PERFORMANCE OF THE CATALYTIC MEMBRANE REACTORS OF DIFFERENT PORE SIZE WITH PALLADIUM AS CATALYTIC PHASE IN HYDROGENATION AND OXIDATION REACTIONS

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Abstract - The catalytic membrane reactors (CMR) were prepared using commercial Hollow Fiber Membranes of corundum with 4 nm or 1400 nm pores and impregnated with palladium. The tests performed were phenol hydrogenation, hydrogen peroxide generation to oxidize phenol by advanced oxidation processes and chromium (VI) reduction. Reactions were performed in aqueous solution, at mild temperature and under atmospheric pressure. For all tests, the hydrogen passed through the membrane to be activated with palladium. The test with phenol showed that, in the absence of oxygen, the activated hydrogen reacts with the organic matter, leading to the formation of hydrogenated products; in the presence of oxygen, active hydrogen reacts with oxygen to form hydrogen peroxide and subsequently hydroxyl radicals that attack the organic matter until its mineralization. Furthermore, the CMR is capable of reducing chromium (VI) to chromium (III). The CMRs of smaller pore size presented better performance in all reactions.

Keywords: Catalytic membrane reactors; Advanced oxidation processes; Palladium nanoparticles; Hydrogenation; Phenol; Chromium (VI) reduction.

INTRODUCTION

A membrane reactor is a device that combines a membrane separation or distribution process with a chemical reaction in one unit (Lin, 2007). Among the different types of membrane reactors, Catalytic Membrane Reactors (CMRs), devices with catalytic perm-selective membranes or made with an ordinary membrane with a catalyst deposited in or on it, are a good choice to develop efficient and safe catalytic reactions (Caro, 2014; Miachon and Dalmon, 2004). The CMR can be used as a contactor to intensify the contact between reactants and catalysts (Westermann and Melin, 2009). The interfacial contactor mode allows contact between catalyst and the reagents fed from opposite sides of the Hollow Fiber Membrane (Pinos-Vélez et al., 2017). This disposition permits the reaction between reagents in different phases, e.g., liquid and gas with a solid catalyst (Dalmon et al., 2007; Volkov et al., 2011). Catalytic Membrane Reactors in the interfacial contactor mode are therefore good options to develop hydrogenation and oxidation reactions, providing a catalytic interface (Sanchez and Tsotsis, 2002). Using a Hollow Fiber Membrane presents some advantages due to the high chemical, thermal and mechanical resistances of the applied material, in addition to the membrane geometry, which provides a large surface area per...
unit volume of membrane module (Terra et al., 2016).

For instance, Catalytic Membrane Reactors are used in environmental applications to eliminate organic pollutants by advanced oxidation processes (AOP), which are one of the most effective methods because they are a highly competitive water treatment technology for organic pollutants not treatable by conventional techniques (Oller et al., 2011; Poyatos et al., 2010; Pires et al., 2015). These processes are characterized by using the high reactivity of OH radicals to oxidize the organic matter to obtain less hazardous pollutants or until complete mineralization; AOPs include \( \text{O}_2/\text{H}_2\text{O}_2 \), \( \text{UV/UV}_2 \), \( \text{UV/H}_2\text{O}_2 \), \( \text{O}_2/\text{UV/H}_2\text{O}_2 \), \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \), and photocatalysis (Andreozzi et al., 1999; Mohanty et al., 2017).

