# Enhanced-performance Membrane-Based Water Treatment Systems

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## ABSTRACT

Membrane systems have gained considerable attention for their ability to produce high quality water. Nevertheless, membrane fouling is the major cause of deterioration in performance of these treatment systems. Surface modification is an attractive option for controlling organic and biological fouling of membranes. Making the membrane hydrophilic and bactericidal can lead to low retention of organic matter and lower biological growth, which in turn culminates in increasing the longevity of membrane performance. In this study, we present our findings on ultrafiltration polyvinylidene difluoride (PVDF) membranes, which were modified by poly(aniline-co-3-aminobenzoic acid) (3ABAPANI) through ex-situ modification processes. FTIR and SEM analysis results confirmed the modification of membrane with 3ABAPANI. The results showed that coating the membrane with 3ABAPANI increased the contact angle from $60^{o}$ to $83^{o}$, which corresponds to a decrease in membrane hydrophilicity. The good bactericidal activity of 3ABAPANI against Gram-positive and Gram-negative bacteria plays a crucial role in antifouling process. These characterisation data will be presented at the conference to illustrate the potential for improving the performance of membrane treatment processes.

## KEYWORDS

PVDF membrane, antimicrobial, Coating, 3ABAPANI

# 1. Introduction

Water scarcity is a growing global issue, fuelled by a continual increase in water demand and an uneven distribution of water supply worldwide. An emerging solution to this global matter of concern is water recycling. Being economical, environmentally friendly, easy to use and effective has made the membrane as promising candidate for the purpose of water treatment(H. Huang & Schwab, 2009).

Membrane treatment processes such as ultrafiltration and reverse osmosis play a crucial role in such strategies. While these technologies are widely recognised for the consistent high quality drinking water they produce, flux decline due to fouling remains a critical unresolved issue. In general, fouling happens on the surface of the membrane or within the pores, which decreases the membrane permeability. Inhibition in membrane performance increases operating costs and reduces membrane longevity, rendering membranes economically unattractive for industrial application(Kim et.al, 2009)(Kang et.al, 2004).

Current physical and chemical processes such as backwashing and the use of cleaning agents have provided limited success in reducing fouling due to the irreversible nature of this phenomenon and the strong adhesive forces between the membrane surface and fouling materials (Dolina et.al, 2015). Fouling also can be controlled by membrane surface modification(Rana & Matsuura, 2010). Making the membrane antimicrobial can kill the bacteria, preventing the bacteria from growing and dispersing in the water(Kaplan et.al, 2003)(Izano et.al, 2008).

Polyaniline (PANI), is a conductive material of interest in membrane modification due to its easy and facile synthesis, environmental stability and antibacterial capability(Gizdavic-Nikolaidis et.al, 2010)( Gizdavic-Nikolaidis et.al, 2012). Fan et.al(Fan et.al, 2008)(Fan et.al, 2008) studied the preparation of PANI/polysulfone nanocomposite membrane and showed that PANI makes the membrane work as an antifouling agent. The main obstacle to PANI commercial application is its low solubility in common solvents such as Dimethyl Sulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP)(Gizdavic-Nikolaidis et.al, 2010). In order to increase the solubility, aniline can be polymerized with functionalised anilines to form fPANIs such as 3ABAPANI(Gizdavic-Nikolaidis et.al, 2010). Studies indicate that the mechanism of cell inhibition of both PANI and fPANI's include a wide range of gene interactions that include the repression of the genes responsible for both cell wall synthesis and the formation of biofilms. This is a factor, which lends itself to use in the reduction of biofouling. The chemical structure of 3ABAPANI emeraldine salt (ES) form is presented in Figure 1.

