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M.N. Nguyen, Patrick Loulergue, N. Karpel, B. Teychene. Electron beam irradiation of polyvinylidene fluoride/polyvinylpyrrolidone ultrafiltration membrane in presence of zwitterions molecules evaluation of filtration performances. *Radiation Physics and Chemistry*, 2019, 159, pp.101-110. 10.1016/j.radphyschem.2019.02.029 . hal-02090014

**HAL Id: hal-02090014**

**<https://univ-rennes.hal.science/hal-02090014v1>**

Submitted on 16 Apr 2019

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Membrane in Presence of Zwitterions Molecules evaluation of filtration performances

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**Abstract:**

In this research, the commercial PVDF/PVP membrane was irradiated at 10 and 100 kGy with electron beam (EB) to improve its fouling resistance capacity. Membrane irradiation was conducted in the presence of zwitterionic molecules (L-Cysteine, Phosphocholine) and with 2-(Dimethylamino)ethyl methacrylate). The main goal was to investigate the impact of irradiation in presence of zwitterions on the modification route of PVP within the polymer blend and to relate it to filtration performances. Globally, EB irradiation enhanced the membrane's filtration performance but this improvement cannot be sustained after several filtration cycles. Membranes irradiated with the lower absorbed dose (10 kGy) displayed higher permeate flux and lower cake resistance than membranes irradiated with the 100 kGy dose. The best sustainable anti-fouling capacity was observed for the membrane irradiated with 10 kGy in the presence of L-Cysteine. Membrane characterization showed that the membrane surface was modified by EB irradiation, with features such as smoother surface, modification of PVP and increased amount of crosslinking emphasizing the potential formation of PVP hydrogels. Despite obvious changes observed on membrane surface depending on the chosen compounds used for irradiation, membranes' analyses failed to identify sulphur, phosphorous grafted moieties. From this study, it is confirmed that membranes EB irradiation in presence of zwitterionic molecules is a promising technique to modify the PVDF/PVP blended polymer.

**Keywords :** electron beam, fouling, ultrafiltration modification, PVDF, PVP, zwitterions.

Due to their significant advantages, membranes processes are becoming popular separation technologies in water treatment field [1]. The membrane properties and physico-chemical interactions with filtrated compounds are a key factor in process efficiency [2]. Indeed, polymeric membranes (such as PVDF, PES and polyamide) dominate the water and wastewater treatment market. Such materials are mostly hydrophobic and induce strong interactions with fouling compounds, leading to an inevitable irreversible resistance build-up at the membrane surface or inside its pores during process operation. Such phenomenon, defined as fouling, inevitably causes membrane replacement, which increases the water production costs and induces environmental impacts. Therefore, controlled or reduced membrane-foulant interactions might lead to a sustainable separation process.

In the recent years, several works were dedicated to membrane modification as reviewed [3, 4]. Due to their excellent mechanical and chemical properties, much attention has been paid to PVDF polymer membranes modification and processing in the past years [5]. Beyond directly blending with additives (such as poly(N-vinylpyrrolidone)) or bulk modification before polymerization process, modifications of membrane surface by crosslinking, coating or deposits have been widely investigated to change the membrane properties [6]. The modified membranes can be applied in fuel cell, pharmaceutical, and pollution remediation [7, 8].

Among all existing modification routes of already polymerized membranes, irradiation techniques, such as with electron beam (EB) or plasma, seem to be one of the most efficient, since they usually require no or little solvent, no catalyst or additives and can be done at ambient temperature [9, 10]. Since the first report written by Timmerman and Greyson (1962), EB irradiation of PVDF materials has been intensively studied [11]. Due to the oxidative conditions caused by the EB irradiation process, changes such as carbon double bond formed under inert atmosphere and carboxyl group formation, mainly formed in presence of oxygen, are commonly observed in FTIR absorbance polymer spectra [12, 13].

Several works were dedicated to the development of low fouling membranes using zwitterion molecules grafting upon membranes' surface [14]. Zwitterions bear both cationic and anionic groups; consequently, electrostatic charges, hydrogen bonds and hydration properties might be tuned depending on pH, facilitating water transport through the membrane [15]. Alswieleh et al. (2014) demonstrated that amino acid-based antifouling materials might be used to strongly reduce biofouling [16]. Such zwitterion molecules mimic nature and conducted to low protein adsorption by inducing strong hydration layer near the membrane surface which is suitable for biofluids filtration operation [17, 18]. Shi et al. (2011) found that lysine-grafted PAN membranes exhibited fouling resistance both during static and dynamic filtration when exposed to protein suspension at neutral pH [19]. Indeed, at neutral pH, the amino and carboxyl groups of lysine are protonated and deprotonated respectively inducing strong repulsive forces preventing protein adsorption.

Most of membrane manufacturers add poly(N-vinylpyrrolidone) (denominated PVP) during polymerization process in order to increase membrane hydrophilicity and control pore structure [3]. Due to its properties (electrostatic interactions, PVP-water hydrogen bonds...), PVP might be considered as zwitterions in water [20, 21] and its zwitterionic properties might be enhanced by EB irradiation [22, 23]. Intensive works were done on the modification of PVP through pulsed EB irradiation [24]. In aqueous deoxygenated solutions, reactive radical intermediates are formed in the PVP polymer chains (called carbon-centred free radicals) due to water radiolysis products: hydroxyl radicals, ( $\bullet\text{OH}$ ,  $0.29 \mu\text{mol J}^{-1}$ ), hydrated electrons ( $e_{\text{aq}}^{-}$ ,  $0.29 \mu\text{mol J}^{-1}$ ) and protons ( $\text{H}\bullet$ ,  $0.06 \mu\text{mol J}^{-1}$ ), together with  $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ ,  $\text{H}^+$  and  $\text{OH}^-$  [25]. Carbon-centred free radicals can recombine via inter- or intra-molecular cross-linking, disproportionation, chain scission, radical transfer (through H-abstraction) and radical recombination [26]. It has been shown that inter-molecular crosslinking was usually observed at low doses (5 kGy) while intra-molecular recombination predominated at higher dose [24].

In the present study, the impact of PVP modifications through EB irradiation on membrane filtration performances (fouling resistance and organic matter rejection) was assessed through lab scale multi-

cycle filtration tests. In order to better control potential degradation effect of PVP during irradiation process, it was proposed to irradiate membrane materials in presence of two zwitterions (L-(+)-Cysteine and phosphocholine) and the 2-(Dimethylamino)ethyl methacrylate. The follow research questions will be taken into account (i) Does EB irradiation enhance the anti-fouling capacity of commercial UF PVDF/PVP membrane and is this improvement sustainable for long term membrane use? (ii) Do polymer modification routes might be controlled by the presence of zwitterion compounds during irradiation?