One option to develop AOPs using CMRs is to obtain hydrogen peroxide in situ to generate hydroxyl radicals in order to oxidize organic pollutants such as phenol (Osegueda et al., 2012; Osegueda et al., 2015). CMRs are capable of performing the entire Fenton process due to the generation of \( \text{H}_2\text{O}_2 \) and formation of OH radicals for organic matter oxidation. Phenol oxidation comprises different consecutive steps: catechol is the primary oxidation product, indicating that hydroxylation takes place predominantly at the ortho position. The concentration of the other oxidation products, such as hydroquinone (para-hydroxylation), resorcinol (meta-hydroxylation), and \( p\)-benzoquinone are less predominant than catechol. The ring opening of the aromatic intermediates leads to the formation of organic acids such as muconic acid, maleic acid, formic acid and malonic acid. As a result, a decrease in the pH takes place. In fact, all of the intermediates are finally oxidized to formic acid and oxalic acid. Formic acid is also oxidized to CO\(_2\) and H\(_2\)O, whereas oxalic acid shows quite refractory behavior and may remain in solution (Pignatello et al., 2006).

Catalyst Membrane Reactor preparation

Corundum Hollow Fiber Membranes (HFM) made of alpha alumina (\( \alpha \)-A1203) for ultra and nano filtration manufactured by Ceparation\textsuperscript{TM} of 4 nm and 1400 nm porous size were used as the starting material. The porosity of the membranes varied from 10% to 15%. The fibers have an inner diameter of 2 mm and an outer diameter of 3 mm with a total length of 300 mm. Each of the Catalytic Membrane Reactors was prepared by using a 150 mm fragment of the membrane. The procedure to prepare Catalytic Membrane Reactors of corundum impregnated with palladium has been described in previous works (Pinos-Vélez et al., 2016a; Pinos-Vélez et al., 2016b). Briefly, the precursor solution of palladium salt, PdCl\(_2\), (Johnson Matthey) with 59.83% of the noble metal, was added into Milli-Q water, while stirred. Then, concentrated hydrochloric acid (37%, Sigma-Aldrich) was added in a drop-wise manner into the solution until the salt was completely dissolved. Finally, the concentration was adjusted with Milli-Q water in order to achieve approximately 1% of weight of Pd per weight of the membrane. The palladium precursor solution was used to impregnate the membranes of 1400 or 4 nm.
Once the impregnation was complete, the Catalytic Membrane Reactors were dried in a special vessel in a vacuum for 30 min. In this step, the CMR was rotated along the horizontal axis in order to avoid preferential deposition of the salts onto the membrane. The CMR was dried at 120°C for 5 h and finally calcined at 450°C overnight. The palladium loaded onto the CMR was further activated by reduction under 20 sccm/min flowing hydrogen at 350°C for 3 hours. The amount of palladium deposited into the Hollow Fiber Membranes was calculated by the weight difference between the original and the modified membrane. The data for the CMRs obtained are summarized in Table 1.

<table>
<thead>
<tr>
<th>CMR</th>
<th>Pore size (nm)</th>
<th>% Pd</th>
<th>% Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMR1400</td>
<td>1400</td>
<td>0.9</td>
<td>15</td>
</tr>
<tr>
<td>CMR4</td>
<td>4</td>
<td>0.75</td>
<td>10</td>
</tr>
<tr>
<td>HFM1400</td>
<td>1400</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>HFM4</td>
<td>4</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

CMR, Catalytic Membrane Reactor; HFM, Hollow Fiber Membranes.

Characterization of catalytic membrane reactors

Transmission electron microscopy (TEM) - Transmission electron microscopy was employed to examine the Pd nanoparticles in the catalytic membrane reactor. The equipment used was a transmission electron microscope, TEM, JEOL model 1011 from Servei de Recursos Científics i Tècnics of URV. A piece of the CMR was crushed and the powder was dispersed in ethanol for the samples obtained by impregnation, sputtering and microemulsion. The nanoparticles obtained by the polyol route without the support were analyzed directly. Then, a drop of the sample in suspension was placed onto a copper grid. The grid was dried and placed in the TEM to be observed. The sizes of the observed Pd particles were determined using the ITEM software by Olympus.