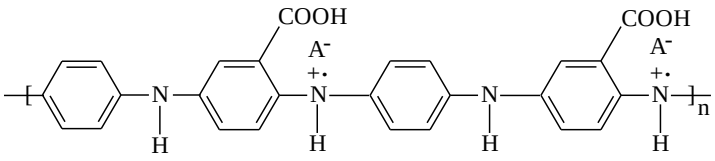


*Figure 1: Basic chemical structure of 3ABAPANI ES form*

There are a huge number of studies on in-situ modification of the membranes(Zhao et.al, 2010)(Huang et.al, 2016); however, a few studies have been focused on ex-situ treatment of the membranes, which is a promising method because it consumes much less amount of solution for modification process, especially in industrial scale.

In this work, we study the ex-situ modification of an ultrafiltration membrane with 3ABAPANI, in order to improve the antifouling properties of the membrane. SEM, FTIR and flux measurement of the membrane also confirms the modification.

# 2. Experimental Section

## 2.1 Materials

Aniline and 3-aminobenzoic acid (3ABA) monomer were purchased from Sigma-Aldrich. Aniline was distilled under reduced pressure and stored in the dark under nitrogen. Oxidising agent, potassium iodate ($KIO_3$) was obtained from Ajax Finechem. 3ABAPANI was chemically synthesised as described previously by Gizdavic-Nikolaidis et al, 2010.

NMP solvent and whatman grade 1 filter paper were purchased from Sigma-Aldrich and PVDF ultrafiltration membrane was purchased from Sterlitech.

## 2.2 UV-Vis Spectroscopy

As the membrane modification is through ex-situ coating of the membrane, to investigate the PVDF membrane degradation in NMP, a UV–vis absorption spectrum was recorded on a Shimadzu UV-1240 spectrophotometer over the wavelength range 220–400 nm.

## 2.3 Membrane modification

An ex-situ method of deposition was used to coat the surface of the membrane with pre-synthesised 3ABAPANI powder. 3ABAPANI powder was synthesised using a conventional method(M. R. Gizdavic-Nikolaidis, Zujovic, et al., 2010) and dissolved in the NMP solvent with 2wt%. The producing suspension of the 3ABAPANI nanoparticles used for the ex-situ modification of membrane.

## 2.4 Membrane characterisation

### 2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectrum was recorded with resolution 4 $cm^{-1}$ using a Nicolet 8700 FT-IR spectrometer with KBr pellet. 150 scans were averaged for the sample.

### 2.4.2 Contact angle measurements

Contact angle measurements were performed using a contact angle goniometer (Rame´-Hart Model 200) with DROP image Standard software version 2.4 (Rame´-Hart Instrument Co., Netcong, NJ).

### 2.4.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was done on 3ABAPANI powder and modified membrane. Dry powder samples were mounted on 10 mm diameter aluminium studs using adhesive graphite tape, and sputter coated using Quorum Q150RS Sputter Coater at 20 mA using Pt as a target for 60 seconds. SEM was then carried out using a Philips XL30S SEM equipped with a Field Emission Gun and a SiLi

(Lithium drifted) EDS Detector with Super Ultra Thin Window. Images were taken at an accelerating voltage of 5.00 kV.

## 2.5 Antimicrobial analysis

### 2.5.1 Calibration of Victor Perkin Elmer 2030 Victor TM Light Luminescence Reader

To convert the microbial luminescence readings from lux to the number of cells on the membrane surface, a calibration procedure involving measuring the luminescence of a known number of cells of *Escherichia coli* 25922 *rrnG*::*luxCDABE* and *Mycobacterium smegmatis* $mc^2$ 155 [pMVhspLuxABG13CDE] (BSG200) bacterial strains was undertaken. 100 µL of TSB broth was pipetted onto 30 mm diameter circles of membrane placed in each well of Corning Incorporated 6 well Culture Cluster Plates. 300 µL of $10^8$, $10^6$, $10^5$ CFU/mL were produced from a $10^9$ CFU/mL overnight culture of each bacterial strain. Uncoated PVDF membranes were placed into each well of the Culture Cluster Plates apart from one row. 100µL of each dilution was pipetted onto the centre of 3 of these membranes. Luminescence readings were obtained for each dilution of the bacterial strains 10 min after inoculation then 2 and 24 h after this process using a Victor Perkin Elmer 2030 Victor TM Light Luminescence Reader. Between readings, the Culture Cluster Plates containing the membranes were kept in a sealed plastic container laden with moistened paper towels to prevent external effects from causing desiccation of these devices.