## 2. Materials and method

### 2.1. Materials and reagents

The membrane modified in this study was a commercial flat-sheet PVDF product with 0.1  $\mu\text{m}$  pore size (PLEAIDE® ORELIS Environment Co., France). The membrane consists of two layers: a functional layer made of PVDF and PVP and a supporting layer consisting of unwoven polyesters. The exact molecular weight of PVP and potential other additives are not known as the membrane fabrication process is patent protected but it is nevertheless understood that relatively high molecular weight of PVP ( $\approx 90$  kDa) are preferred to the sake of processing [27]. Information about the zwitterionic molecules is shown in Table 1. Two zwitterionic molecules were chosen the L-(+)-Cysteine and the phosphocholine. These compounds are part of many protein, enzymes and were chosen in order to influence PVP recombination during irradiation (radicals scavenging) and to potentially introduce sulphur or phosphorous moieties [28, 29]. The 2-(Dimethylamino)ethyl methacrylate (DMAEMA) is commonly used as crosslinker with PVP [30-32]. L-Cysteine (CAS 52-90-4) was purchased from Fluka; phosphocholine chloride calcium salt tetrahydrate (CAS 72556-74-2) and 2-(Dimethylamino)ethyl methacrylate (DMAEMA, CAS 2867-47-2) were purchased from Sigma-Aldrich. From the above, zwitterion molecules solutions (0.1 wt%) in Milli-Q water were prepared by dissolving 0.25 g of L-Cysteine and phosphocholine salt powder and DMAEMA liquid in 250 mL of Milli-Q water. The foulant surrogate selected for the filtration

test was sodium alginate (CAS 9005-38-3, purchased from Sigma-Aldrich, USA), which has been shown to efficiently mimic the properties of bio-macromolecular foulant naturally occurring in surface water [33]. The feed water contained sodium alginate at a concentration of 5 mg/L. The pH of the feed was kept constant at 7.6 using a buffer of NaCl and Na<sub>2</sub>CO<sub>3</sub>.

## 2.2 Membrane modification procedure

PVDF membranes were prepared in circular pieces with a diameter of 4.5 cm, thus allowed an effective filtration area of 13.4 cm<sup>2</sup>. All membranes were thoroughly cleaned and submerged in Milli-Q water for 48 hours at 4°C to remove the preservative inside the pores. Subsequently, the permeability tests were conducted with Milli-Q water at various transmembrane pressures ranging from 0.5 to 1 bar. The permeability of all the investigated membranes was equals to  $900 \pm 5 \% \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ , outlier membranes were discarded in order to reduce experimental error. . Prior to EB irradiation, all membranes except the pristine membrane (PVDF-Pristine) and the irradiated membrane without any molecules (PVDF-Water) were submerged in 25 mL of their respective 0.1 wt% graft solutions for 24 hours. Pristine and PVDF-Water were submerged in Milli-Q water instead. The radiation dose of choice was 10 kGy, although a higher dose equals to 100 kGy was selected to study the effect of absorbed dose variation on the membrane's filtration performance. It is noted that the PVDF membrane can tolerate a very high EB irradiation dose of 1,000 kGy, so no membrane disintegration is expected [34]. EB irradiation of the membranes was performed with a pilot scale Van De Graaff electron beam accelerator (Vivirad France, 3 MeV, 0.5 mA, 43 cm scan width).

For the wet-phase irradiation process, the membranes were taken from the solutions and placed inside plastic bags filled with nitrogen gas. Subsequently, the bags were placed on a belt-conveyor to be exposed under the beam and moved back and forth at a speed of 1.0 cm/s. The operating voltage and current of the EB accelerator were 2,600 kV and 195 μA, respectively. The absorbed dose depended on the number of passes of the membranes through the EB, with one pass

### 2.3. Filtration set-up and procedure

#### 2.3.1 Total organic carbon (TOC) analysis

The organic content throughout the filtration experiment was controlled by thermal TOC measurement with a Shimadzu TOC-V<sub>SSH</sub> (Shimadzu Co., Japan) in non-purgeable organic carbon mode. The detection limit was 0.1 mg<sub>C</sub> L<sup>-1</sup>. Each permeate sample was analyzed in triplicate. The calibration curve was obtained using potassium hydrogen phthalate solutions with concentrations ranging from 0 to 10 mg L<sup>-1</sup>.

#### 2.3.2 Filtration

All filtration tests were conducted at room temperature (20±2 °C). Prior to filtration tests, the irradiated membranes were submerged in Milli-Q water for 48 hours and filtrated with at least 500 mL of Milli-Q water to remove any potential homopolymers formed during irradiation process. Membranes cleaning was stopped when TOC values reached approx. 0.1 mg L<sup>-1</sup> (i.e. approaching the TOC value of Milli-Q water).

Then the membranes were placed inside a 50 mL Amicon® stirred cell (EMD Millipore Corp., USA) connected to a 10 L dispensing pressure vessel (EMD Millipore Corp., USA), containing the alginate feed water. For every filtration experiment, 5 mg L<sup>-1</sup> of sodium alginate solution in NaCl/Na<sub>2</sub>CO<sub>3</sub> buffer was used as the feed (feed volume of 5 L). The pH of the feed solution was maintained at 7.6. The measured TOC content of the feed solution was approximately 1.75 mg L<sup>-1</sup>, which is representative to natural surface waters [35]. During the filtration stage, a constant transmembrane pressure of 0.5 bar was induced, and the permeate volume was recorded every 10 seconds using an electronic balance (OHAUS Corp., USA) until 150 mL of permeate was obtained. The average permeate flux (over 10 min period) was determined as a function of specific permeate volume (m<sup>3</sup> m<sup>-2</sup>) using Equation 1:

$$J = \frac{1}{S} \frac{\Delta V}{\Delta t} \quad \text{Equation 1}$$

In which,  $J$  is the flux through the membrane ( $\text{L m}^{-2} \text{h}^{-1}$ ),  $\frac{\Delta V}{\Delta t}$  is the volumetric flow rate ( $\text{L h}^{-1}$ ), and  $S = 13.4 \text{ cm}^2$  is the effective filtration area.

When the filtered volume reached  $0.1 \text{ m}^3 \text{ m}^{-2}$ , a backwash step was performed with Milli-Q water. For this, the alginate feed solution in the pressure vessel was removed and the membrane was placed upside-down. Backwashes were performed at 1 bar with 50 mL of Milli-Q water. Subsequently, the conditions were switched for the next filtration cycle. For every membrane, 4 filtration-backwash cycles were operated. An aliquot of permeate was collected at the middle of each cycle for TOC measurement.

