Synthesis of PVDF ultrafiltration membranes supported on polyester fabrics for separation of organic matter from water

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Abstract: Polyvinylidene fluoride (PVDF) membranes supported on non-woven fabrics (NWF) of polyester are reported. The PVDF membranes were fabricated using the phase inversion method followed by modification of the active top layer of the PVDF thin film by adding polyvinylpyrrolidone (PVP) into the cast solution. A PVDF resin was used with N-methyl-2-pyrroldione (NMP) as a solvent. Sessile drop contact angle measurements and scanning electron microscopy (SEM) were used to study the physical properties of the membranes. Membrane rejection of humic acid was studied using a cross-flow membrane testing unit. The contact angle results revealed that the hydrophilicity of PVDF membranes increased as the PVP concentration was increased from 3 to 10 wt%. SEM analysis of the membranes revealed that the membrane pore sizes increased when PVP was added. AFM analysis also showed that membrane roughness changed when PVP was added. Total organic carbon (TOC) analysis of water samples spiked with humic acid was performed to test the rejection capacity of the membranes. Rejections of up to 97% were achieved for PVDF membranes supported on polyester NWF1, which had smaller thickness and higher permeability compared to polyester NWF2. The NWFs provided the high strength required for the membranes despite the modifications done on the PDVF surface and microstructure.

1. Introduction

Natural organic matter (NOM) is known to exist naturally in surface and ground waters [1]. It can react with a number of disinfectants to generate disinfection by-products (DBPs) such as trihalomethanes, halonitromethanes, haloacetonitriles, halomides, halofuranones, iodo-acids and others which are known to be carcinogenic and having the potential of being highly detrimental to human life [2-7]. The effective removal of NOM is extremely important in order to prevent the formation of the DBPs and provision of safe drinking water. Moreover, NOM is known to cause fouling of membranes thus requiring high pressures to force water across the membrane.

In order to reduce NOM before disinfection, a direct correlation between TOC and NOM was established as per Standard Methods 5310 and the USEPA’s disinfectants/disinfection by-products rule. Therefore, TOC analysis was chosen for measuring NOM in this study. The TOC analysis permitted the determination of the effectiveness of the NWF supported PVDF membranes in the removal of NOM, particularly humic acid (HA) from water [8,9].
In this study, PVDF membranes supported on two different non-woven fabrics (NWFs) of polyester (Table 1) were prepared using the phase inversion method [10]. We demonstrate the advantages of using the support materials compared to unsupported PVDF. It is well known that NWF materials can effectively be used for the removal of particles larger than 1 µm in the decontamination process in both air and water filtration [12]. Recent studies have shown that NWFs can be used in membrane bioreactors (MBR) to treat waste water [13]. It is also known that modification of polymeric membranes either through chemical functionalization of the surface (active layer) or through addition of nanoparticles compromises the strength of the membranes due to defects caused by these modifications. NWFs were used as support layers for the thin film PVDF membranes, which allowed us to modify the membranes while maintaining the desired strength provided by the intact NWF used as a support layer.

Table 1. Physical properties and chemical structures of the NWFs used as support materials for PVDF membranes.

| Non-woven Fabric | Material | Thickness/µm | Permeability (µms⁻¹) | Repeating unit of the polymer structure |
|------------------|----------|--------------|----------------------|---------------------------------------|
| NWF 1            | Polyester| 95           | 162000               | \(\text{C}_2\text{O}\text{C}\text{O}\text{C}_2\text{H}_4\text{O}\text{C}_2\text{H}_4\text{O}\)\_n \(n\) |
| NWF 2            | Polyester| 134          | 2500                 | \(\text{C}_2\text{O}\text{C}\text{O}\text{C}_2\text{H}_4\text{O}\text{C}_2\text{H}_4\text{O}\)\_n \(n\) |

2. Experimental

2.1 Materials
PVDF resin, N-methyl-2-pyrrolidone (NMP) solvent, polyvinylpyrrolidone (PVP) with molecular weight of 29 KDa and HA powder were purchased from Sigma Aldrich, South Africa. The non-woven fabrics were purchased from Ahlstrom Co and Hirose Co in the USA. All chemicals were used without further purification. The physical-chemical properties of the NWFs are given in Table 1.

2.2 Membrane preparation
A 17 wt % of PVDF resin was dissolved in NMP with stirring over a period of 24 h to form a PVDF viscous homogenous solution. The PVP additive was varied between 3 wt %, 5 wt % and 10 wt % respectively. The resulting solution was allowed to stand for 24 h in order to allow the gas bubbles generated during the reaction to settle. The solutions were subsequently cast on the NWFs using a casting knife with a blade height set at 200 µm.

2.3 Membrane characterization
Water contact angles of the membranes were measured using a sessile drop method using a Data Physics optical goniometer, which is a contact angle measuring instrument with the droplet size controlled using a Gilmont syringe. Deionised water was used for analysis. The advancing angle was measured as water droplet was added spreading over the membrane surface. Droplets from the syringe were directed to come into contact with the membrane at several different points on each membrane sample to obtain a series of contact angle pairs. All measurements were executed at room temperature. The surface and cross-sectional analysis of the membranes were carried out using a JEOL-JSM-7500F scanning electron microscope using an energy source of 200 kV. The samples were first cryogenically
fractured in liquid nitrogen. They were then securely mounted on aluminium stubs and coated with gold, in order to induce their capacity to conduct. Membranes were ultimately studied in order to understand the morphology of the bare membranes relative to the modified ones.

