amount of adsorbent, but with GAC 0.50 mm and PAC 0.041 mm, which show a slight decay after 3 h of permeation and on the initial normalized flows, respectively. However, after those drops, normalized flows were maintained throughout further permeation. Processes that use GAC usually show higher fouling resistance on the surface of the membrane. Dialynas & Diamadopoulos (2008), for instance, reported an increase in transmembrane pressure, thus pores blocking, after the addition of 2.5 g/L PAC (0.15 mm particle size). On the other hand, Pradhan et al. (2012), Johir et al. (2013) and Shanmuganathan et al. (2017) resolved that GAC can substantially diminish mechanical scouring on the membrane rather than smaller AC particle size.

The increase in AC concentration to 2 g/L favored the decline on the permeation flux for all particle sizes of AC tested (Figure 5), thus, the initial normalized flows of GAC 0.50, PAC 0.137, and PAC 0.041 mm could not be maintained in the first hours, although after 5 h of operation the permeation flow was stabilized until up to 7 h of operation. This occurs precisely due to the increase in the concentration of AC, which increases the concentration of solids in the feed tank, making permeation more difficult in the first hours.

The mean normalized permeate flow data ($J/J_0$) of each test from Figure 5 was statistically evaluated to verify the existence of any influence of AC particle size towards permeation flow. For this, the two-sample t-test was calculated for each possible combination between the experiments with the same concentration of AC, which gave a total of six possible combinations (Figure 6).

Among all combinations performed, just the ones with 1 g/L GAC 1.01 mm vs. 1 g/L PAC 0.041 mm and 1 g/L GAC 0.5 mm vs. 1 g/L PAC 0.041 mm were statistically different regarding their particle sizes; and no significant differences was observed between 1 g/L GAC 1.01 mm vs. 1 g/L PAC 0.5 mm. In another words, 1 g/L GAC with particle size higher than 0.5 mm could efficiently maintain the permeation flux, while PAC, as discussed before, is a challenge to fouling resistance. For 2 g/L of AC, all the experiments were, instead, statistically the same, i.e., flux reduction showed no difference between the AC particle sizes due to high amounts of AC, thus worse effects towards fouling occurrence.

Regarding the combination for the evaluation of different AC concentration, the two-sample t-test from Figure 5 is represented in Figure 7.

**Figure 5** | Profile of permeation flow with time. Conditions: AC particle size ranging from 0.041 to 1.01 mm; 1 and 2 g/L AC concentration; 0.3 bar; 8/10 backwash cycle; and 20 L/h air purge.
Whereas different particle sizes did not statistically affect the permeation flux with 2 g/L of AC (Figure 6), when the comparison regards 1 g/L PAC 0.041 mm vs. 2 g/L PAC 0.041 mm, the fluxes are statistically different. No significant effect was observed when rationalizing 1 g/L GAC 0.5 mm vs. 2 g/L GAC 0.5 mm conditions. Those behaviors might be due to the higher surface area of 0.041 mm than 0.5 mm of AC, in which the first one is capable of adsorbing more compounds than

![Box plot graphs related to two-sample t-test (p-value <0.05) of the data from permeate flux experiments with 1 and 2 g/L activated carbon and 0.041–1.01 mm particle size.](image)

Figure 6 | Box plot graphs related to two-sample t-test (p-value <0.05) of the data from permeate flux experiments with 1 and 2 g/L activated carbon and 0.041–1.01 mm particle size.
the AC with larger particle size. Therefore, when adding higher concentrations of PAC 0.041 mm, the adsorption capability of the system is favored, resulting in less fouling occurrence during permeation through a microfiltration membrane. However, one should consider that this adsorption effect has also an optimum point, thereafter, the adsorption capability is reduced, ultimately impacting on fouling resistance. By analyzing Figure 5, this behavior precisely occurs with 2 g/L PAC 0.041 mm, where flux is initially higher than 1 g/L PAC 0.041 mm, and then it reduces.