X-ray diffraction (XRD) - To identify the palladium and corundum crystals, pieces of the catalytic membrane reactor were analyzed using X-ray diffraction. XRD measurements were performed using a Bruker-AXS D8-Discover diffractometer equipped with a parallel incident beam (Göbel mirror), a vertical θ-θ goniometer, an XYZ motorized stage and a General Area Diffraction System (GADDS). Samples were placed directly on the sample holder and the area of interest was selected with the aid of a video-laser focusing system. An X-ray collimator system allowed the analysis of 500 μm areas. The X-ray diffractometer was operated at 40 kV and 40 mA to generate CuKα radiation. The GADDS detector was a HI-STAR (multwire proportional counter of 30 x 30 cm with 1024 x 1024 pixels) placed 15 cm away from the sample. A frame (2D XRD patterns) covering 24 – 56 2θ was collected. The exposure time was 900 s per frame and it was chi-integrated to generate the conventional 2θ vs. intensity diffractogram. Image scale: small lines separation corresponds to ≈ 100 μm. The average area analyzed was represented by an ellipsoid centered in the cross with a constant short axis of 0.5 mm (N-S direction) and a variable long axis (from 1.5 to 0.6 mm in the W-E direction). The analysis of the XRD diffractogram was performed by the ICDD database (release 2007) using Diffracplus Evaluation software (Bruker 2007).

Tests

Test of generation of hydrogen peroxide - Both CMR were introduced in a vessel containing 100 mL Milli-Q water. Hydrogen flow of 6 sccm/min was supplied to one end of the CMR whilst the other end was kept closed. In this way, the hydrogen passed across the membrane wall reaching the external surface. Air was bubbled into the water as an oxygen source in the reactor vessel. High performance liquid chromatography, a Shimadzu HPLC equipped with LC 20AB system and with a diode array detector SPD-M10Avp, was used. Hydrogen peroxide was analyzed at a wavelength of 193 nm after direct injection of the sample without a column. The mobile phase was Milli-Q water, 1mL/min.

Test of treatment of 100 ppm of phenol in aqueous solution - A 100 ppm synthetic water solution of phenol was prepared using Milli-Q water and phenol (98.5%, Riser S.A). The Catalytic Membrane Reactors were tested with 100 ppm of phenol in water solution in semi-batch mode. The hydrogen flow was adjusted using a mass flow controller and supplied to one end of the reactor while the other end was kept closed. The hydrogen supply was 6 sccm/min. The hydrogen crossed the membrane wall reaching the external surface. The CMR was submerged into a glass reactor containing 100 mL of the phenol-water solution. The tests were performed at 60°C for 7 hours at atmospheric pressure. Thereafter, the experiments were divided into three groups: (a) hydrogenation with no external gas supply, and with Ar supply as sweep gas; (b) oxidation with pure oxygen supply; (c) oxidation with air supply to the reaction vessel containing the model solution. In order to saturate the solution when an external gas was supplied, this gas was bubbled into the vessel 10 minutes before introducing the membrane with hydrogen. The experimental set ups are shown in Figure 1.

In order to determine the elimination of the organic substances by stripping, individual tests for phenol, cyclohexanol and cyclohexanone were done. The stripping test for phenol was done in the same condition as the oxidation tests with air and with Argon, but using
a Hollow Fiber Membranes without palladium. The stripping tests for cyclohexanol and cyclohexanone were done with a Hollow Fiber Membrane in the same conditions of the hydrogenation tests but using argon as a sweep gas.

High performance liquid chromatography, Shimadzu HPLC equipped with LC 20AB system and with a diode array detector SPD-M10Avp, was used to measure the concentrations of phenol as well as the intermediates in phenol oxidation. A C-18 column (ID. 4.6 mm, length 250 mm, Omnisphere, Varian) was used to separate the reaction intermediate products from the phenol. The concentrations of phenol during the tests were measured every hour. The analysis of the phenol was made at a wavelength 254 nm. The mobile phase of 1 mL/min was a mixture of 60% water at pH 3 adjusted with acetic acid and 40% of acetonitrile (Aldrich).

