Modification of tubular ceramic membranes with carbon nanotubes using catalytic chemical vapor deposition

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ABSTRACT

In this study, carbon nanotubes (CNTs) were successfully grown on tubular ceramic membranes using the catalytic chemical vapor deposition (CCVD) method. CNTs were synthesized at 650 °C for 3–6 h under a 120 mL min⁻¹ flow of C₂H₆ on ceramic membranes impregnated with iron salt. The synthesis procedure was beforehand optimized in terms of catalyst amount, impregnation duration and reaction temperature, using small pieces of tubular ceramic membranes. The yield, size and structure of the CNTs produced were characterized using thermogravimetric analysis and microscopic imaging techniques. Afterwards, preliminary filtration tests with alginate and phenol were performed on two modified tubular membranes. The results indicate that the addition of CNTs on the membrane material increased the permeability of ceramic membrane and its ability to reject alginate and adsorb phenol, yet decreased its fouling resistance.

Key words | carbon nanotube, CCVD, ceramic membrane

INTRODUCTION

Due to their high robustness, membrane processes have been employed in many industrial applications, such as textile, pharmaceutical, food and beverage processing, biotechnology industries, as well as water and wastewater treatment. Indeed membrane separation might reduce the number of unit operations in the production chain and could be easily automated (Drioli & Romano 2001; Saffaj et al. 2004; Kajitvichyanukul et al. 2011; Zhu et al. 2014). For harsh conditions such as high temperature (up to 350 °C) and aggressive chemicals, ceramic membranes are widely preferred by membrane operators (Luque et al. 2008).

Carbon nanotubes (CNTs) are nanoscale cylinders of rolled-up graphene with exceptional properties such as high mechanical strength, aspect ratio and electrical conductivity (Che et al. 1998; Hinds et al. 2004; Sears et al. 2010). In addition, the inherent porosity resulting from the tubular structure of CNT makes it become an interesting material for applications in separation processes. Previous works have demonstrated that CNTs can be added to membrane materials in order to create composite materials exhibiting high mechanical resistance, electrical conductivity and separation performances (Upadhyayula et al. 2009; Schnorr & Swager 2010). Thus, introducing CNTs to membrane technology might create a nexus for the development of innovative processes. Specifically, hybrid CNT/membrane materials could pave the way for interesting separation applications such as oil-in-water emulsion separation/stabilization, micropollutant removal and energy sensor technologies (de Lannoy et al. 2012; Gallagher et al. 2013).

Several attempts to fabricate CNT/polymeric composite membranes have been reported (Wu et al. 2010; Shawky et al. 2011; Celik et al. 2011). In contrast, the idea of modifying ceramic membranes with CNTs is still fairly new. Previously, CNTs were implanted in pore channels of a Y₂O₃–ZrO₂ membrane using chemical vapor deposition with nickel catalyst (Chen et al. 2012). However, no-one has performed CNT synthesis on a full-scale tubular ceramic membrane, nor has the performance of such a membrane been tested.

In this study, the modification of commercial tubular ceramic membranes with CNTs using the catalytic chemical vapor deposition (CCVD) method was investigated. To this end, metal catalyst precursors were formed on ceramic membranes by impregnation method using commercial FeCl₃ solution, while C₂H₆ was chosen as the carbon
source, as it has been reported to be an appropriate source for large-scale synthesis of CNTs (Gulino et al. 2005). The main objective of this work is to define the appropriate conditions for CNT growth on tubular ceramic membranes. Moreover, in order to preliminarily evaluate the filtration performances of the modified membranes, fouling and adsorption tests were performed at laboratory scale.

**METHODS**

**Membrane sample preparation**

The tubular ceramic membranes used in this study were purchased from Novasep (Kerasep® Mineral Membranes). These membranes exhibited a pore size of 0.2 μm and a filtration surface (inside–out) of about 50 cm² (length 23 cm, internal diameter 0.7 cm). The separation layer was made of ZrO₂-TiO₂ and the support layer consisted of monolithic TiO₂-Al₂O₃. To prepare samples for CNT synthesis optimization, a tubular membrane was cut into small crescent-shaped fragments of about 1 cm² in area. Before using, these pieces were washed thoroughly in milli-Q water (pH 6.8, 18 MΩ cm at 25 °C), dried overnight and stored separately in glass vials containing milli-Q water.

**Catalyst precursor preparation**

Metal salts were deposited onto the membrane pieces by wet impregnation method. Commercial FeCl₃ solution (41%, density = 1.45) and CaCl₂ (solid, 97%) were used as metal catalyst precursor and support, respectively. The impregnation of small membrane pieces was performed with solutions containing various iron/calcium weight ratios. The pieces were immersed in these solutions at room temperature for 1 h, then rinsed by compressed air and dried for at least 5 h at 105 °C. In necessary cases, double impregnation was applied by repeating the above impregnation method one more time using the exact procedure.

