Highly hydrophilic copolymer based PES hollow fibre ultrafiltration membranes

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Abstract

Bio-fouling is a major issue in all membrane-based water treatment systems and there are several cleaning methods available to address this problem. Current membrane modification methods are focused on improving the hydrophilicity of membranes by blending hydrophilic additives or blending antibacterial compounds with the dope solution. In this study, we demonstrate a new method to impart bio-fouling resistance to a membrane surface by developing a water insoluble unique copolymer additive, namely poly (acrylonitrile co maleic acid co di-amino maleio-nitrile) (PANCMACDAMN) with highly hydrophilic carboxylic and amine functional groups. Hydrophilic polyethylene glycol functionalized with silver (Ag) was grafted to the copolymer backbone to further improve the hydrophilicity. The final additive PEG-Ag attached PANCMACDAMN was used to modify polyethersulfone (PES) ultrafiltration (UF) membrane. Characterization tests indicate that the innovative surface chemistry increases the hydrophilicity of the membrane by reducing the water contact angle (CA_w) by 78.1% and increases its permeability by 120% compared to the control membrane. More importantly, the innovative surface chemistry prevents protein attachment and exhibits inhibition to microbes even after 720 min of continuous protein solution filtration.

Keywords: Biofouling, ultrafiltration, self-cleaning, hydrophilic membrane, surface modification.

Introduction

Insufficient access to clean freshwater is one of the most pervasive problems afflicting mankind throughout the world [**1,2,3**]. Membrane-based filtration systems have led to their proliferation in wastewater treatment due to their reliability and ease of operation. However, bio-fouling is one of the most serious problem in all membrane based separation processes and it is very difficult to control in wastewater treatment [**4,5**].

Physical [**6**], chemical [**7,8**] and biological [**9,10**] treatment methods have been proposed to control bio-film on the membrane surface. As prevention is better than cure, preventing the attachment of bacteria on the membrane is more effective in managing membrane fouling. This requires membrane engineering methods to modify the membrane surface in terms of reducing or preventing bacterial adhesion [**11**]. The current state of art membrane modification techniques include the blending of either hydrophilic additives or an antibacterial compound into the membrane matrix [**12**], with silver being more commonly employed [**13,14,15**].

Poly (N-vinyl pyrrolidinone) (PVP) [**16**] and polyethylene glycol (PEG) [**17**] are the well-known hydrophilic polymer additives for the modification of ultrafiltration (UF) membranes. However, elution of these highly hydrophilic additives from the membrane matrix is unavoidable in real field application with harsh operation conditions [**18**]. Recently, in an attempt to prevent elution, monomers of these additives or monomers with highly hydrophilic functional groups (hydroxyl, carboxylic and amine) were polymerized with water insoluble monomers to produce a matrix with stable hydrophilicity [**12, 19, 20**].

In our recent study, we showed that the hydrophilicity and the antifouling property of the PES UF membrane can be improved by blending the highly hydrophilic, water insoluble poly (acrylonitrile-co-maleic acid) (PANCMA) grafted with polyethylene imine-silver (PEI-Ag) [**12**] and polyethylene glycol-silver (PEG-Ag) [**20**]. The findings proved that these highly hydrophilic hydroxyl, carboxyl and amine functional groups containing water insoluble additives not only improve the hydrophilicity of the membrane but, also impart long lasting antifouling properties to the membrane via a killing and cleaning mechanism. **Fig. 1** shows a schematic comparison of the anti-fouling mechanism exhibited by the silver modified membrane and the proposed self-cleaning biofouling resistant membrane.

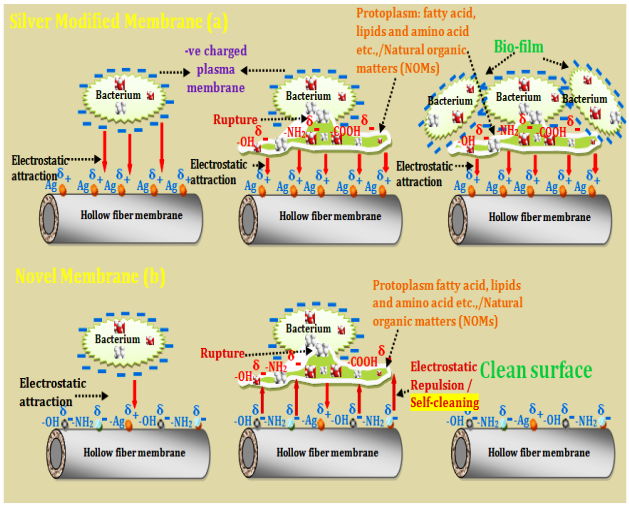

Fig. 1. Schematic representation of the silver modified membrane (a) and the proposed self-cleaning biofouling resistant membrane (b).