### 2.3.3 Specific cake fouling resistance

It is assumed that concentration polarisation only occurs at the very beginning of each filtration tests, *i.e.* the foulant concentration at the membrane surface is equal to that in the bulk. Thus, the specific cake fouling resistance  $\alpha$  can be calculated using Equation 2:

$$\frac{t}{V} = \frac{\mu}{S \Delta P} \left( \frac{\alpha C_{bulk} V}{2 S} + R_m \right) \quad \text{Equation 2}$$

In which,  $\alpha$  is the specific cake resistance ( $\text{m kg}^{-1}$ ),  $R_m$  is the membrane hydraulic resistance ( $\text{m}^{-1}$ ),  $\mu$  is the dynamic viscosity of the feed solution at  $20^\circ\text{C}$  ( $\text{Pa s}$ ),  $C_{bulk}$  is the TOC content of the feed solution ( $\text{kg m}^{-3}$ ),  $S$  is the effective filtration area ( $\text{m}^2$ ), and  $\Delta P$  is the transmembrane pressure ( $\text{Pa}$ ).

It was assumed that the viscosity of the feed solution was similar to that of pure water.

Compared to the classical fouling layer hydraulic resistance, the cake layer specific resistance takes into account the amount of deposited foulant on membrane surface. It thus allows the



straightforward comparison of fouling extent of membranes having different rejection ability (and thus different amount of deposited material).

#### 2.4. Membrane material characterization

Atomic Force Microscopy (AFM) was performed in tapping mode with the AFM 5500 equipment (Keysight Inc., USA). The probes used were the AppNano ACT-50 (NanoScience Instruments Inc., USA). A new probe was used for each membrane analysis. The images were generated for a surface size of  $5.0 \times 5.0 \mu\text{m}$ . The topography images were produced for calculating the membrane roughness, Feret's diameter, defined as the equivalent pore size diameter, (using ImageJ software) and the phase images were for identifying polymer properties modifications (hydrophobicity and stiffness). From the topographic patterns, it was possible to develop the Material Ratio curves (also known as the Abbott–Firestone curves), which allowed to obtain the surface roughness profile, including the root-mean-square (*RMS*) roughness [36, 37].

Attenuated Total Reflectance – Fourier Transform Spectroscopy (ATR-FTIR) was performed with the Thermo Nicolet NEXUS spectrometer (GMI Inc., USA), in the wavenumber range of  $4000\text{--}650 \text{ cm}^{-1}$  and at a resolution of  $4 \text{ cm}^{-1}$ . A total number of 16 scans were recorded for each membrane sample.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed with the Q600 SDT thermal analyser and TA Universal Analysis software (TA Instruments Inc., USA). The membrane samples were prepared in small pieces ( $2\text{--}4 \text{ mm}^2$  in size) and placed in a  $40 \mu\text{L}$  platinum sample pan. For each measurement, the mass of membrane in the sample pan was  $3.5\text{--}5.0 \text{ mg}$ . The samples were heated in air from room temperature to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}$  per minute.

X-ray Photoelectron Spectroscopy (XPS) was performed with the KRATOS Axis Ultra DLD equipment (KRATOS Analytical Ltd., UK), deploying a monochromatic Al excitation source at  $150\text{W}$ . The resolutions were  $1.0 \text{ eV}$  for survey scans (pass energy  $160 \text{ eV}$ ) and  $0.1 \text{ eV}$  for high

resolution scans in the carbon region (pass energy 20 eV). The analysed membrane surface area was  $300 \times 700 \mu\text{m}$  and the X-ray penetration depth was 10 nm. The sensibility factors were selected according to Wagner (1983) [38].

The zeta potential of the membranes was determined by mean of transversal streaming current measurements. A SurPASS electrokinetic analyzer (Anton Paar GbmH, Austria) was used. It is equipped with an adjustable-gap cell containing 2 membrane samples (length 2 cm and width 1 cm) fixed using double-sided adhesive tape. The distance between the 2 membrane samples was set to  $100 \pm 2 \mu\text{m}$  thus forming a channel in which the electrolyte solution ( $\text{KCl } 10^{-3} \text{ mol L}^{-1}$ ) can flow. After equilibration by circulating the electrolyte solution for 2 hours, the streaming current was measured by means of a pair of large-area Ag/AgCl electrodes and recorded for increasing pressure difference up to 300 mbar. The flow direction was changed periodically. All experiments were performed at room temperature ( $20 \pm 2 \text{ }^\circ\text{C}$ ) under a controlled atmosphere (nitrogen gas).

### 3. Results and discussion

#### 3.1 Filtration performances evaluation

Filtration performances were investigated through multicycle dead-end filtration tests using alginate solution and performed at 0.5 bars ( $20^\circ\text{C}$ , unstirred condition). At the first moments, the initial flux was selected at the point where approximately 1 mL of permeate had been obtained. As shown in Figure 1 and Table 2, the initial permeate flux (obtained after 10 min of filtration) was equal to  $114 \text{ L h}^{-1} \text{ m}^{-2}$  for the pristine membrane. This value was much lower than the pure water flux obtained at the same pressure ( $450 \text{ L h}^{-1} \text{ m}^{-2}$ ). Such strong decrease might be attributed to the concentration polarisation phenomena quickly building up at the very beginning of the unstirred filtration test [39].

Irradiated membrane at 10 kGy (Water-10kGy) exhibited similar initial permeate flux equals to  $132 \text{ L h}^{-1} \text{ m}^{-2}$  whereas 100 kGy irradiated membrane (Water-100kGy) showed a lower flux equals to

102 L h<sup>-1</sup> m<sup>-2</sup>. Beside concentration polarisation phenomena irradiation at 100 kGy might change membranes' structure and surface properties (e.g: electrostatic charge, hydrophobicity, pore size) causing a lower permeate flux. During the first filtration cycle (up to 0.1 m<sup>3</sup> m<sup>-2</sup>), permeate flux strongly decreased for the three membranes with the highest and lowest fluxes observed for the Water-10kGy and pristine membranes, respectively. The specific cake resistances (Eq. 2) calculated for the first cycle with the pristine membrane was equal to  $44.5 \times 10^{15} \text{ m}^{-1} \text{ kg}^{-1}$  which is a classical values observed for organic matter surrogates fouling layer [40, 41]. Interestingly, whatever the investigated irradiation dose the specific cake resistance was strongly reduced for the same filtered volume (0.1 m<sup>3</sup> m<sup>-2</sup>). The lowest value was obtained during the alginate filtration on the Water-10kGy membrane and was about  $8.6 \times 10^{15} \text{ m}^{-1} \text{ kg}^{-1}$ . Irreversible fouling after the first filtration cycle were equal to 40 %, 20 % and 18 % for the pristine, Water-10 kGy and Water-100 kGy, respectively.

After the third backwash, all membranes started with a similar permeate flux equals to an average of  $66 \pm 5 \text{ L h}^{-1} \text{ m}^{-2}$ . As demonstrated by these results, irradiation of PVDF membrane under EB in deaerated water improves filtration performances at the very beginning of filtration process, but this positive effect cannot be sustained for long term filtration, since irreversible fouling continuously accumulate near the membrane surface leading to similar performances as the pristine PVDF/PVP membrane. Thus, even if PVDF/PVP membrane properties were modified under EB irradiation, the surface properties modifications due to alginate deposition at the membrane surface will govern the membrane's filtration performances after a certain period of time.