The total organic carbon was measured with a Shimadzu TOC-L CSN equipment. Only the initial and the final samples were assessed.

The hydrogenated products at the end of each experiment were extracted from the aqueous solutions, previously saturated with NaCl, with ethyl acetate (Sigma). Hydrogenation products of phenol extracted were assessed using the gas chromatograph Shimatzu GC-2010 with ZEBRON ZB-WAX column and FID detector. The analyses GC conditions were: 115 kPa head column pressure, helium flow 144 mL/min, split ratio 15, injector and detector temperature 250°C. The temperature ramp was from 60°C to 180°C and held for 5 min. The obtained values were corrected by a relative response factor (Rome et al., 2012). A calibration curve was prepared for phenol, cyclohexanone (Fluka), for cyclohexanol (Sigma-Aldrich) and for 2-cyclohexen-1-one (Aldrich), from 0.5 to 100 ppm and R of 0.999.

In the reaction vessel, the dissolved oxygen was measured in each experiment using a SG6 (MettlerToledo) dissolved oxygen meter.

**Chromium Reduction** - In order to test the dissimilarities between CMRs of different pore size, experiments to achieve the reduction Cr (VI) to Cr (III) were performed. The procedure was previously described elsewhere (Pinos-Vélez et al., 2016a). A water solution of 8 mg/L of Cr (VI) was prepared from K$_2$CrO$_4$ salt (Panreac) and adjusted to pH 3. Samples were prepared in accordance with the standard methods 3500-Cr (colorimetric method for the examination of water and wastewater) (Apha, 2012). 1,5-biphenyl carbazide was added to the samples as an indicator and its absorbance was measured at 540 nm each hour using the Jasco V-630 Spectrophotometer.

**RESULTS AND DISCUSSION**

The Catalytic Membrane Reactors obtained are described in Table 1. The Catalytic Membrane Reactors achieved have a palladium concentration around 1% considering the weight of the Hollow Fiber Membranes. The porosity of the CMRs did not differ from the porosity of the original Hollow Fiber Membrane.

**Characterization**

In Figure 2, spherical dark brown palladium nanoparticles can be seen over corundum. The results obtained through the TEM showed a mean nanoparticle size of 6 nm with a standard deviation of 2 nm. No differences were found between palladium nanoparticles loading in CMR4 and CMR1400.

Figure 3 shows the XRD analysis; in HFM (a), only the characteristics peaks of corundum were found.
as was expected. In the CMR samples (b and c), the characteristic peaks of corundum and palladium can be seen at 39.9 degrees for palladium and at 37.7, 41.65, 43.3 and 46.1 degrees for corundum. No differences between membranes can be found.

Hydrogen Peroxide generation

The CMRs tested reached the maximum concentration of \( \text{H}_2\text{O}_2 \) after twenty minutes. Subsequently, no more hydrogen peroxide was produced. A possible reason to explain this apparent inactivity can be attributed to palladium deactivation caused by the \( \text{H}_2\text{O}_2 \) produced (Osegueda et al., 2012). The results of this test are presented in Table 2. The reaction pathway proposed is the hydrogen passing through the CMR where a dissociative absorption is produced. The atomic hydrogen reacts with the oxygen dissolved in the water to form hydrogen peroxide and water.

CMR1400 gave the best performance and, as was expected, the Hollow Fiber Membranes did not react. In both cases, CMR 1400 and CMR 4 produced enough \( \text{H}_2\text{O}_2 \) to be tested in Advanced Oxidation Processes to eliminate phenol.

![Figure 3. XRD analysis of CMR4 and CMR1400.](image)

A possible drawback in the process is the peroxide decomposition caused by the palladium. In order to check this, once a maximum in the peroxide concentration was reached, the hydrogen supply was stopped and the \( \text{H}_2\text{O}_2 \) concentration was monitored. No variation in the peroxide concentration was measured for at least 20 min.