Figure 8(a) shows TOC removal (TOC\textsubscript{0} = 24.1 ± 7.5) during AC/SMF operation with different particle sizes of AC. The highest TOC removal (89% in 7 h) was observed when 2 g/L PAC 0.041 mm was added in the feed tank, fitting the refinery effluent, i.e., 3.4 mg/L TOC, to the requirements of the next process for reuse purpose, which should be less than 10 mg/L for EDR. In fact, due to its higher surface area, Figure 8(a) endorses the hypothesis of PAC having better performance towards organic matter removal than GAC. The latter presented TOC removal up to 35% in 10 h of permeation when adding 1 g/L of GAC 0.50 mm and GAC 1.01 mm. By decreasing the concentration of PAC 0.041 mm to 1 g/L, the efficiency of the process was compromised (73% in 5 h), leading to a higher content of organic matter in the permeate stream, i.e., 8.5 mg/L TOC. This outcome was also demonstrated elsewhere with PAC achieving 60% DOC (dissolved organic carbon) removal, while GAC could reach up just 36% (Dialynas & Diamadopoulos 2008). Analogous removal results were achieved by Ahmad et al. (2018) with 39% of TOC removal in submerged ceramic membrane system with fluidized GAC. It is also reported that the increase in AC concentration in AC/SMF system may not lead to better performance on TOC removal (Vigneswaran et al. 2007), which is the case of GAC 0.50 mm in this current work. In addition, Corwin & Summers (2010) stated that GAC particle size influences the adsorption capacity rather than its concentration in the reaction media. These discussions agree with the normalized permeate flux previously considered.

Figure 8(b) shows the COD removal at the end of permeation in SMF (without AC) and AC/SMF system for different particle sizes and concentrations of AC. Microfiltration alone is able to remove at some extent the COD (19%), although, in general, higher removals (up to 65%) were achieved by adding AC. Unlike the influence of particle size of AC towards TOC removal, COD in the permeate stream decreased with higher AC particle size, e.g., 1 g/L GAC 1.01 mm, 1 g/L GAC 0.5 mm, and 1 g/L PAC 0.041 mm, achieved 65, 60, and 15% of COD removal, respectively. However, by increasing GAC 0.50 mm concentration (from 1 to 2 g/L), COD concentration remained the same, while 2 g/L PAC 0.041 mm led to higher COD removal (53% removal).

Figure 8(c) shows that the analysis of ABS\textsubscript{254 nm} followed the same trend as TOC, with high influence of the particle size of the AC. For instance, 2 g/L CAP 0.041 mm could decrease up to 97% ABS\textsubscript{254 nm} signal, while 2 g/L PAC 0.137 mm and 2 g/L PAC 0.50 mm was around 76%. Similar results, up to 82.4% of ABS\textsubscript{254 nm} signal decrease, were reported when using 20 g/L of PAC with a grain size range of 0.149 to 0.045 mm (Gai & Kim 2008). When minor amounts of AC were added, in this current work, 1 g/L GAC 0.50 mm performance towards ABS\textsubscript{254 nm} was the same as with 2 g/L GAC 0.50 mm (~47% in 18 h of operation), yet, 1 g/L PAC 0.041 mm decreased its performance to from 97% to 81%. Variations on PAC performance for
ABS$_{254\text{ nm}}$ removal is also demonstrated when 0.022 and 0.045 mm in a concentration range of 0 to 40 g/L was applied (Kim et al. 2005).

The contradictions verified between COD and TOC/ABS$_{254\text{ nm}}$ analysis may suggest that other contaminants, different from organic (and aromatic) compounds, is still present in the effluent, which show less affinity with Norit AC active groups, and are easily permeated through the microfiltration membrane. Kusworo et al. (2018) used a two-step bed column (PAC 0.177 mm particle size and bentonite clay) to reduce both organic matter and salt content from oil field produced water as a pre-treatment for nanofiltration membranes. As a result, the adsorption step could increase just 12% of COD removal, while salinity reduction was up to 40% due to the presence of a specific adsorbent, i.e., bentonite clay, to remove such species.

Finally, by using AC/SMF system to fit refinery industry effluent to tertiary process, PAC showed better results regarding the removal of organic contaminants than GAC due to higher surface area of the former adsorbent. On the other hand, the latter could prevent severe fouling, and be more prone to backwash operation, hence improving permeation flux.

**CONCLUSION**

This study evaluated the use of AC associated with the SMF system for treatment of refinery effluent in order to suit it for further EDR treatment and generate reused water. Assays carried out with AC in solution allowed the selection of the best
AC brand for organic matter removal, that is Norit 1240 W. Convective permeation experiments demonstrated that both aeration and backwash are ultimately important to achieve the best performance of SMF system. The addition of AC to SMF system efficiently improved organic matter removal through the analysis of TOC, COD, and ABS254 nm, which was also dependent on the particle size of AC, as well as its concentration. Therefore, the results showed that by adding 2 g/L of Norit 1240 W PAC in the feed tank of SMF system, the effluent was acceptable to the EDR process.

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The authors declare no competing interests.

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DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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