2.4 Membrane rejection studies

The fabricated PVDF NWF supported membranes were assembled in the cells of a cross flow unit. The membranes were then compacted at a pressure of 344.7 KPa using deionised water for 4 h. The water flux was then determined for all the membranes in the cross flow system. In this work, a 5 litre of 20 mg/L solutions of humic acid (HA) was prepared to be used in rejection studies. The pH of the solution was adjusted to be between 8 and 9 using NaOH to ensure complete dissolution of HA (HA is insoluble at lower pH values). The concentration of HA was kept at 20 mg/L with the aim of simulating the HA concentration found in natural surface waters. The flux of the membranes was determined at a pressure of 137.9 KPa by noting the time taken to collect 20 ml of the permeate volume, which was varied over 30 min intervals. The low pressure was used to conserve energy. A typical sea water reverse osmosis plant uses pressure in the region of 6000 KPa to 8000 KPa [14]. As membranes begin to foul the high pressure demand increases in order in to drive water across the membranes.

The concentration of the collected feed and permeate for each of the membranes was determined quantitatively using a An Apollo 9000 TOC Analyzer by TEKMAR DOHRMANN. The instrument uses the High Temperature Combustion–Infrared Method–5310B, which is more accurate than the UV-Persulfate method. The instrument was calibrated using a series of Potassium Hydrogen Phtalate (KHP) standard samples. The calibration curve was used to calculate the TOC values of unknown samples. These concentrations were then used to calculate percentage rejections (% R) of each membrane.

3. Results and Discussion

3.1 Contact angle measurements

The contact angles of the PVDF membranes supported on two NWFs are given in figure 1. A declining trend in contact angles was observed with the addition of PVP. Membrane contact angles declined sharply as the concentration of PVP was increased from 3 wt % to 10 wt % which suggested improved hydrophilicity of the membranes, thus improving their water flux properties. There were no noticeable differences between the supported membranes with those not supported by the NWFs. There effect of PVP addition was similar with all the membranes. An explanation to this observation was that the contact angle measurements were taken on the membrane surface. Since the NWF was located below the membrane surface, it did not make a contribution to the contact angle values. The contact angle graphs of the unsupported PVDF membranes (figure 1 b) illustrate the declining contact angle values, which showed that even the unsupported membranes became more hydrophilic with the increase in PVP concentration. The incorporation of PVP has a similar effect of making the membrane hydrophilic even if the membrane was not supported by NWFs.
Figure 1. Surface water contact angles of PVDF membranes supported on NWF 1 (A) and unsupported PVDF membranes (B).

3.2 Scanning electron microscopy analysis
SEM surface and cross-sectional morphologies of the PVDF membranes supported on NWF 1 are given in figure 2. The SEM micrographs gave information about size, shape, and orientation of the pores present in the synthesised PVDF membranes. The bare PVDF membranes (i.e. without PVP) on the NWFs were found to comprise considerably smaller surface pores of about 10 nm and their cross-sectional view possessed a broad “finger-like” shape (figure 2 a and b). The bare membranes could be distinguished from the PVP modified membranes due to their increase pore sizes and asymmetric properties. When the concentration of the PVP was increased to 10 wt% in the casting solution, the size of the pores on the membrane surface increased to about 35 nm and the finger-like pores (macrovoids) on the membrane cross-section increased correspondingly and appeared to form asymmetric orientation when compared to relatively small macrovoids in the bare membranes (figure 2 c and d). Similar results were obtained when NWF2 was used as a support.

Figure 2. Surface (a) and cross-sectional (b) SEM images for PVDF bare membranes supported on NWF1 and surface (c) and cross-sectional (d) SEM images for PVDF membranes with 10 wt% PVP supported on NWF 1.
3.3 HA membrane rejection studies
The PVDF membranes supported on the polyester NWFs were all found to effectively reject HA from water. The highest rejection recorded for was 97% for PVDF membranes supported on NWF1 (figure 1) compared to the 95% for membranes supported on NWF 2 (data not shown). Incremental addition of PVP was found not to be consistent with rejections for most of the membranes, as shown in figure 1. It was presumed that this variation could be due to the fact that reject was not only influenced by pore size but also by interaction of the HA with the membrane surface.

![Figure 3](image_url)

Figure 3. HA rejection for PVDF bare and PVP modified membranes supported on NWF1.

4. Conclusion
The effect of using NWFs as supports for PVDF membranes fabricated using the phase inversion method has been studied. Contact angle analysis of the membrane surfaces showed that the addition of PVP enhances hydrophilicity. The pore sizes of the membranes also increased with increase in PVP concentration. The PVDF membranes supported on NWF 1 all gave higher humic acid rejections compared to NWF 2 due to the permeability and thickness properties of NWF1. However the key results on the tensile strength of the membranes demonstrated that the use of NWF 1 and NWF 2 as supports provided advantages that could allow modification of the thin film PDVF membranes without compromising the strength. The tensile strength of the unsupported PDVF membranes decreased with increase in PVP concentration while the strength was not affected when the membranes were supported on the NWFs. The interactions between the PVDF membranes and NWFs were found to be good thus providing materials with robustness and flexibility that is desired for membrane materials.

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