CHEMICAL ENGINEERING TRANSACTIONS

VOL. 60, 2017

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Luca Di Palma, Elisabetta Petrucci, Marco Stoller

ISBN 978-88-95608- 50-1; **ISSN** 2283-9216

DOI: 10.3303/CET1760049

Modification of Hollow Fibre Membranes through Electron Beam Irradiation

Minh N. Nguyen, Nathalie Karpel Vel Leitner, Benoit Teychené

Institut de Chimie des Milieux et des Matériaux de Poitiers (UMR CNRS 7285) École Nationale Supérieure d'Ingénieurs de Poitiers (ENSIP), Université de Poitiers. 1 rue Marcel Doré, Bâtiment 1, 86022 POITIERS CEDEX, France.
benoit.teychene@univ-poitiers.fr

The capacity for secondary effluent filtration of hollow fiber polypropylene membranes grafted with several zwitterionic molecules and multi-walled carbon nanotubes was evaluated. In particular, all the modifications result in significant improvement of filtration performances. The anti-fouling properties of the membrane had been increased without damaging the membrane as observed from FTIR, TGA/DTA analyses. The loading of MWCNT increased both the resistance of the membrane to organic matters fouling and permeate quality thank to the adsorption on carbon nanotubes. However, upon irradiation of PP-MWCNT membranes, a proportion of CNT was degraded and some of its adsorptive characteristics deteriorated, although the membrane's filtration capability was still very impressive. Among the zwitterionic molecules, the best performers were the cysteine-modified membrane, followed by phosphocholine and DMAEMA.

1. Introduction

The swift expansion of the global population and economies has led to the occurrence of water scarcity and water quality degradation in many parts of the world. In this context, the research and development of efficient water treatment technologies is needed more than ever to meet the world's growing demand for fresh and clean water. Among the existing treatment technologies, membrane-based processes have become the most robust technique to treat polluted water. Indeed, thanks to their properties (various pore sizes, hydrophilicity…) membrane are able to simultaneously separate a wide variety of pollutants (bacteria, viruses and organic compounds) from many water sources without using toxic or harmful chemicals (Mulder, 1996) . However, membranes suffer from fouling, which refers to the accumulation of rejected matter at the membrane surface. Fouling strongly impacts treatment operating cost by increasing cleaning procedure frequency, and consequently reducing membrane life time (Cha et al. 2000; Chen & Fane, 2008). Many studies were dedicated to understand and mitigate membrane fouling. As intensively reported, a sustainable membrane for water treatment should have a hydrophilic surface in order to avoid the adsorption of foulant species (Liu et al. 2009; Ochoa, 2003; Zhao et al. 2013). The most common method to improve membrane hydrophilicity is to blend membrane polymer with polyvinylpyrrolidone (PVP). However, many works report on the leakage of PVP during membrane cleaning due to chlorine (Causserand et al. 2015) . Therefore, other routes to improve membrane hydrophilicity and fouling resistance are needed.
The present study investigates the modification of commercial membranes by electron beam irradiation in order to improve filtration performances. Electron beam irradiation is a versatile technique to induce cross linking in polymers (Le Moel et al. 2986; Zhu & Xu, 2006; Nasef et al. 2006; Schulze et al. 2010 & 2013). Indeed, irradiation induced changes in polymer matrix due to radical-involved reactions, recombination without the need of strong chemicals for pre-treatment and consequently might be considered as a "green routes" to modify membranes materials. In this study, three zwitterionic molecules were grafted on the polypropylene hollow fibre membranes induced by electron beam (EB) irradiation. It had been reported that zwitterionic molecules could effectively alleviate membrane fouling (Lin et al. 2014; Zhao et al. 2013). In addition, the modification of hollow fibre with multi-walled carbon nanotubes (MWCNT) was tested and the impact of electron beam irradiation on the MWCNT-loaded membrane was investigated. MWCNT is known for its

Please cite this article as: Nguyen M., Karpel Vel Leitner N., Teychene B., 2017, Modification of hollow fiber membranes through electron beam irradiation, Chemical Engineering Transactions, 60, 289-294 DOI: 10.3303/CET1760049

adsorptive properties towards organic foulants (Lu & Su, 2007; Pan & Xing, 2008; Wang et al. 2009), thus preventing cake formation at the membrane surface.