### 2.5.2 Control testing

Luminescence readings were obtained for 2wt% 3ABAPANI and uncoated PVDF membranes. The control test readings were obtained without the addition of microbes. This would determine if the membranes had a natural luminescence and if the effect was compounded with the addition of filter paper. To obtain the luminescence readings of the coated membranes, each membrane was placed in a single well of a Corning Incorporated 6 Well Culture Cluster Plate. Measurements were obtained for 2 samples using Victor Perkin Elmer 2030 Victor TM Light Luminescence Reader. The effects of the filter paper with broth on the luminescence of the membranes were obtained by pipetting 100 µL of TSB broth on 30 mm discs of filter paper placed in a single well of the Culture Cluster plate. Each respective membrane was placed in the same well used for the previous test to ensure a fair result was obtained. Measurements were recorded using the same Luminescence Reader.

### 2.5.3 Analysis of bacterial inhibition

Antimicrobial analysis was conducted using luminescent strains of Gram-negative *E. coli* and Gram-positive *M. smegmatis*. 30 mm diameter pieces of filter paper moistened with 100 µL of TSB broth were placed at the bottom of each well of Corning Incorporated 6 well Culture Cluster Plates. Tests were conducted in triplicates using the same sample types as the control tests. The uncoated membranes served as controls for the tests by allowing for the effects of the membrane coating on microbial inhibition to be observed. 100 µL of $10^9$ CFU/mL of each bacterial strain was pipetted onto the centre of each membrane sample. Luminescence readings were obtained 10 min after the initial inoculation and every half hour after this process for 6 h. In addition, measurements were taken both 24 h and 48 h after the cells were applied to establish the longevity of the coatings on bacterial inhibition. To ensure that external effects did not affect the measurements recorded, the 6 well Culture Cluster Plates were placed in a sealable plastic container laden with moistened paper towels.

## 2.6 Pure water flux cross-flow filtration

The pure water flux of the membrane was measured using a UF experimental apparatus with effective membrane area of 80 $cm^2$. The pure water flux was measured at 0.20 MPa TMP and 0.1 m/s cross-flow velocity. The pure water flux was calculated using Equation 1.

$$J_w = \frac{V}{A \times \Delta t} \quad (1)$$

Where $J_w$ ($L/(m^2.h)$) is the pure water flux, V (L) is the permeate volume, A($m^2$) is the effective membrane area and $\Delta t$ (h) is the permeation time.

# 3. Result and Discussion

## 3.1 UV-Vis Spectroscopy

In order to see the membrane degradation in NMP, the PVDF membrane was soaked in the solvent for 5 h. The result showed that PVDF membrane is resistant to the NMP solvent (Figure 2). Indeed, it can be seen that there is a little shift of NMP in the solution of PVDF membrane in NMP compared to the pure NMP.