Permeate flux trends against specific filtered volume are reported on Figure 2 (A & B) for all investigated irradiation conditions in presence of additives (Metha, Cyst & Phos at 10 & 100 kGy, respectively). Once again, the initial permeate fluxes are strongly reduced compared to the pristine membrane's pure water flux (450 L/h/m<sup>2</sup>). According to results reported in Table 2, the highest initial flux was obtained for the Cyst-10kGy membrane while the lowest flux, equals to 58 L/h/m<sup>2</sup>, was observed for both Cyst-100kGy and Phos-100kGy membranes. Similarly, the lowest specific

cake resistance after the first filtration cycle (for a filtered volume of  $0.1 \text{ m}^3 \text{ m}^{-2}$ ) was observed for the Cyst-10kGy and Metha-10kGy (equal to  $7.0 \times 10^{15} \text{ m}^{-1} \text{ kg}^{-1}$ ) membranes (Table 2). The highest specific cake resistances for the first cycle was found for both the Cyst-100kGy and Phos- 100kGy membranes ( $2.7 \times 10^{16}$  and  $3.0 \times 10^{16} \text{ m}^{-1} \text{ kg}^{-1}$ , respectively). However, the specific resistances values for the modified membranes are always lower than the one obtained for the pristine PVDF membrane.

At a low dose of 10 kGy, compared to irradiated membranes in deaerated water, presence of DMAEMA and L-Cysteine during irradiation has no impact on specific cake resistance. However, a slight increase in specific cake resistances was observed when irradiation was conducted in presence of phosphocholine compounds.

After membrane backwash, the permeate flux losses were mostly recovered with the best recovery ratio equals to 100 % and 92 % observed for the Phos-100kGy and Metha-100kGy, respectively. As previously observed, during the third and fourth cycles the positive effect of EB irradiation is reduced and the flux decline trends tend to be similar to the pristine membrane (except for the Cyst-10kGy membrane). Once again, presented results demonstrate that after several filtration cycle, the irreversibly deposited alginate governs the filtration performances of the modified PVDF membranes. However, the positive effect of irradiation is sustained on the Cyst-10kGy membranes. Indeed, the initial permeate flux at the fourth cycle was equal to approximately  $120 \text{ L h}^{-1} \text{ m}^{-2}$  which is much higher than the other membranes at the same filtered volume and similar to the initial permeate flux of the pristine membrane.

To conclude, these results show that EB irradiation in presence of zwitterionic compounds or solely is able to positively affect filtration performances in term of flux decline but this improvement is difficult to sustain for most of the investigated conditions. However, in presence of cysteine at low absorbed dose (10 kGy), the improvement seems to be sustainable for four filtration cycles. Based on these observations, cysteine seems to be the most suitable zwitterionic compound for membrane modification using low dose EB irradiation.

This result underlines that filtration performances of modified membranes should be evaluated through multi-cycle filtration tests instead of single filtration experiments, which only give a partial picture of the impact of the membrane modification on filtration performances.

### 3.2 Total organic carbon measurement

TOC rejection reported in figure 3 for the pristine membrane was constant throughout the filtration cycles and equal to approximately 60% (the average bulk TOC concentration ( $C_{OM}$ ) was  $1.77 \pm 0.02$  mg<sub>C</sub>/L). In contrast, the first-cycle TOC rejections for the modified membranes (except for Phos-10kGy and Cyst-10kGy) were relatively lower. However, TOC rejection increased with the filtration cycle and most of modified membranes displayed similar TOC rejection to that of the pristine membrane from the second or third cycle onward. The only exception was for membrane irradiated in presence of methacrylate (at both radiation doses, Metha-10 kGy and Metha-100 kGy), with a low rejection of about 40% throughout the filtration test. DMAEMA is polymerized by irradiation-assisted process, and the breakdown of these polymeric structures contributed to the higher concentration of low MW foulants flowing through the membrane pores [42]. Nevertheless, the other irradiated membranes induced a higher resistance to fouling capacity with a negligible degradation in the permeate quality.

To sum-up, taking into account the results of filtration flux, membrane retention and membrane anti-fouling ability, the most interesting performance are obtained for the Cyst-10kGy membrane which present an increase permeate flux and resistance to fouling after 4 filtration-cleaning cycles compared to the pristine membrane.

### 3.3. Membrane surface characterization

As numerous characterization techniques were used in this study, only membranes exhibited the best filtration performances were reported here. Therefore, all membranes irradiated at 10 kGy were investigated and compared to the pristine polymer. A specific attention was brought to the Cysteine

modified PVDF membrane at 10 kGy (Cyst-10kGy) previously shown as the best performing modified membrane.

Atomic Force Microscopy (AFM) allows the investigation of membrane surface changes caused by irradiation. The AFM phase images of the pristine PVDF membrane and irradiated membranes with 10 kGy absorbed dose are shown in Figure 4. As seen in Figure 4-a, the pristine membrane reveals a highly porous surface while irradiated membranes showed a smoother surface (Fig.4 b-e upper row). In addition, similar phase lag degree was observed for the pristine, Water-10kGy and Phos-10kGy membranes (Fig.4 a, b & d bottom row), while a slight decrease was obtained for the Metha-10kGy and Cyst-10kGy (Fig.4 c & e, bottom row). Phase images might be linked to a sample's stiffness and hydrophobicity indicating that Metha-10kGy and Cyst-10kGy membranes were more flexible and hydrophilic than other investigated membranes [43].

Irradiated membranes revealed a smoother surface with lower peak height, valley depth, Roughness values ( $R_{MS}$ ) compared to pristine membrane (Table 3). The smoother surface was found for the Metha-10kGy membrane (Table 3). The Feret's diameter ( $d_{50\%}$ ) of the pristine membrane (i.e : likened to pore diameter) was equal to 80 nm (Fig. 4-a & Table 3), closed to the pore size given by membranes' manufacturer (0.1  $\mu\text{m}$ ). The lowest Feret's diameter ( $d_{50\%}$ ) of irradiated membranes, equals to 50 nm, was obtained for the Water-10kGy and Cyst-10kGy membranes (Table 3), whereas no change was observed for the Metha-10kGy and Phos-10kGy membranes ( $d_{50\%} = 73$  nm).

AFM analysis revealed that whatever the irradiation conditions, membranes' surface was smoothed which might be associated to the enhanced anti-fouling capacity as observed in the filtration tests [44-46]. Interestingly, pore size might be controlled by the presence of phosphocholine or DMAEMA compounds.