2. Materials and methods

2.1 Feed water characteristics and filtration procedure

Filtration tests were carried out with a secondary effluent (SE) sampled from Saint Julien l'Ars wastewater treatment plant (June 2016, Poitiers, France). The effluent was prefiltered using a 200 µm sieve to remove coarse materials and stored in dark at 4 °C for a maximum of 10 days. All the experiments were conducted at room temperature (approximately 20 °C). The total organic carbon (TOC) content of the secondary effluent was approximately 7 mg_C/L.

Prior to every filtration test, the permeability of the pristine or modified hollow fibre membranes was evaluated with the flow step procedure by varying permeate flux from 1 to 4 mL/min using Milli-Q water (20 °C). Filtration tests were carried out using a fully automated lab-scale filtration unit using home-made membrane modules (consisting of 2 fibres 20 cm in length; 15 cm^2 of surface area) according to the procedure described elsewhere (Touffet et al. 2015). The filtration was operated in dead end inside-out mode at 80 $L/h/m^2$ (2 mL/min) for 45 minutes, interspersed by membrane backwash (outside-in mode using permeate solution) at 127 $L/h/m^2$ (4 mL/min) for 2 minutes. The filtration tests duration was set for 24 h or until reaching a maximum pressure of 1.5 bars in order to avoid membrane bursting. The extent of fouling was characterized by the cake fouling resistance R_C (m^{-1}), which could be calculated using Eq(1).

$$J = \frac{\Delta P}{\mu_{20^\circ C}(R_m + R_c)} \qquad (1)$$

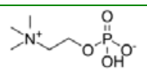
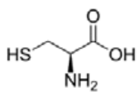
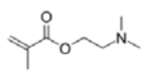
In which J is the permeate flux ($L/h/m^2$), ΔP is the transmembrane pressure (bar), $\mu_{(20°C)}$ is the water viscosity (bar.s) and R_m and R_C are the membrane hydraulic resistance and cake fouling resistance (m^{-1}), respectively.

2.2 Membranes and modification procedures

The hollow fibre membranes were purchased from ACCUREL®, (PP300/1200 Membrana, 3M GmbH). The membranes consisted of polypropylene fibre with an inner diameter of 1.8 mm, a wall thickness of 300 µm and a nominal pore size of 0.2 µm. According to the manufacturer, the permeability of the membrane module was 3060 L/h/bar and the bubble pressure was 1.17 bar.

Membranes were modified using L-Cysteine, DMAEMA, phosphocholine and MWCNT followed by electron beam irradiation. The respective chemical structures of the investigated molecules are given in Table 1. The three graft molecules were purchased from Sigma (Aldrich, France) and the MWCNTs (O.D: 10−20 nm and 10−30 µm in length) were purchased from CheapTube (USA).

Table 1: Properties of the investigated molecules

Molecule	Full product name	Formula	MW (Da)	Log P (ACD predicted values / ChemSpider)
Phosphocholine	Phosphocholine chloride calcium salt tetrahydrate		183.143	−4.99
Cysteine	L-Cysteine > 99.5%		121.158	0.23
DMAEMA	2-(Dimethylamino)ethyl methacrylate		157.210	1.50

For grafting with hydrophilic molecules, prior to irradiation, the membranes were filtrated with and submerged in the respective 10 mg/L graft molecule solutions (dissolved in Milli-Q) for 24 hours. The filtration with graft molecules was performed to enhance the interactions between the graft molecules and the inner surface of the membrane module. In contrast, membranes containing MWCNT (5 mg/m^2) were produced according to the previous reported procedure (Gallagher et al. 2013). This methodology allows producing stable MWCNT mats on the membrane lumen. The pristine and EB membranes were submerged in Milli-Q water only. Electron beam irradiation was performed on a semi-industrial electron accelerator (3 MeV Van de Graaff, VIVIRAD, France). In the irradiation process, the selected membrane modules were concealed inside plastic bags filled with nitrogen gas. Subsequently, the bags were placed on a conveyor and delivered through the electron beam source (2600 kV, 195 μA) at a speed of 0.6 cm/s. The corresponding irradiation dose was set at 10 kGy. It has to be noted that the polypropylene membrane cannot withstand an irradiation dose above 50 kGy (Makuuchi & Cheng, 2011).