Once the optimized impregnation conditions were defined, two tubular membranes were impregnated using FeCl₃ solution only (the reason for this is explained in the result section). The first membrane (denoted K1) was impregnated by filtrating in inside–out mode an FeCl₃ solution containing 10 g Fe L⁻¹ for 15 min at 0.5 bar. The second membrane (denoted K2) was closed at one end and filled with a more concentrated FeCl₃ solution containing 135 g Fe L⁻¹. This membrane was left vertically for 1 h for impregnation.

**Synthesis of CNTs**

All impregnated membranes were calcined at 400 °C for 5 h in order to turn the deposited precursors into metal oxide forms. Temperature-programmed reduction (TPR) was performed afterwards on the test pieces to study the reduction profiles of the calcined samples, which determined the reaction temperature for the reduction step.

The reductions and CNT synthesis were performed, for both tubular membranes and test pieces, in a tubular quartz reactor placed inside a vertical furnace. In the first step, a 120 mL min⁻¹ flow mixture of H₂:He (ratio 1:1) was introduced to the reactor while the furnace was heated up to 650–750 °C and maintained at that temperature for 1 h. Subsequently, the H₂:He flow was replaced by a 120 mL min⁻¹ flow of C₂H₆ while the furnace temperature was adjusted to 650 °C to start the CNT synthesis process. The reaction time of CNT synthesis varied between 3, 6 and 16 h. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on the membrane pieces afterwards for CNT characterization.

**Filtration procedure on tubular ceramic membranes**

A laboratory-scale, crossflow ceramic membrane pilot (TIA, France) was used for all filtration tests. The setup includes a module for one single tubular ceramic membrane and a feed tank with a maximum volume of 5 L connected to a centrifugal pump. The crossflow rate can be controlled by adjusting the frequency of the pump while the operating pressure can be adjusted using the concentrate control valve. In all experiments, crossflow velocity was fixed at 3.12 m s⁻¹ (turbulent regime). All filtration tests were performed in inside–out mode at constant pressure. Two pressure sensors were installed before and after the module to measure the average transmembrane pressure (TMP). During filtration, temperature of the feed tank was kept at 20 ± 0.5 °C using a water bath circulator (Proline RP 845, LAUDA). Permeate volume was recorded by measuring the permeate weight every 10 seconds during filtration using an electronic balance (Sartorius, France). The membrane permeability was obtained by the pressure step method with different TMP values equal to 0.5, 0.75 and 1 bar using milli-Q water and was controlled before and after every filtration test or backwash. Backwash cleaning (outside in filtration) was performed at 1 bar in dead end mode using a pressure vessel of 5 L (Sartorius, France).
Alginate filtration tests were performed by filtrating 5 mg L\(^{-1}\) aqueous solution of sodium alginate at 1 bar, followed by backwashing the membrane with a mixture of 1:1 NaOH 0.25 M and NaClO 26% at 1 bar until a backwash volume of 500 mL was reached (Katsoufidou et al. 2010). Phenol filtration tests were performed by filtrating 50 mg L\(^{-1}\) aqueous solution of phenol at 1 bar, followed by backwashing by milli-Q water at 1 bar (Akay et al. 2002). During filtration tests, water samples from the permeate stream and feed tank were regularly taken for analysis. Alginate rejection was assessed by total organic carbon (TOC) measurements of the samples using a TOC-V<sub>CSH</sub> Analyzer (Shimadzu), while phenol concentration was analyzed by measuring the sample absorbance at 270 nm using a Cary® 50 UV-visible spectrophotometer (Varian). After each run, the pilot was cleaned by circulating milli-Q water several times to remove chemical residues. All filtration tests were performed on both the virgin and CNT-modified membranes to compare the potential effects that CNTs have on ceramic membranes.

### RESULTS AND DISCUSSION

#### Optimization of CNT synthesis on small membrane pieces

TPR and TGA were performed on samples prepared under different synthesis conditions as reported in Table 1. Four samples were double-impregnated for 1 h and then calcined at 400°C for 5 h before being analyzed by TPR. The results are presented in Figure 1(a).

The sample impregnated with only Fe (Fe-1) exhibited two reduction peaks at 382 and 500°C and the reduction of iron oxides was completed at around 575°C. The addition of Ca clearly had an effect on the reduction temperature, as for all three samples impregnated with both Fe and Ca, reduction processes only started at 500°C. The reduction peaks were observed at around 580 and 675°C, and the reduction could only be completed at above 700°C. The variations in Fe:Ca ratio among samples did not show a noticeable impact on their TPR profiles. Nevertheless, these results did determine the required reduction temperature to form metal catalyst particles on ceramic membranes, which has to be over 575°C for samples impregnated with Fe and over 700°C for samples impregnated with both Fe and Ca.