In order to activate the CMRs, the reactors were removed from the reaction vessel and cleaned with Milli-Q water. Then, hydrogen was passed through the membrane for 10 minutes.

Phenol test

The results of the tests can be seen in Table 3 and Figure 4. All tests were performed at 60°C and atmospheric pressure in semi-batch mode at neutral pH. The only exception was the test where \( \text{Fe}_2(\text{SO}_4)_3 \) was added to improve the oxidation performance; in this case, the pH was set to 2 with hydrochloric acid to maintain the iron solubilized. HFM 1400 and HFM 4 were tested as blanks using \( \text{H}_2 \) that passed through the membrane and bubbling air. In the blank tests, leaching of palladium was measured by ICP MS; no

<table>
<thead>
<tr>
<th>CMR</th>
<th>Trans-membrane pressure (barg)</th>
<th>Max ( \text{H}_2\text{O}_2 ) Mg/L</th>
<th>% Efficiency ( \text{mol H}_2\text{O}_2 / \text{mol H}_2 )</th>
<th>( \text{mol H}_2\text{O}_2 / \text{h.mol Pd}^* )</th>
<th>( \text{mol H}_2\text{O}_2 / \text{h.m}^2 \text{ membrane} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMR1400</td>
<td>2.3</td>
<td>11</td>
<td>0.45</td>
<td>0.57</td>
<td>0.06</td>
</tr>
<tr>
<td>CMR4</td>
<td>3.7</td>
<td>7</td>
<td>0.22</td>
<td>0.34</td>
<td>0.03</td>
</tr>
<tr>
<td>HFM1400</td>
<td>0.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HFM4</td>
<td>3.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Initial hydrogen peroxide generation rates measured in the first ten minutes of the tests.
Table 3. Results of the test of the phenol oxidation and hydrogenation.

<table>
<thead>
<tr>
<th>CMR</th>
<th>Test</th>
<th>mg/L DO</th>
<th>mg/L Conversion, LC</th>
<th>% Selectivity</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mineralization, TOC</td>
</tr>
<tr>
<td>1400</td>
<td>H$_2$</td>
<td>26</td>
<td>00</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>H$_2$</td>
<td>44</td>
<td>00</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>H$_2$, 25°C</td>
<td>0.34</td>
<td>16</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>52</td>
<td>73</td>
</tr>
<tr>
<td>1400</td>
<td>O$_2$, H$_2$</td>
<td>23.6</td>
<td>32</td>
<td>59</td>
</tr>
<tr>
<td>4*</td>
<td>O$_2$, H$_2$</td>
<td>39</td>
<td>32</td>
<td>68</td>
</tr>
<tr>
<td>1400</td>
<td>H$_2$, Air bubble</td>
<td>34</td>
<td>43</td>
<td>46</td>
</tr>
<tr>
<td>4*</td>
<td>H$_2$, Air bubble</td>
<td>53</td>
<td>67</td>
<td>26</td>
</tr>
<tr>
<td>1400</td>
<td>H$_2$, Air by diffusor</td>
<td>36</td>
<td>46</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>H$_2$, Air by diffusor</td>
<td>52</td>
<td>26</td>
<td>38</td>
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<tr>
<td>1400</td>
<td>H$_2$, Air, Fe</td>
<td>42</td>
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<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td>71</td>
</tr>
</tbody>
</table>

Dissolved oxygen, DO; cyclohexanone, C=O; cyclohexanol C-O; * values taken from Pinos-Vélez et al. (2016b).

Figure 4. Tests of hydrogenation and Advanced oxidation processes using 100 ppm of phenol in aqueous solution at 60°C and atmospheric pressure.

leaching of palladium was detected. The reaction rate fit best with a zero order reaction with respect to the phenol concentration.