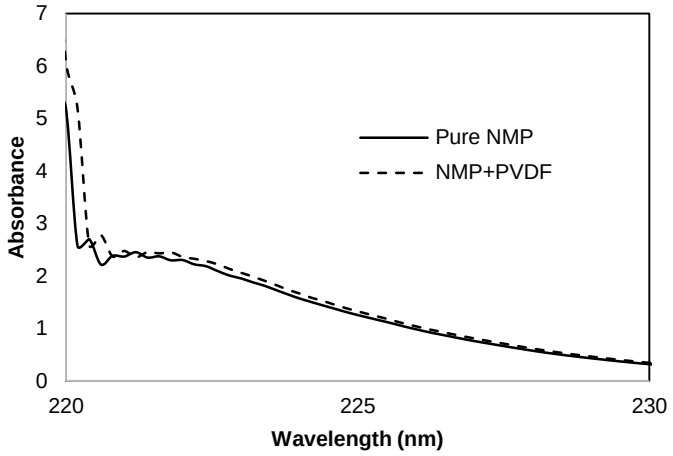


*Figure 2: UV-Vis spectroscopy of the solution of NMP including PVDF membrane*

## 3.2 Membrane Characterisation

### 3.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3 shows the FTIR spectra of 3ABAPANI powder, uncoated PVDF membrane and PVDF coated membrane with 3ABAPANI.The FTIR spectra confirms that sample fabricated using the ex-situ method demonstrates the characteristic peaks of 3ABAPANI copolymer, despite the minimal shifting between the 3ABAPANI and membrane coated with 3ABAPANI. The peak at 1717 $cm^{-1}$ demonstrates the C=O band, confirming incorporation of ABA unit in the copolymers. The bands at 1568 and 1497 $cm^{-1}$ correspond to the C-C ring stretching vibrations of the quinoid and benzenoid structures, respectively. The band at 1231 $cm^{-1}$ in the spectra corresponds to C-N stretching modes of the benzenoid ring. The peak at 827 $cm^{-1}$ is ascribed to the out-of-plane C-H bending mode.