In this present study, we developed a novel biofouling resistant self-cleaning membrane by using a copolymer with hydrophilic carboxyl and amine groups immobilized with PEG and positively charged silver nanoparticle. In order to achieve this objective, monomers with the desired functional groups (acrylonitrile, maleic acid and di-amino maleio-nitrile) were chosen and polymerized to obtain the final polymer poly (acrylonitrile co maleic acid co di-amino maleio-nitrile) (PANCMACDAMN). PEG grafted with silver nanoparticles were covalently attached to the prepared copolymer additive by a thermal grafting method. The functionalized copolymer was then blended with PES to produce ultrafiltration membranes.

Experimental

Materials

Polyethersulphone (PES) powder was purchased from Sumitomo Chemicals pte ltd, Japan. Acrylonitrile, maleic anhydride, azoisobisbutyronitrile (AIBIN), silver nitrate ($AgNO_3$) and polyethylene glycol (PEG) of molecular weight 400 were purchased from Sigma Aldrich with 99% purity. High purity ethanol, N-methyl-2- pyrolidone (NMP), polyvinyl pyrolidone (PVP-K30) and diethylene glycol (DEG) were also purchased from Sigma Aldrich and used as received. Water used for the reaction was distilled and de-ionized (DI) with a Milli-Q plus system from Millipore, Bedford, MA, USA.

Methods

Synthesis of poly (acrylonitrile co maleic acid co di-amino maleio-nitrile) (PANCMACDAMN)

Copolymerization of acrylonitrile, maleic anhydride and diaminomaleionitrile was performed using AIBN as initiator. Typically, to a reactor with 250 ml DI water at 90°C, 9.8 g maleic anhydride, 5.3 g acrylonitrile and 10 g of diaminomaleionitrile were added. The reactor was equipped with a mechanical stirrer, thermometer, and nitrogen inlet tube. After complete dissolution, 1.85 g AIBIN was added into the stirring solution while maintaining the reaction temperature at 90°C under nitrogen atmosphere. The copolymerization was continued for 5 hrs, after which, the precipitated copolymer was filtered and washed with excess de-ionized water and ethanol to remove residual monomers. After thorough drying in a vacuum oven at 70°C overnight, the synthesized PANCMACDAMN was further functionalized with PEG and Ag before being used as an additive to prepare the PES dope solution.

Attachment of PEG and Ag with PANCMACDAMN

To further functionalize the copolymer, 25 g of PANCMACDAMN was dissolved in 200ml of NMP. After complete dissolution, about 10 g of PEG and 1 g of silver nitrate was added to the solution and allowed to stir at 80°C for about 8 hrs. 10ml of 0.1 M solution of sodium borohydride was slowly added to the above solution and allowed to stir at the same temperature for another 3 hours. Finally, the solution was precipitated in methanol and filtered and washed with ethanol to obtain functionalized PANCMACDAMN. **Fig. 2,** shows the schematic representation of the Synthesis of PANCMACDAMN and attachment of PEG and Ag with PANCMACDAMN.

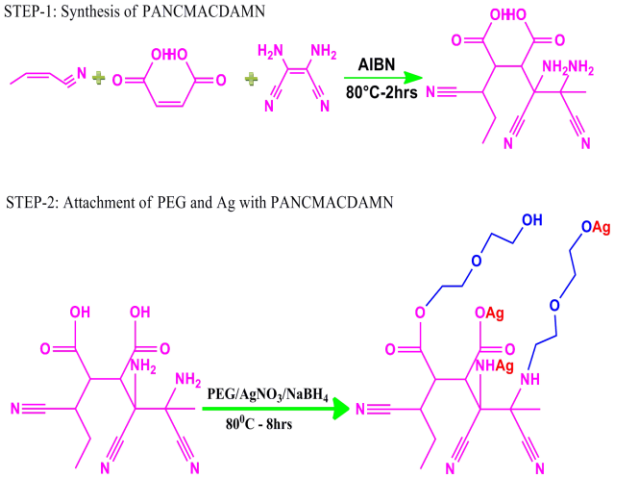

Fig. 2. Synthesis of PANCMACDAMN and attachment of PEG and Ag with PANCMACDAMN.