In linear regressions for the hydrogenation reaction, the $R^2$ obtained was 0.987 for CMR4 and 0.992 for CMR1400; when argon was added into the reaction, the $R^2$ was 0.966 for CMR4 and 0.984 for CMR1400; for the test of hydrogenation at atmospheric temperature $R^2$ was 0.968. In the reaction with hydrogen and oxygen, the $R^2$ was 0.999 for CMR4 and 0.980 for CMR1400; for the test of hydrogenation at atmospheric temperature $R^2$ was 0.968. In the reaction with hydrogen and air, the $R^2$ was 0.984 for CMR4 and 0.951 for CMR1400, when the diffusor was used, the values were 0.997 for CMR4 and 0.998 for CMR1400. Finally, in the test where hydrogen, air, and Fe were added, the values were 0.992 for CMR4 and 0.998 for CMR1400.

The CMRs prepared with a ceramic Hollow Fiber Membrane and Pd as the active phase are able to catalyze different reactions in one set-up, depending on the operational conditions and reagents. This proves that the CMRs are capable of developing different reactions due to their versatility (Sanchez and Tsotsis, 2002).

Table 3 and Figure 4 show that both CMR successfully reacted in each condition. Despite the lower content of Pd, in the hydrogenation reaction, CMR4 obtained better results. Hence, a smaller pore size favors the reaction due to improved hydrogen diffusion. Cyclohexanone and cyclohexanol were found as hydrogenation products. In the test at 25°C, very poor results were obtained, almost comparable with the blank results obtained with the HFMs. The hydrogenation tests with phenol were performed again, but using argon as sweep gas. Surprisingly, the total organic carbon decreased in the same sense of the amount of phenol; furthermore, less hydrogenation products were found in comparison of the hydrogenation tests without Ar, see Table 3. Then, stripping tests with phenol, cyclohexanol and cyclohexanone were performed, see Figure 5. The tests
found that the cyclohexanone and cyclohexanol were easily stripped. In order to determine the stripping in each reaction, a connection to collect the gases of the reaction, with a known amount of ethyl acetate, was adapted in the set up. The ethyl acetate was analyzed by gas chromatography. The reactions using the CMRs were repeated with this new set up; cyclohexanone and cyclohexanol were found in the sample corresponding of the stripping. A little conversion variation between the test with no external gas and with Ar was found; that is, when a product is eliminated, the equilibrium will be recovered and generates more of the eliminated product.

Fenton reactions to oxidize phenol were performed using a) oxygen, b) air as oxygen source, and c) air and Fe to improve the reaction. In the reaction with bubbled oxygen, no important difference was found between the performances of the CMRs. Between them, CMR4 achieved a better conversion. In the samples to corroborate stripping, no hydrogenation products were found; in the extracted final samples, hydrogenation products were under the detection limit. Furthermore, through HLPC, typical intermediates of phenol oxidation were found, such as catechol, hydroquinone, resorcinol, and p-benzoquinone (Pignatello et al., 2006). Hence, we can conclude that only oxidation is produced when oxygen is used due to the large amount of this gas available in the reaction.