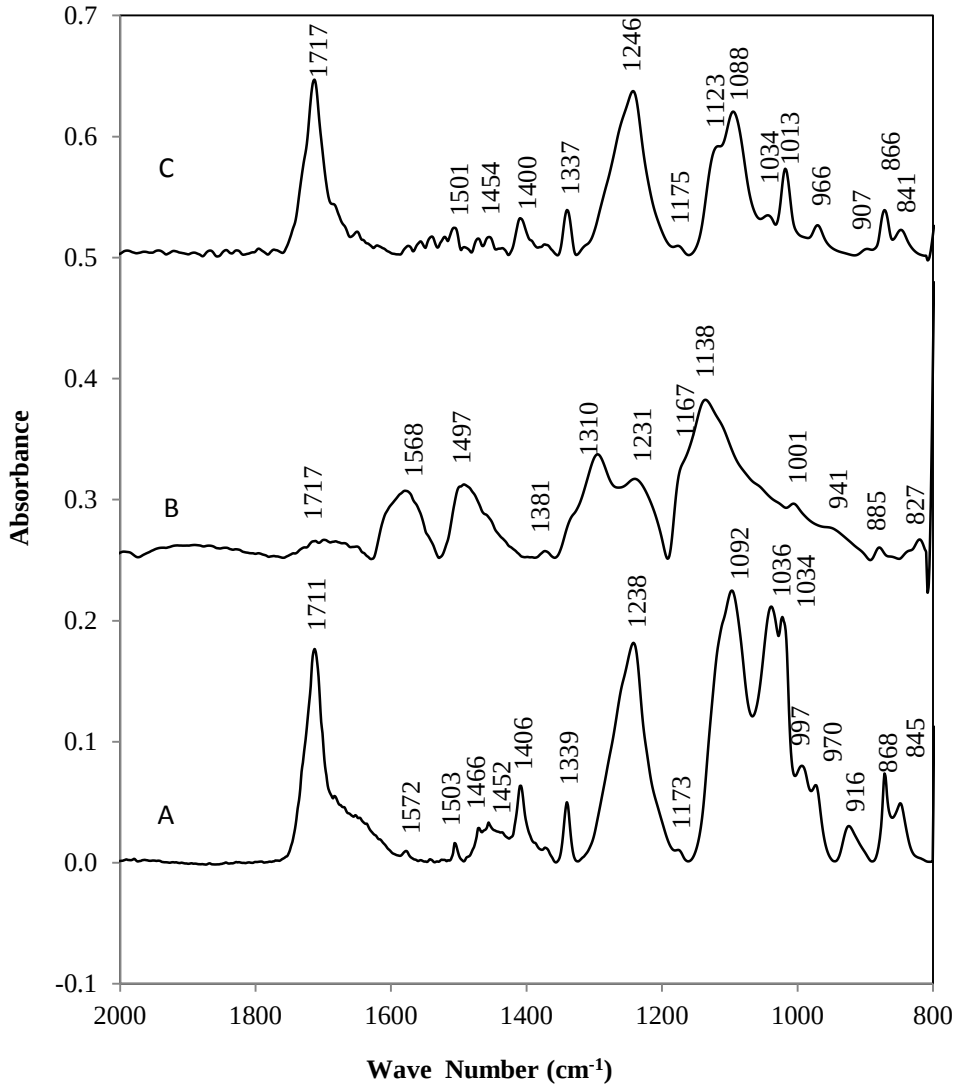


*Figure 3: FTIR spectra (A) Uncoated PVDF membrane (B) 3ABAPANI powder (C) 3ABAPANI on PVDF membrane*

### 3.2.2 Contact angle measurements

Contact angle measurements were carried out to determine the hydrophilicity of both uncoated and coated membranes. In which case, deionised water was used for the measurement. It is acknowledged that a hydrophilic membrane allows a high membrane flux to be exhibited. Results in Table 1 indicate that coating the membrane with 3ABAPANI makes the membrane to become less hydrophilic (Table 1), although the contact angle is still below 90º (within hydrophilic range). On the other hand, the antimicrobial property of the membrane compensates the decrease of the hydrophilicity.

*Table 1: Water contact angle of uncoated and coated PVDF membrane*

| Membrane | Water Contact Angle |
|---|---|
| Uncoated PVDF | 60 |
| 3ABAPANI coated PVDF | 83 |

### 3.2.3 SEM characterisation

SEM micrographs depicting the morphologies of 3ABAPANI, uncoated and coated membrane with 2wt% 3ABAPANI can be seen in Figure 4. The membranes coated using the ex-situ method exhibit the granular morphology, which is consistent with the structure of the 3ABAPANI material used. The morphology of PANI is amorphous. However, the 3ABAPANI shows two features, one amorphous and the other a crystalline domain. The crystalline morphology is due to the intramolecular hydrogen bonded amino benzoic acid units(Rao & Sathyanarayana, 2002).

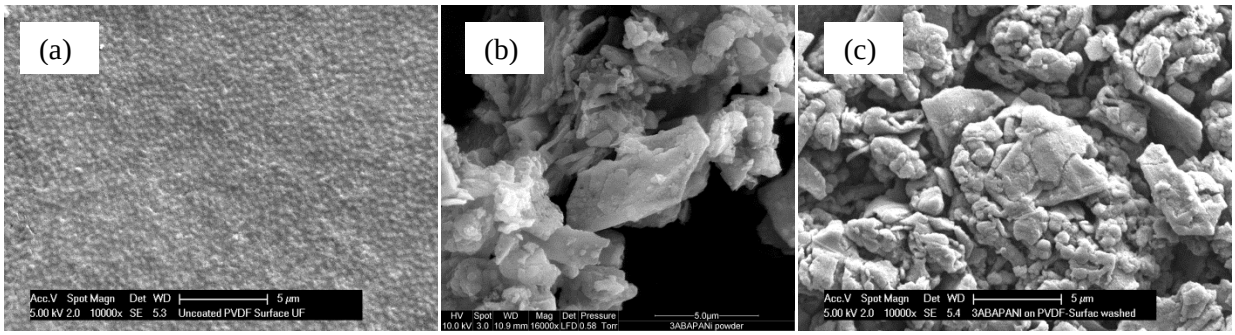


*Figure 4: Scanning Electron Microscopy (SEM) image of (a,b) Uncoated PVDF membrane, (c,d) 3ABAPANI powder (e,f) PVDF modified membrane with 3ABAPANI at 10000x magnification*

## 3.3 Antimicrobial analysis

### 3.3.1 Calibration results

Following the calibration procedure described in section 2.5.1, the equations shown below were obtained from the plotting the data using Microsoft Excel and converting the results to the number of bacterial cells using curve fitting.