Streaming potential was measured to determine the surface charges of the pristine and modified membranes. Figure 5 shows the zeta potential values for pristine membrane, as well as Cyst-10kGy and Water-10kGy at both irradiation doses (10 kGy and 100 kGy). All membranes was negatively charged with the isoelectric points (IEP) between 2 and 3. These value of IEP was unusually low for

PVDF membranes which usually exhibits IEP around 3-4 in absence of ionisable additives [47, 48]. However, such low values have previously been reported for the hydrophilic Durapore (Millipore) membrane, which contains other components beside carboxylated fluorocarbon copolymer [49, 50]. Similar range of IEP were also obtained by Schulze et al (2016) for PVDF-COOH modified membrane using hyperbranched polymers with the aim to generate a high density of hydrophilic functional groups at the membrane surface [51]. These results suggest that the pristine membrane used in this study contained carboxylated additives.

Above a pH value of 3, the pristine and modified membranes exhibited negative zeta potential. This behaviour is classically obtained for uncharged membranes. It can be postulated that this charge originated from the specific adsorption of hydroxide ions due to water structuring at the liquid-membrane interface [52]. A negatively charged surface is desirable in order to prevent fouling caused by negatively charged alginate thanks to electrostatic repulsion [40], and these repulsive forces increased at higher pH values.

Compared to pristine membrane, the Water-10 kGy and Cyst-10 kGy membranes had lower magnitudes of zeta potential  $\zeta$ . At pH 7.0, the  $\zeta$  values of both the 10 kGy irradiated membranes were  $-28$  mV, compared with  $-35$  mV as seen for PVDF-Pristine. This could be due to either the changes of PVDF/PVP at low irradiation dose within the membrane, or the irradiation that modified the adsorption equilibrium of hydroxide ions at the membrane interface.

The membranes irradiated with 100 kGy absorbed dose had the most negative  $\zeta$  values ( $-52$  mV at pH 7.0). Such increase in zeta potential associated with a slight decrease of the IEP towards the low pH value can be ascribed to an increase of acidic feature of the material surface [53]. Increase in the negative surface charge value due to polymer EB irradiation has previously been observed and attributed to polymer oxidization (leading to the formation of  $-\text{COOH}$  groups) [54].

Electrostatic repulsion between the 100 kGy irradiated membranes and alginate was an important driving force for membrane fouling resistance ability (in particular high fouling reversibility) [40].

Despite the deficit of electrostatic interactions with alginate, the irradiated membranes with 10 kGy

dose are good at fouling resistance because the antifouling capacity is dependent on both the electrostatic interactions and surface hydrophilicity [55].

Whatever the irradiation dose, there was no substantial difference in the zeta potential values between irradiated membranes in presence of water or cysteine solution. To explain this behaviour, it was suggested that the amount of grafted cysteine was insufficient to alter the surface charge and consequently modifications were only linked to PVP modifications. This remark agreed with the following XPS and FTIR observations. In order to quantify the elemental composition featured at the membrane surface XPS characterization was performed. Table 4 gives information about the composition of elements in the pristine and modified membranes with 10 kGy absorbed dose. The N1s and O1s peaks were present in the pristine membrane due to PVP and other additives, since nitrogen and oxygen elements are not present in pure PVDF. N1s and O1s peaks were observed in similar level on all the modified membranes, indicating that membrane chemical composition was not changed after irradiation. Nevertheless, the XPS results were insufficient to determine the presence of graft molecules, as the respective peaks corresponding to S2p (Cyst-10kGy) and P2p (Phos-10kGy) were absent (or in similar intensity as the baseline noise). This might be due to the low concentration of grafted molecules at the membrane surface inducing low XPS signals, such as S2p and P2p, not separable from noise. All modified membranes shows negligible difference in surface elemental composition compared with the pristine membrane. High intensity scans in the carbon and oxygen regions (Supporting Information, Figure S1) also show little compositional changes between the bonding types, such as C-C, C-H<sub>2</sub> and C=O. Similar issues have been previously encountered with XPS characterization for grafted molecules with EB irradiation [56, 57]. As indicated by XPS, It is concluded that irradiation induces little effect on the membrane surface composition.

ATR-FTIR results reported on figure 6 confirms the slight change in membrane composition upon irradiation [58, 59]. Figure 6 represents ATR-FTIR spectra of 10 kGy irradiated membranes. The spectra of all membranes (Figure 6) had the common features for PVDF. Two bands at 2980 and



3024  $\text{cm}^{-1}$  indicated the symmetric and asymmetric stretching modes of  $\text{CH}_2$ , respectively (not shown). Another band at 1403  $\text{cm}^{-1}$  corresponded to the wagging vibration of  $\text{CH}_2$  and bands in the 1300 – 1100  $\text{cm}^{-1}$  region corresponded to  $\text{CF}_2\text{-CF}_2$  stretching [34, 60]. According to FTIR results, most of identified bands correspond to PVDF  $\alpha$ -phase. The peaks corresponding to the C–F bond at 1000–1400  $\text{cm}^{-1}$  are similar for all the observed membranes, which indicate that no dramatic changes occurred to the C–F bonds of PVDF. This conclusion agrees with Jaleh et al. (2015), in which no significant effect on the PVDF structure was observed up to an absorbed dose of 300 kGy [34]. In addition, ATR-FTIR failed to identify any change in the polyester fingerprint fabric for the virgin, water 10kGy and Cysteine 10kGy membranes (data not shown).

The most obvious difference between the pristine and the irradiated membranes are the presence of a broad band centred at 1650  $\text{cm}^{-1}$ , corresponding to the C=O stretch vibrations in lactams-like compounds. This band indicates the presence of polyvinyl-pyrrolidone additives (PVP) [61]. During EB irradiation significant amount of PVP might be oxidized due to hydroxyl radicals' actions [62]. Interestingly, a broad band centred at 1750  $\text{cm}^{-1}$  seen on irradiated membranes, which could be linked to the formation of succinimide compounds induced by radical oxidation of PVP [62]. Sabatino et al. (2013) demonstrated that succinimide groups might be formed during PVP irradiation [63]. Such structure indicates a potential crosslinking of PVP during low dose irradiation (< 40 kGy) leading to inter-molecular recombination through the C-O-C bands formation. Interestingly, oxidation of PVP and formation of succinimide compounds (during membrane chlorination) is associated to higher water permeability and higher fouling propensity [53]. Therefore, these results suggest that EB irradiation induces a different PVP modification routes than chlorination oxidation. More investigation are needed to demonstrate the PVP modification mechanisms upon EB irradiation (crosslinking, chain scissions...).

No bands indicating the presence of phosphorus and sulphur moieties was observed in the spectra of the Phos-10kGy and Cyst-10 kGy, respectively. It was suggested that the zwitterion molecules were

present in relatively small quantities to give a detectable FTIR signal. Another explanation is that there is similarity between the spectral patterns of zwitterions molecules, PVP and the PVDF membrane [64]. However, two distinct bands ( $1540$  &  $1570\text{ cm}^{-1}$ ) were observed for the Phos-10kGy membranes and might be attributed to NH bending in amide II compounds [65].