TGA was performed to qualitatively and semi-quantitatively study the presence of CNTs in the test pieces. A similar pattern can be observed among the TGA curves (Figure 1(b)), which is one major mass-loss event occurring between two very small mass-gain events. The mass-loss events occurred in a distinctive, non-stepwise fashion starting at near 500°C and ending at around 650°C. These losses could be attributed to the decomposition of CNTs, as amorphous carbon decomposes at around 200–500°C while the decomposition temperature

**Table 1** | Summary of samples for TPR and TGA analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Impregnation solution ((V = 15 \text{ mL})) contains</th>
<th>Synthesis time</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-1(^a)</td>
<td>1 g Fe</td>
<td></td>
<td>TPR</td>
</tr>
<tr>
<td>Fe/Ca-21(^a)</td>
<td>1 g Fe + 0.5 g Ca</td>
<td></td>
<td>TPR</td>
</tr>
<tr>
<td>Fe/Ca-11(^a)</td>
<td>1 g Fe + 1 g Ca</td>
<td></td>
<td>TPR</td>
</tr>
<tr>
<td>Fe/Ca-12(^a)</td>
<td>1 g Fe + 2 g Ca</td>
<td></td>
<td>TPR</td>
</tr>
<tr>
<td>Fe-3 h</td>
<td>2 g Fe</td>
<td>3 h</td>
<td>TGA</td>
</tr>
<tr>
<td>Fe-16 h</td>
<td>2 g Fe</td>
<td>16 h</td>
<td>TGA</td>
</tr>
<tr>
<td>Fe/Ca-3 h</td>
<td>2 g Fe + 2 g Ca</td>
<td>3 h</td>
<td>TGA</td>
</tr>
</tbody>
</table>

\(^a\)Samples double-impregnated.
of CNTs is higher in most cases, and has been reported to be around 500–700 °C (Murakami et al. 2003; Mansfield et al. 2010; Mezalira et al. 2011). The two small mass-gain events could be attributed to the re-oxidation of metallic contents in the samples upon increasing temperature. The amount of CNTs thus can be estimated from the mass-loss percentages obtained from TGA curves.

As expected, a longer reaction time (16 instead of 3 h) led to a higher amount of CNTs produced, as can be seen when comparing the mass loss percentages of the two samples impregnated with Fe (Figure 1(b)). However, sample Fe-16 h was partly broken after synthesis, suggesting it is not recommended to perform CNT synthesis on ceramic membranes at this temperature over such a long duration. The addition of calcium for impregnation resulted in better CNT yield than using iron only, as can be seen when comparing the mass loss percentages between sample Fe-3 h and Fe/Ca-3 h. This could be explained by a better iron dispersion in the presence of calcium; thus, more-accessible Fe catalyst particles were provided for CNT growth. It should also be noted that despite undertaking the same synthesis conditions, the membrane piece impregnated with Fe and Ca could only be reduced at a higher temperature, 750 °C, compared to 650 °C for the ones impregnated with Fe alone.

SEM images of a calcined sample impregnated with iron (Figure 2(a), (b)) show that iron particles were present throughout the membrane thickness. More importantly, the presence of CNTs could be observed in the samples after synthesis (Figure 2(c)). The diameter of the CNTs ranged from 20 to 50 nm while their length could be up to a few micrometres (Figure 2(c)). Finally, the TEM images reveal that the CNTs synthesized were multi-walled CNTs and the iron particles can be seen trapped inside the tubes (Figure 2(d)).

To summarize, CNTs were successfully synthesized on the membrane pieces using unsupported Fe catalyst and supported Fe/Ca catalyst. However, the latter method, despite producing better CNT yield than the former, required the reduction step to be performed at 750 °C, a high temperature that caused damage to the tubular membrane in one of our experiments. Hence, in the next phase of this study, only Fe precursor was used to impregnate tubular membranes. Synthesis was performed at 650 °C for 3–6 h under the same conditions applied to the membrane pieces.