<u>*E. coli*</u>

$$x = 1000000000 - 141421\sqrt{50014369 - 500y} \quad (2)$$

<u>*M. smegmatis*</u>

$$x = 31622.8\sqrt{1000y - 28249} - 4000000 \quad (3)$$

In both scenarios:
$x$=*Number of bacterial cells*

$y=Lux$

It was evident from the original calibration curves of the bacterial species that the cell count was effectively zero when the lux value was approximately 29 and 44 for *E. coli* and *M. smegmatis* respectively. The shape of the calibration curves for both bacteria is parabolic, which is because they provide realistic results.

### 3.3.2 Control testing

The measurements obtained from membranes without microbes confirmed that both uncoated and coated membranes exhibited a natural luminescence. Furthermore, with the addition of a filter paper moistened with TSB broth beneath the membrane, it was determined that there was no significant difference between readings obtained using this method and the previous method described. This indicates that the luminescence readings obtained with microbes added to the membrane surfaces were unaffected by the addition of a filter paper and broth. Consequently, due to the large standard deviations recorded for the obtained results and the time dependent variability in the measurements taken, for all antimicrobial testing, the effects of the natural luminescence of the membranes were not deducted.

### 3.3.3 Analysis of bacterial inhibition

When tested with *E. coli* as shown in Figure 5, the 2 wt% 3ABAPANI membrane showed a fast inhibition of cell growth. It is acknowledged that below 100 bacteria remained after modification of the membrane. The sample continued to show significant bacterial inhibition 24 and 48 h after inoculation. This result is corroborated with the fact that the number of cells on the uncoated membrane was not significantly inhibited over the 48 h testing period.

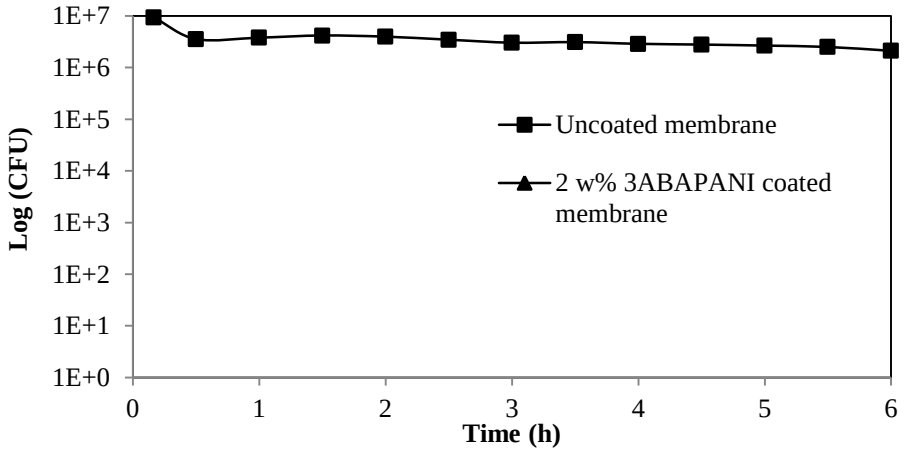


*Figure 5: Number of E. coli cells after exposure to the membrane surfaces over time*

Figure 6 demonstrates the effect of 3ABAPANI on the *M. smegmatis* cell inhibition, which decreases the number of cell growth compared to uncoated membrane about 10%. *M. smegmatis* appears to be more difficult to inhibit than *E. coli* on the membrane surface, as there was a larger number of cells present throughout testing compared to *E. coli*. It is possible that due to the hydrophilicity of the membrane and hydrophobicity of *M. Smegmatis* bacteria, this strain can adhere to the membrane surface, weakly.