TGA/DTA measurements were performed to investigate the effect of irradiation on the composition and thermal stability of the modified membranes. Representative DTA thermograms for Pristine, Water-10kGy and Cyst-10kGy are shown in Figure 7. All membranes displayed similar thermal weight loss patterns. From the thermograms (Fig 7-a & b), two main decomposition stages occurred between  $400^{\circ}\text{C}$ - $470^{\circ}\text{C}$  and  $500$ - $550^{\circ}\text{C}$  corresponding to the oxidation of PVDF polymer and the polyester fabric, respectively. For the pristine membrane, another decomposition stage from  $100^{\circ}\text{C}$  to  $220^{\circ}\text{C}$  was observed, which caused a weight loss of 10% and an exothermic peak (Fig 7-a & b). This weight decrease corresponds to the removal of PVP and other additives [66]. The smaller widths and heights of these peaks for the modified membranes (Water-10kGy and Cyst-10kGy) indicated that PVP and other additives were oxidized/modified during irradiation process and only residual unchanged PVP occurred in the polymer matrix. According to the weight loss patterns, more additives were removed at the higher absorbed dose (Figure S2).

At around  $426^{\circ}\text{C}$ , the decomposition peaks of PVDF-PVP blend are distinctive between PVDF-Pristine and the modified membranes (Fig 7-a). These peaks correspond to exothermic processes (Fig 7-b) related to oxidation followed by decomposition. Upon irradiation, the peak was either segregated into a doublet or increased in intensity. Either of the phenomena implied that the modified membranes were less stable than the pristine one. Similar results was observed on the 100kGy irradiated samples but with lower peak height (Figure S2) emphasizing the decrease of thermal polymer stability under higher irradiation dose. Interestingly, this new decomposition peak observed at  $426^{\circ}\text{C}$  might be associated to the thermal decomposition of PVP crosslinked as already reported elsewhere [67].

Thermogravimetric analysis failed to give distinctive observations for different graft molecules

(i.e. L-Cysteine with a degradation temperature around 250°C), because it only allowed studying the bulk property of the membrane, and the amount of graft molecules was insignificant compared with other membrane components, such as PVDF and polyesters. However, it was confirmed that polymer irradiation mechanisms were modified in presence of cysteine compounds compared to irradiation done in deaerated water.

According to presented results, electron beam irradiation at 100 kGy strongly reduced membrane additives (i.e: PVP) and increased the negative charges at the membrane surface. Membranes irradiated at 10 kGy exhibited similar thermal weight loss partner but the membrane surface was smoother. Among all investigated conditions, the most obvious difference between pristine and irradiated membranes was a decrease of the C=O stretch vibrations bands of PVP additives.

### 3. Conclusion

The investigated commercial PVDF/PVP membrane product was successfully modified by EB irradiation. As observed with AFM, EB irradiation resulted in a smoother surface and smaller pore sizes (i.e. Feret's diameter). The AFM results agreed with the thermogravimetric and FTIR results, indicating a change in amount of crosslinking, and that additives, such as PVP, were modified to certain extent. Upon irradiation in presence of zwitterion compounds, the majority of investigated membranes show improvement in the anti-fouling capacity, with lower flux decline and prominent flux recovery.

The irradiated membranes with 100 kGy absorbed dose displayed lower initial fluxes compared with the pristine and irradiated membranes with 10 kGy dose. The best performer is the 10 kGy irradiated membrane in presence of L-cysteine. It was also discovered that TOC was not reduced for most irradiated membranes, ensuring that the membrane integrity was not affected by EB irradiation. Interestingly, it was shown that the presence of zwitterion molecules during irradiation process influenced PVDF/PVP modification routes as strong differences in membrane morphology was observed according to the zwitterion nature. These results suggest that commercial PVDF membranes' pore size and roughness might be tuned and controlled through irradiation of PVP

using EB process in presence of zwitterion. Nevertheless further investigation are needed to state on the PVP recombination (inter- or intra-molecular) mechanisms within the membrane.

However, after several filtration-backwash cycles, filtration performances show little change compared to the pristine membrane, where the most significant improvement belongs to the Cyst-10 kGy. This emphasizes that irradiation process induced only slight changes in PVP and their effect on fouling resistance might not be sustained for long-term filtration. According to presented results, it is highly recommendable for future studies to evaluate membrane modification impact based on multiple filtration-cleaning cycles instead of single filtration experiments as classically reported in literature.

#### **Acknowledgement:**

The authors acknowledge financial support from the European Union (ERDF) and "Region Nouvelle Aquitaine". The authors express their thanks for the useful and valuable assistance given by Audrey Allavena during the electron beam experiments.

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**Figure 1.** Multiple-cycle permeate flux for the pristine, Water-10 kGy and Water-100 kGy membranes

**Figure 2.** Multiple-cycle permeate flux for the Metha, Cys and Phos modified membranes irradiated at (A) 10 kGy and (B) 100 kGy.

**Figure 3.** TOC rejection (%) observed during multi-cycle filtration tests for all the investigated membranes

**Figure 4.** AFM phase images (top) and topography (bottom). (a) pristine and (b-e) modified membranes: (b) Water-10kGy; (c) Metha-10 kGy (d) Phos-10 kGy; (e) Cys-10kGy.