2.3 Analytical tools

The membrane surfaces were characterized by ATR-FTIR (Thermo Nicolet NEXUS, GMI Inc.) and X-ray microtomography (Viscom X8050-16, France). The thermal properties of the materials were investigated through Differential Thermogravimetric Analysis (TGA/DTA) (SDT Q600, TA Instruments, France). Organic matter rejection during filtration tests were analysed by Liquid Chromatography − Organic Carbon Detection (LC-OCD). The LC-OCD system contained a 0.5 μm size-exclusion chromatography (SEC) column (ReproSil 200, France). The mobile phase consisted of 20 mmol L^{-1} of Na_2HPO_4 at pH 6.8. The flow rate was set at 1 mL/min[1].

3. Results and discussions

3.1 Characterization of the modified hollow fibre membranes

As shown in TGA results (Figure 1-a), the degradation of the pristine PP membrane occurs between 200 °C and 400 °C. As expected, adding MWCNT onto the membrane lumen did not change the thermal degradation of the membrane, and results show that MWCNT thermal degradation occurred between 400 °C and 600 °C. Figure 1-b shows that a thin MWCNT layer was deposited on the membrane inner surface. The membranes grafted with zwitterionic molecules (PP-CYSTE is shown Figure 1-a) show similar TGA results as the pristine, demonstrating that little polymer deterioration was induced by the low irradiation dose used (10kGy).

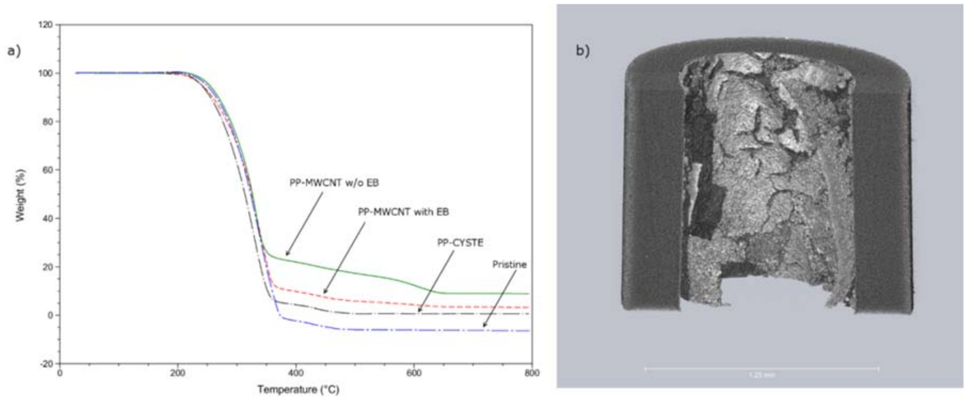


Figure 1: (a) TGA results obtained for the pristine, PP-CYSTE membrane and PP-MWCNT (5 mg/m^2) membranes with and without irradiation. (b) 3D cross-section of hollow fibre obtained by X-ray microtomography of a PP-MWCNT (5 mg/m^2) membrane dried at room temperature. Surface cracking comes from MWCNT layer shrinkage during drying.

The FTIR spectra for the internal surface (Figure 2-a) of the irradiated module without molecule grafting confirmed the chemical changes in the PP, probably due to oxidation resulting in the formation of carbonyl or amide groups (Mirabedini et al. 2004). The doublet at 1631 and 1659 cm^{-1} might be related to the carbonyl groups. The O−H stretching vibrations were represented by two peaks at 3184 and 3358 cm^{-1} (data not shown). These peaks decreased in intensity seen for the modules in the presence zwitterionic molecules, suggesting that the presence of these molecules reduce the occurrence of functional groups formed by EB. However, as shown in Figure 2-a, the variation between membranes in the presence of different zwitterion molecules was not significant.

In contrast, strong changes were observed on the external surface of irradiated HF membranes (figure 2-b). As indicated, four main changes were observed at 1409, 1425, 1631 and 1659 cm^{-1}, respectively. These changes might be attributed to the formation of hydrophilic groups induced by irradiation and the grafting of the zwitterions. Interestingly, the presence of different graft molecules varied the intensity of these bands observed for the outer surface. The bands increase follows this order: EB-only, phosphocholine, cysteine and DMAEMA. According to Log P values reported in table 1, DMAEMA is the most hydrophobic compound; consequently, it is more susceptible to adsorption on the hydrophobic polypropylene membrane before irradiation, thus the band intensity is highest because the grafting was most efficient with DMAEMA.