Preparation of membranes by dry wet spinning

The PES hollow fiber membranes were prepared by dry wet spinning method. PES was used as the base polymer, NMP was the base solvent, DI water was used as a non-solvent and two additives, PVP-K-30 as pore forming agent and hydrophilic PEG and silver grafted PANCMACDAMN were used to improve the surface property of the membrane. The composition of the casting solution consists of 21 wt% PES, 5 wt% PVP-K-30, 5wt% DEG, 59~69 wt% NMP and 0-10wt% PANCMACDAMN, (M1-0%, M2-2.5%, M3-5%,

M4-7.5% and M5-10%) respectively. The composition of the dope solutions and the phase behavior of the dope solutions are shown in **Fig. 3.**

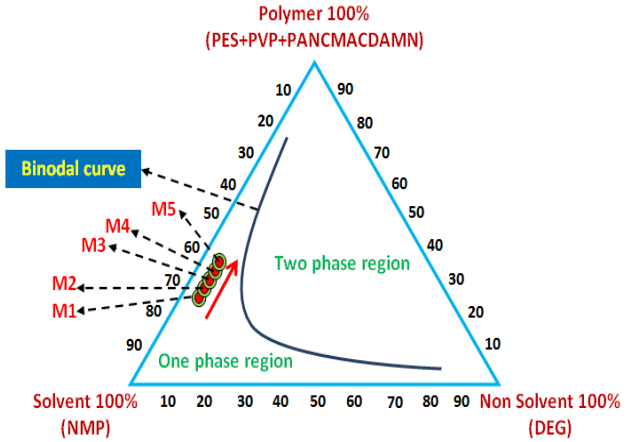

Fig. 3. Phase diagram of the dope composition with optimization direction.

PVP powder was first added into the NMP/DEG mixture in a round bottom (RB) flask and the solution was stirred by a mechanical stirrer for at least 1 hour. After complete dissolution of PVP, PEG-Ag grafted PANCMACDAMN and PES were added and allowed to stir at a constant speed of 250~350 rpm for at least 24 h at 80^{o} C, to obtain a completely dissolved homogeneous polymeric solution. All dope solutions from M0-M5 were used to fabricate the membranes. The dope solution was poured into the polymer tank and degassed at a vacuum pressure of -0.6 bar for 20 min. Nitrogen gas was purged into the dope tank to create an inert atmosphere and to push the polymer to the polymer pump. NMP and water were mixed in 80:20 volume ratio and poured into the bore liquid tank. The polymer solution and the bore liquid were pumped to the spinneret (OD 1.2mm, ID 0.6 mm). The air gap was fixed at 10mm. The hollow fiber membranes were fabricated at around 25^{o}C and at around 65% relative humidity with a take up speed of 0.25 m/s. The membrane turned opaque soon after coming into contact with water which indicates that the coagulation and precipitation of PES from the solution and finally a translucent, white hollow fiber membrane was formed. The membrane was then collected from the winder and left inside a water tank (post coagulation tank) for a minimum of 24 hrs to washout the residual NMP, DEG and PVP that was not removed from the solution at the point of coagulation. All the prepared membranes were immersed into a post treatment solution of 40% ethanol and 60% glycerin before testing the clean water flux.

Results and discussion

Molecular weight analysis

Gel Permeation chromatography (GPC) was used to study the molecular weight (Mw) and the molecular weight distribution of the synthesized polymer with respect to polystyrene standards. From the analysis, the molecular weight of the polymer was found to be around 95971 g/mol. The number average molecular weight was around 75800 g/mol. The polydispersity index (Mw/Mn) was calculated to be 1.27. This analysis confirms the high molecular weight of the synthesized polymer with controlled polymer width.

Fourier Transform Infra-Red analysis (FTIR)

PES and PES/PEG-Ag grafted PANCMACDAMN hybrid hollow fibers were successfully fabricated by using the dry wet spinning process. FTIR analysis was used for the structural confirmation of incorporation of PEG-Ag grafted PANCMACDAMN into PES matrix. The FTIR spectrum is shown in **Fig.4**.