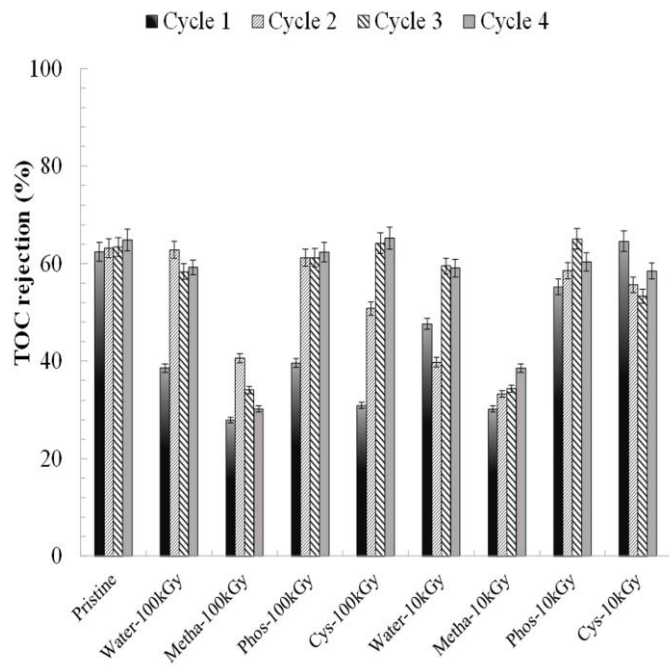
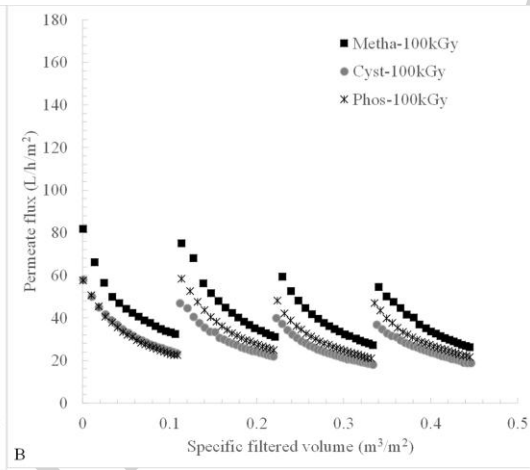
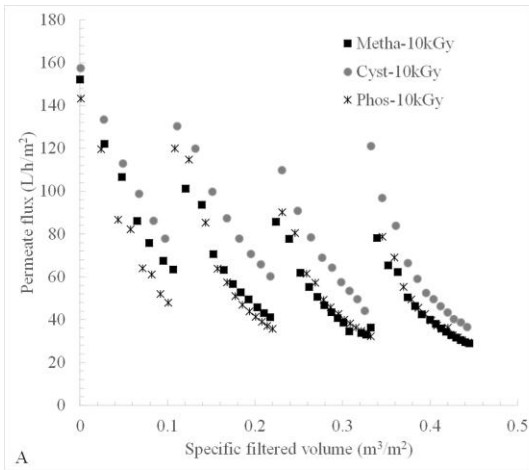
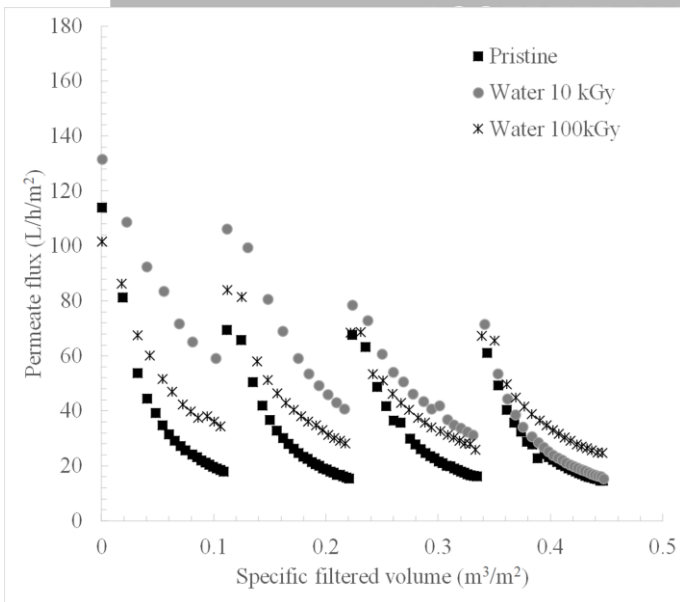
**Figure 5.** Zeta potential values for PVDF-pristine and modified membranes: Water 10 & 100 kGy and Cyst 10 & 100kGy.

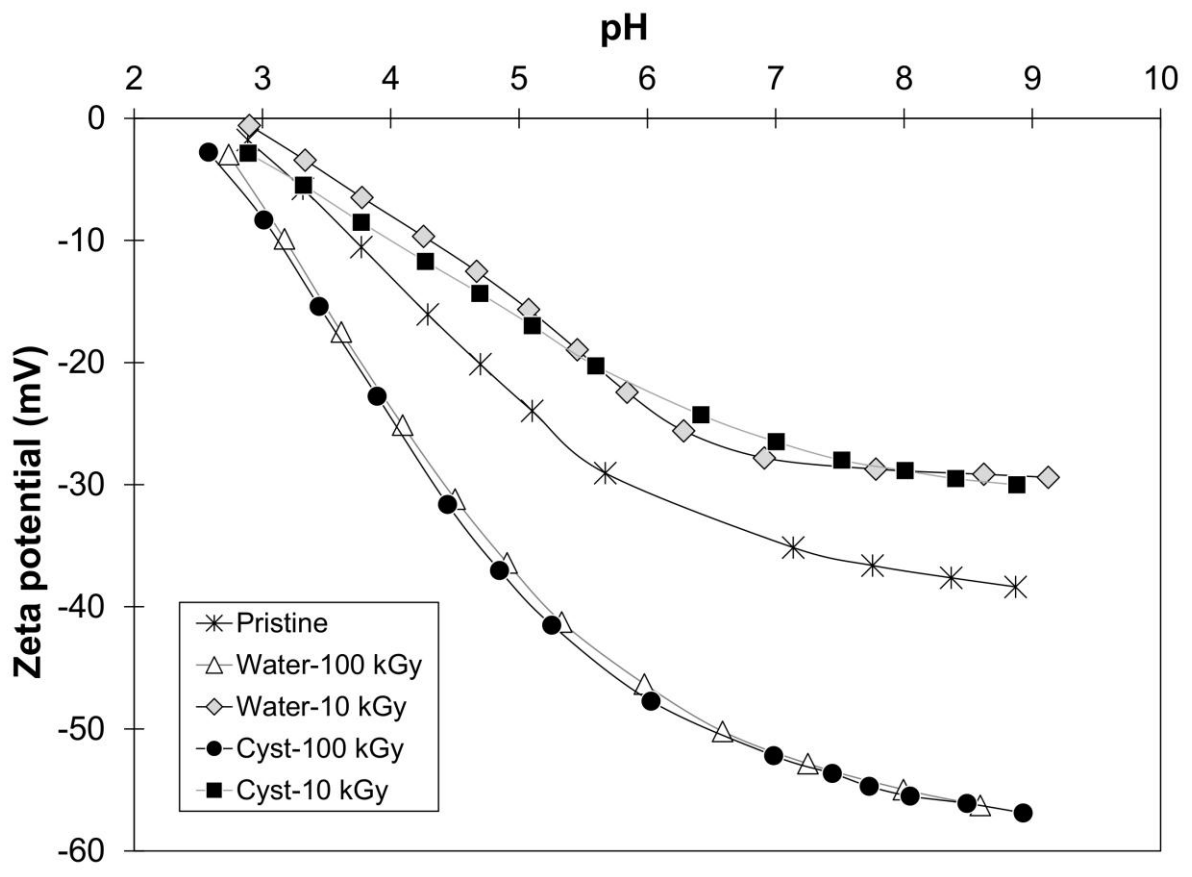
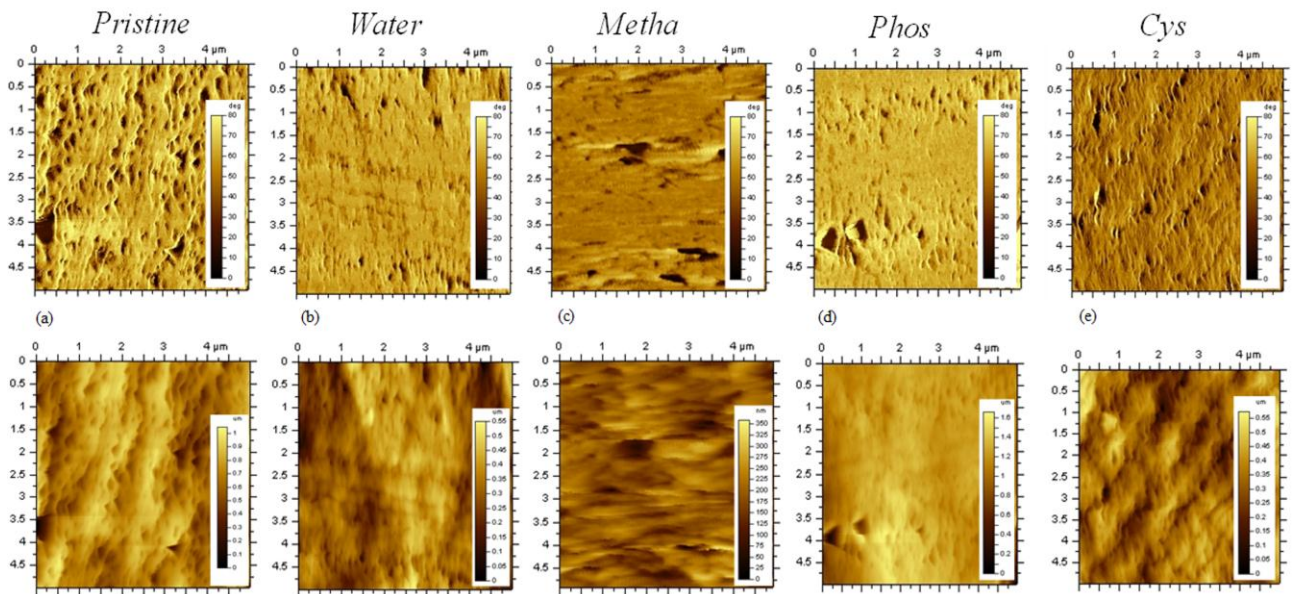
**Figure 6.** ATR-FTIR spectra of PVDF-Pristine and PVDF-EB 10kGy membranes ( $2000-700\text{ cm}^{-1}$ ). Insert: zoom on the  $1400-2000\text{ cm}^{-1}$  region. Spectra were normalized to  $874\text{ cm}^{-1}$  and intensities were vertically shifted for better clarity.