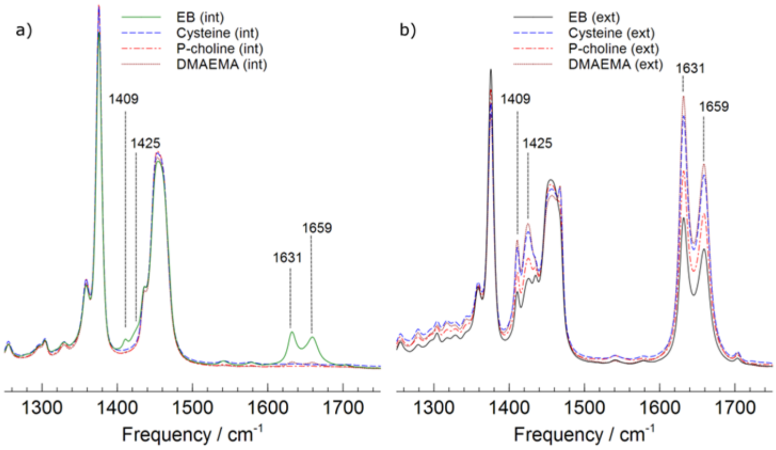


Figure 2: ATR-FTIR spectra obtained for the modified membranes on the internal surface (a) and external surface (b).

3.2 Filtration performances of modified membranes

As shown, in Figure 3-a&b, the transmembrane pressure strongly increases during the filtration of SE on pristine PP membranes. As reported, the maximum pressure equals to 1.5 bars was reached in only 320 minutes corresponding to a filtered volume of 274 L m^{-2} (7 cycles). These results demonstrate that membrane backwash are not enough efficient to remove fouling and irreversible fouling layer quickly accumulate in the membrane lumen (Nasef et al. 2006, Ye et al. 2005) . Adding MWCNT inside the membrane lumen strongly reduce the TMP increase and allow longer filtration time. Indeed, the maximum pressure allowed by the filtration system was reached after nearly 861 L m^{-2} of filtration corresponding to 22 cycles. As previously reported, MWCNT might protect the membrane surface from pore blockage by adsorption phenomena and might also structure fouling layer to avoid highly compressible organic matter layer formation at higher pressure (Gallagher et al. 2013, Wang et al. 2009). Irradiation of the pristine membrane has also a beneficial effect of TMP increase. In early stage of filtration, the TMP quickly increases and then levelled off. The maximum TMP was observed after 18 cycles (704 L m^{-2}) indicating that the slight change observed on the irradiated membrane has a strong impact on membrane resistance to fouling. This might be attributed to a possible change in materials hydrophilicity after electron beam irradiation, due to the formation of hydrophilic functional groups (C=O, O-H, COOH) on membrane surface. Irradiation on the PP-MWCNT membrane has further positive effect in the fouling resistance of the membrane (25 cycles of filtration). Similarly, modification of the membrane with zwitterion molecules shows significant improvement in membrane filtration performances. The best performers were the cysteine-modified membranes with an average filtration volume of 821 L m^{-2}, followed by phosphocholine (704 L m^{-2}) and DMAEMA (626 L m^{-2}).

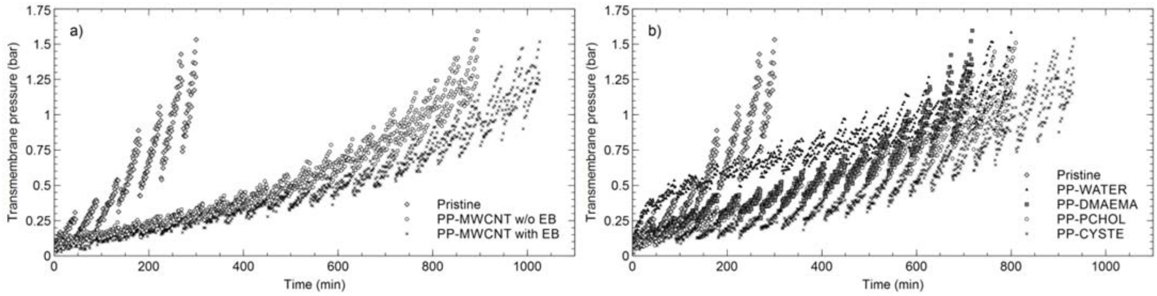


Figure 3: Transmembrane pressure (TMP) increase during filtration of SE through the pristine and modified hollow fibre membranes - (a) with MWCNT with and without irradiation at 10 kGy, and (b) with zwitterionic molecules. Inside-out filtration in dead end mode at a constant flux of 52 L/h/m^2).