CNT synthesis on tubular membranes

After the reduction step at 650 °C, CNT synthesis on tubular membranes was performed at 650 °C for 3 h for membrane

![Figure 2](https://iwaponline.com/wst/article-pdf/72/8/1404/466302/wst072081404.pdf)
K1 and 6 h for membrane K2. By appearance, after synthesis the color of both membranes turned dark, which was similar to the case of the membrane pieces. Unfortunately, due to the analytical tools used in this study, characterization of produced CNTs on tubular membranes was not possible, as SEM imaging and TGA would require breaking the membranes. Thus, electrical resistance was measured to serve as an indicator for the presence of CNTs (Hinds et al. 2004; de Lannoy et al. 2012). Indeed, virgin membrane was found to be not electrically conductive, while electrical resistance values of about 10 kΩ were recorded on both modified membranes. This suggests that the modified membranes were conductive materials, which is attributed to the presence of CNTs.

**Filtration performances of membranes modified with CNTs**

The same ceramic membrane, before and after synthesis, was used for alginate filtration tests. Membrane K1 was the virgin membrane and exhibited a pure water permeability of 850 L h⁻¹ m⁻² bar⁻¹. After alginate filtration at 1 bar for 42 min, its permeability decreased to 495 L h⁻¹ m⁻² bar⁻¹ and the backwash step revealed a total flux recovery. As shown in Figure 3, the pure water permeability of modified membrane K1-CNT increased dramatically by 60% (from 850 to 1,325 L h⁻¹ m⁻² bar⁻¹) compared to K1. However, after alginate filtration (1 bar, 42 min), its permeability decreased to 258 L h⁻¹ m⁻² bar⁻¹, which is 48% lower than the corresponding value of K1. This suggests stronger adsorption of alginate on the modified membrane. In addition, chemical backwash cleaning did not totally recover the pure water membrane permeability (flux recovery = 78%, permeability = 1,033 L h⁻¹ m⁻² bar⁻¹), suggesting an irreversible adsorption of alginate on CNTs. However, this recovered permeability was still higher than that of the virgin membrane K1.

Nevertheless, the alginate rejection rate for K1-CNT was higher. The rejection rate for alginate could be up to 90% for the CNT-modified membrane after 1.5 L of water was filtrated while it was only 75% for the virgin membrane (Figure 4(a)). These preliminary results indicate that CNTs have a positive effect on ceramic membranes in terms of organic matter rejection. Therefore, as suggested by this preliminary filtration test, the modified membrane exhibited a stronger organic matter rejection capability but a stronger
flux decline. However, chemical backwash cleaning showed a lower permeate flux recovery but the permeability value was still higher than that of the virgin membrane. As a preliminary conclusion, these results suggest that the filtration operation on CNT/ceramic membrane provides a better permeate quality but will need more frequent chemical cleanings in order to alleviate the stronger flux decline.

Rejection efficiencies during phenol filtration using virgin membrane K2 and CNT-modified membrane K2-CNT are presented in Figure 4(b). No fouling was observed during phenol solution filtration. In both cases a quick adsorption of phenol to the membranes can be observed at the very beginning of the filtration process. K2 became saturated after a permeate volume of 200 mL, whereas this preliminary filtration test on K2-CNT, despite not showing a significantly higher rejection rate at the beginning, proved to be more durable as it could still adsorb phenol for a longer period than the virgin membrane. The rejection rate of the K2-CNT decreased slowly and reached zero after 1 L of filtration volume. Interestingly, the adsorbed phenol on the modified membrane could easily be washed out later simply by backwashing with water. This opens the potential of repeated usage of the membrane to remove phenol.

CONCLUSIONS

To conclude, CNTs were successfully synthesized in situ on ceramic materials obtained from a commercial tubular ceramic membrane using the CCVD method with Fe as the unsupported catalyst and Fe as the catalyst supported by Ca. The CNTs produced were multi-walled CNTs, with a diameter of 20–50 nm and length up to a few micrometres. Though the method using Fe/Ca catalyst produced better CNT yield, its higher required temperature could potentially damage the tubular membrane. Consequently, the method using unsupported Fe catalyst was chosen for the synthesis of CNTs on tubular membranes. The applied methodology allowed CNT synthesis without damaging the ceramic materials. Thus iron precursor in the form of FeCl3 was chosen to impregnate the tubular membrane and perform reduction and synthesis at 650 ºC for 3–6 h using C2H6 as the carbon source. Preliminary filtration tests on two ceramic membranes using ‘optimal’ synthesis conditions, suggest a stronger rejection efficiency of alginate and phenol but exhibited more difficulty in recovering permeability even using harsh chemical backwash. The low improvement in separation efficiency might be explained by the low amount of CNT produced on the tubular membranes. However, further filtration tests on tubular membranes are needed to fully conclude on the role of CNTs on separation performances and to optimize the cleaning and filtration operations.

REFERENCES


Lueke, S., Gomez, D. & Alvarez, J. R. 2008 Industrial applications of porous ceramic membranes (pressure-driven processes). In: Inorganic Membranes: Synthesis, Characterization and...


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