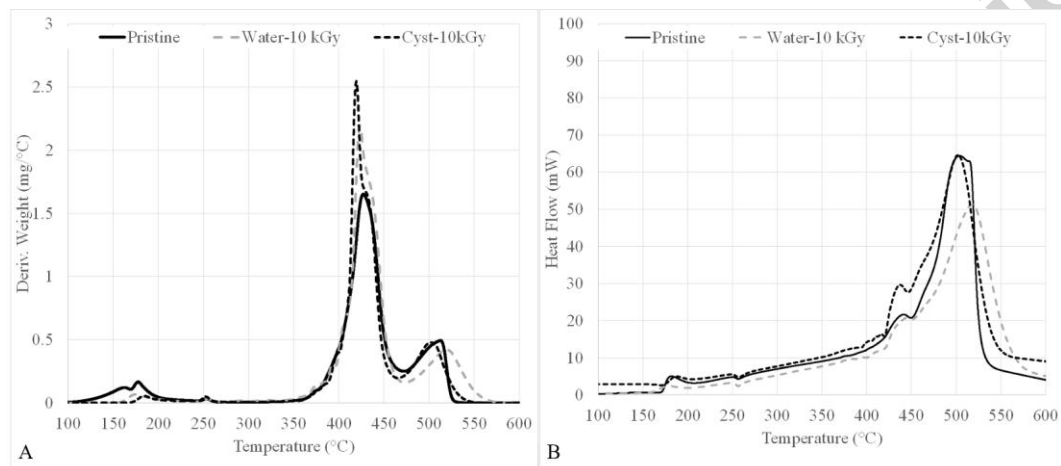
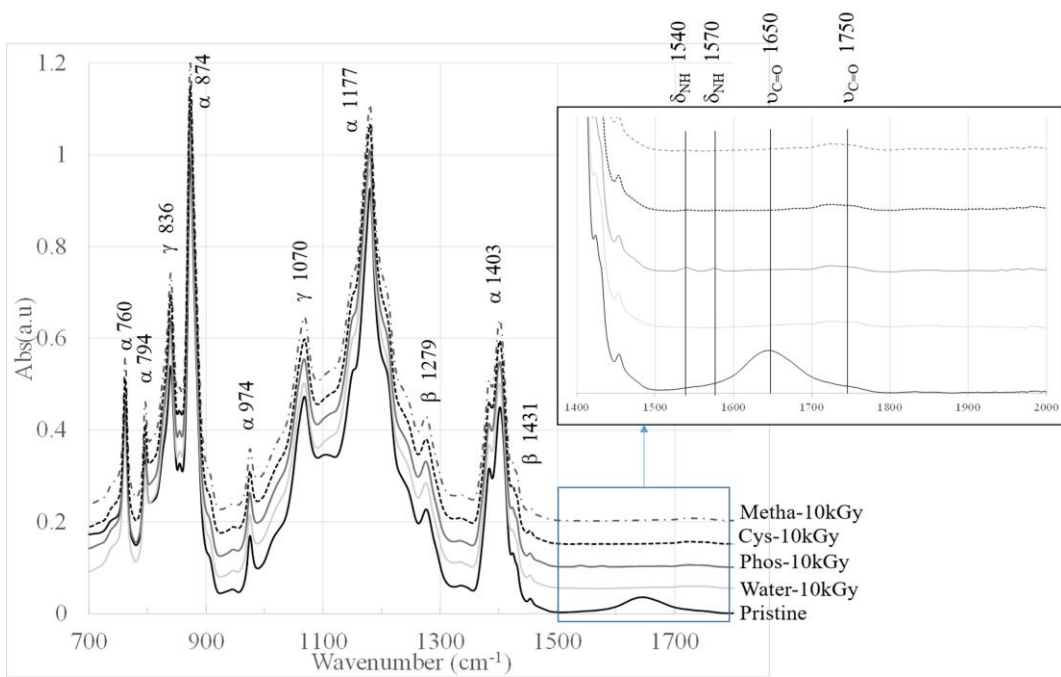
**Figure 7.** Derivative thermogravimetric analysis (DTA) (a) and Heat Flow (b) for the pristine, water-10kGy and Cyst-10kGy membranes.

Highlights:

- PVDF/PVP membranes were successfully modified by electron beam irradiation.
- Membranes irradiated with 10 kGy dose displayed higher permeability.
- The best anti-fouling capacity was obtained Cys-10kGy irradiated membrane.
- Irradiated membranes show smoother surface and lower Feret's diameter.







Accepted