In the oxidation test using air as oxygen source, the CMR4 achieved the best performance in the three variations of the test, which are air supply i) by tube or ii) by diffuser, or iii) air by tube and added iron to improve the Fenton reaction. There was no difference due to the mode of the air supply. This result is explained by the fact that oxygen used in the reaction is the dissolved oxygen; thus, the amount of oxygen depends on the temperature and pressure. In fact, when the amount of oxygen in the water was measured, no differences were found by way of supply. In all varieties of the tests, apart from intermediates of phenol oxidation, hydrogenation products were found. Hence, hydrogenation and oxidation compete in these conditions. Moreover, in the samples to detect stripping, hydrogenation products were found. This mean that not all the Total Organic Carbon eliminated in these reactions is due to phenol mineralization; part of this is due to phenol hydrogenation products being stripped. Regarding the amount of hydrogenation products, a lower quantity was found when the air was bubbled; apparently, the small bubbles originated by the diffusor are less efficient to produce stripping. Since gas transfer occurs through the gas-liquid interface, this operation has to be carried out so as to maximize the opportunity of interfacial contact between the two phases (Glória et al., 2016). In the reaction when iron is added, more conversion was found because iron enhances the hydroxyl radical generated from hydrogen peroxide and promoted the phenol oxidation. Once again, hydrogenation and oxidation products were found. In conclusion, when air is supplied as the oxygen source hydrogenation and oxidation compete. Therefore, it is recommended to use oxygen and not air if an advanced oxidation process is required. This result is reasonable because oxygen is more soluble in water than air; in fact, at 60°C the Henry constant for oxygen is 62200 Pascal, while for air it is 100500 Pascal; furthermore, one must take into account that air content is approximately 21% oxygen. A disadvantage to use oxygen instead of air is that the treatment cost increases; hence, an optimization of the process is needed.

The reaction pathway proposed is hydrogen activation by the palladium nanoparticles over the HFM. This atomic hydrogen can react with the oxygen in water to generate hydrogen peroxide. As a result, $H_2O_2$ releases hydroxyl radical due to Pd or Fe.
These radicals attack the organic matter. In this case, phenol degrades through the formation of catechol, hydroquinone, resorcinol, and p-benzoquinone until mineralization occurs. Alternatively, the activated hydrogen can react directly with the organic matter to produce the hydrogenation products, cyclohexanone and cyclohexanol. Therefore, when hydrogenation is required, only hydrogen should be used in the test, but when an advanced oxidation process is needed, oxygen must be used.

**Chromium reduction**

The results of the test of chromium (VI) reduction to chromium (III) are presented in Figure 6. No differences in performance were found between CMR1400 and CMR4. The calculated rate of Cr(VI) reduction for the first 4h was 1.4 ppm/h in both reactors in similar experimental conditions. In the case of CMR4, the amount of Pd, 0.75%, is lower than that of CMR1400, 0.9%. Considering this difference, it seems that the CMR with a lower nominal pore size is more active. However, considering the differences between the pore sizes of both reactors, the obtained activity is lower than expected. This result can be attributed to the lack in uniformity of the pore size distribution of the starting membrane. Another possibility is that the chromate reduction in this concentration and experimental conditions is kinetically limited.

The reaction results best fit with a first-order reaction with respect to the chromium concentration, as can be seen in Figure 4. R² obtained for these cases were 0.996 for CMR4 and 0.995 for CMR1400. From the results obtained with the CMRs, it can be deduced that part of the hydrogen gas flowing through the porous membrane matrix is activated on the Pd surface. Thereafter, the activated hydrogen reacts with the chromate anions dissolved in the water, reducing them. The reaction takes place predominantly at the solid-liquid-gas contact point (Pinos-Vélez et al., 2016a).

**CONCLUSIONS**

All prepared CMRs appeared to be active for generation of hydrogen peroxide directly from hydrogen and oxygen when tested in contactor interfacial mode at ambient conditions. Moreover, the catalytic membrane reactors with a single Pd catalytic phase are active either for phenol oxidation or for its hydrogenation. The reactions can be carried out under mild conditions (atmospheric pressure and at 60°C) and the prevailing reaction pathway can easily be chosen only by controlling the amount of dissolved oxygen in the solution. Following the oxidation pathway, the phenol can be eliminated through advanced oxidation processes. On the other hand, following the hydrogenation pathway, phenol is transformed into cyclohexanol and cyclohexanone. These findings suggest that a single CMR can successfully be used in AOPs or hydrogenation reactions. The catalytic membrane reactors can successfully be used for Cr (VI) to Cr (III) reduction with only hydrogen as reducing agent. In all cases, the Catalytic Membrane Reactor with smaller pore size presented the best performance. Thus, it was demonstrated that the pore size is important as far as performance is concerned.

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