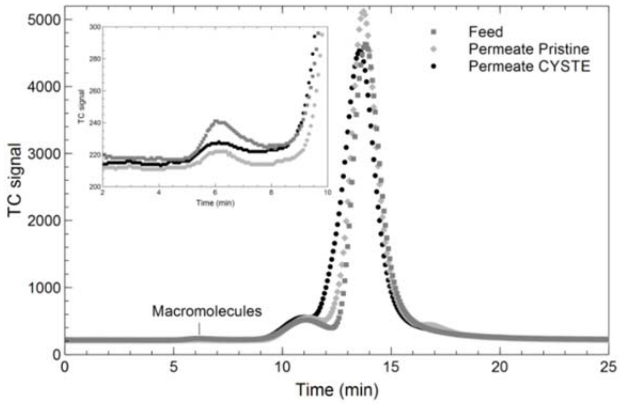


Figure 4: LC-OCD analysis of the SE feed waters, permeate obtained on pristine membrane and cysteine grafted membrane filtration.

Despite the slight change in internal surface modification revealed by ATR-FTIR analysis, hollow fibre membranes undergone electron beam irradiation have a strong resistance to cake fouling during SE filtration. According to Table 1, cysteine has a Log P value close to zero, thus the best performing membranes might be grafted with neither hydrophilic nor hydrophobic molecules. In addition to TMP increase the quality of the permeate solutions was also monitored using LC-OCD analysis. An example of LC-OCD chromatogram was provided in Figure 4 and all results obtained by TOC peak integration for macromolecules were reported in Table 2. As seen, the SE organic matters consist of macromolecular (HMW) compounds with an elution time of around 6 min and low molecular weight (LMW) compounds exhibiting an elution time of about 14 min. As shown, the pristine membrane efficiently removed the macromolecular compounds but has no impact on LMW compounds content. In contrast, PP-Cysteine membrane slightly rejected the HMW compounds but better rejected the LMW. The rejection of HMW compounds obtained on all investigated membranes is reported in Table2. As shown, the lowest rejection was obtained for the PP-DMAEMA membranes with only 15 % of rejection. The highest was obtained for the MWCNT w/o EB membranes with 81 % of rejection. This high value is attributed to the strong adsorption capacity of MWCNT deposited on the membrane. Interestingly, the irradiation MWCNT exhibited similar rejection as the pristine membrane, indicating that irradiation strongly decreased the adsorption capability of CNT.

Table 2: Macromolecule rejection efficiency obtained from TOC peak integration

Molecule	Pristine	PP-WATER	PP-PCHOL	PP-DMAEMA	PP-CYSTE	MWCNT w/o EB	MWCNT with EB
Efficiency (%)	40.6	23.0	30.2	15.2	36.5	81.1	40.5

Despite their strongly improved resistance to fouling, PP-Cysteine membranes showed similar rejection compared to the pristine membranes (Table 2). This results suggest that hollow fiber irradiation in presence of Cysteine molecules led to the development of an efficient membrane material.

4. Conclusions

The hollow fiber PP modules were successfully modified in the presence of zwitterionic graft molecules and MWCNT. All the modifications result in significant improvement at secondary effluent filtration performance. At low irradiation dose (10 kGy), the anti-fouling properties of the membrane had been increased without damaging the membrane, as seen from FTIR, TGA/DTA analysis and TC measurements for macromolecules. Interestingly, the changes in FTIR spectra were correlated to the Log P values of the investigated zwitterionic molecules. The best performer among the investigated zwitterionic molecules was the Cysteine compounds leading to strong fouling reduction and to macromolecular rejection upholding.

The formation of MWCNT mats at the membrane lumen increased both the membrane fouling resistance and permeate quality thank to the adsorption of carbon nanotubes. This unique geometry allow to stabilize the CNT layer indicating the membrane-MWCNT could be backwashed without losing the MWCNT benefit effect. However, upon irradiation of MWCNT-HF membranes, a proportion of CNT was degraded and some of its adsorptive characteristics deteriorated, although the membrane's filtration capability was still very impressive.

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