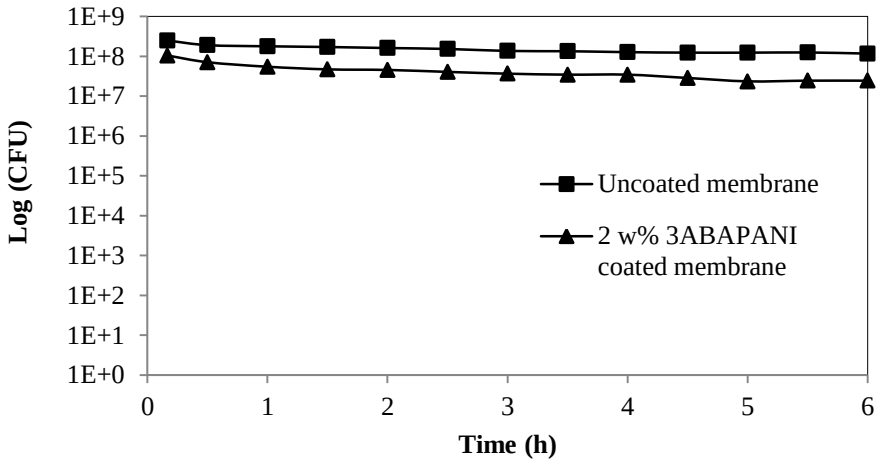


*Figure 6: Number of M. smegmatis cells after exposure to the membrane surfaces over time*

## 3.4 Pure water flux cross-flow filtration

Figure 7 shows the pure water flux of uncoated and coated PVDF membrane with 3ABAPANI, depicting that coating the membrane with 3ABAPANI decreases the pure water flux from around 300 to nearly 130 ($L.m^{-2}.h^{-1}$). Further work is required to optimise the thickness of coating to minimise the mass transfer resistance of the membrane caused by coating material.

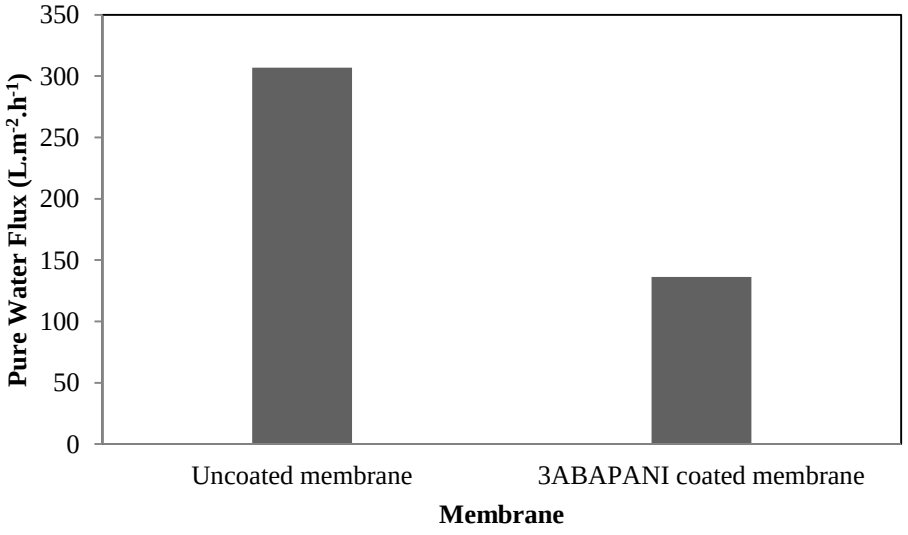


*Figure7: Pure water flux for uncoated and coated PVDF membrane with 3ABAPANI*

## 4. Conclusion

PVDF membrane was successfully coated with 3ABAPANI, using the ex-situ synthesis method. This was confirmed by FTIR spectra, as well. SEM analysis demonstrated that the membrane morphology was consistent with the applied materials whilst the membrane coatings showed increased hydrophobicity

compared to the uncoated equivalent membrane. In addition, the membranes, when tested with *E. coli* and *M. smegmatis* bacterial strains showed bactericidal capabilities supporting the use of the polymer materials as membrane modifications for reducing the fouling effects.

Throughout the investigation, several directions of future research have been identified. Hydrophilicity of the membrane coated with 3ABAPANI may increase by grafting some chemicals or depositing nanoparticles. Study of the effect the coated membrane on organic fouling is also another research gap.

## 5. Acknowledgements

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