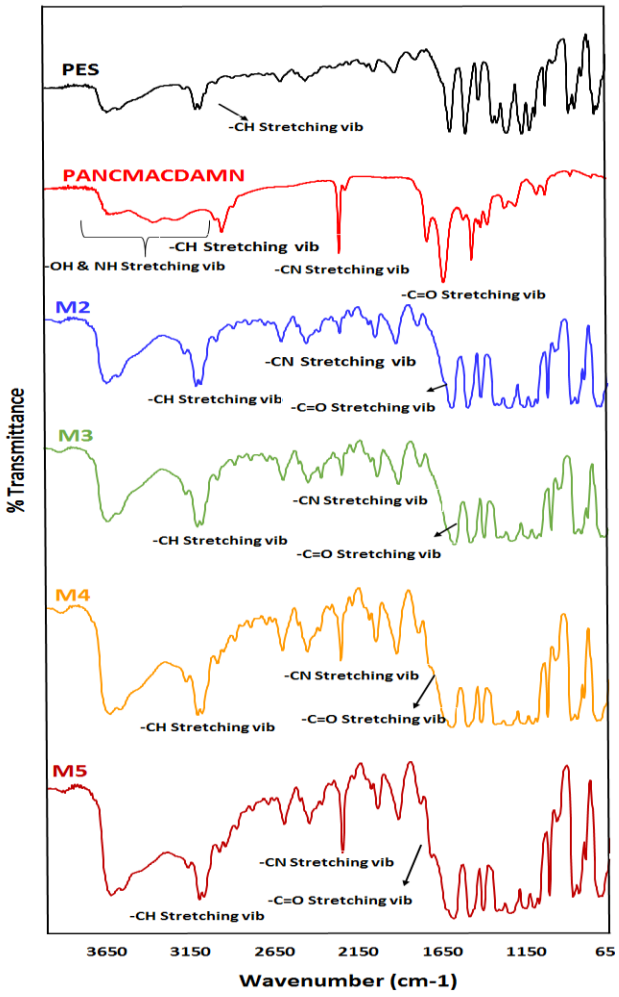

Fig. 4. FTIR spectrum of the new additive PANCMACDAMN and presence of the new additive in the modified PES membranes.

The vibrational peak at 2921cm^{-1} can be assigned to the –CH stretching vibration of the PES, PEG and PANCMACDAMN. The peak at 2241cm^{-1} can be assigned to the CN stretching peak for nitrile group of the co-polymer. The peaks at 3492cm^{-1} and 1690cm^{-1} can be assigned to the OH stretching vibration of the PEG and the carbonyl stretching vibrations of the acid groups in

copolymer respectively. All these peaks confirms the presence of PEG-Ag grafted PANCMACDAMN in PES matrix. It can also be observed that the peak intensity of the copolymer increases with increase in concentration.

Morphological analysis

The hollow fiber membranes fabricated through dry-wet spinning process had an average inner diameter of 0.6mm and an outer diameter of 1.2mm. The cross-section morphology of all the prepared hollow fiber membranes were examined using SEM and the micrographs of the control sample (M1) and the best performing membrane sample (M4) are presented in **Fig.5 (a, b)**.

The morphology analysis shows that the hollow fibers exhibit different internal structures depending on their composition. M1 is the neat PES membrane which shows the presence of large number of macro voids in its internal structure. When the PANCMACDAMN concentration increased from 2.5 wt% to 10wt%, the void structure diminished gradually and formation of uniform sponge like structures over the membrane cross section was observed. This can be explained by the increase in viscosity of the polymer solution with increase in PANCMACDAMN concentration. Generally, an increase in solution viscosity slows down the diffusion of non-solvent into the membrane which in turn decreases the rate of coagulation. The cross-section morphology and uniform distribution of silver in membrane sample M4 can be observed from **Fig. 5 (c)**.

Leaching test for silver

The membrane samples grafted with PEG-Ag functionalized PANCMACDAMN were washed with excess DI water for 2 hours and dried at room temperature before testing. The dried samples of M2, M3, M4 and M5 were immersed in DI water and ultra-sonicated at 37 kW for 60 mins. After ultra-sonication, the water was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-OES). The leached silver was found to be less than 0.01% for all the samples. This confirmed strong covalent bonding of silver with the functional groups of the PANCMACDAMN, which prevents the leaching of silver.

Contact angle

The hydrophilicity of the membrane was measured by their water contact angle and the results are tabulated in **Table 1.**

Sample ID	CAw (°)	Pore size (μm)	PWF (LMH)
M1	64.6± 3.2	0.07 ± 0.02	477.6± 18.2
M2	49.1± 1.7	0.07 ± 0.02	666.2± 22.0
M3	32.4± 2.0	0.06 ±0.025	858.6± 27.1
M4	18.7± 1.3	0.05 ± 0.02	1050.2± 24
M5	14.2± 2.3	0.04 ± 0.02	984.6± 14.1

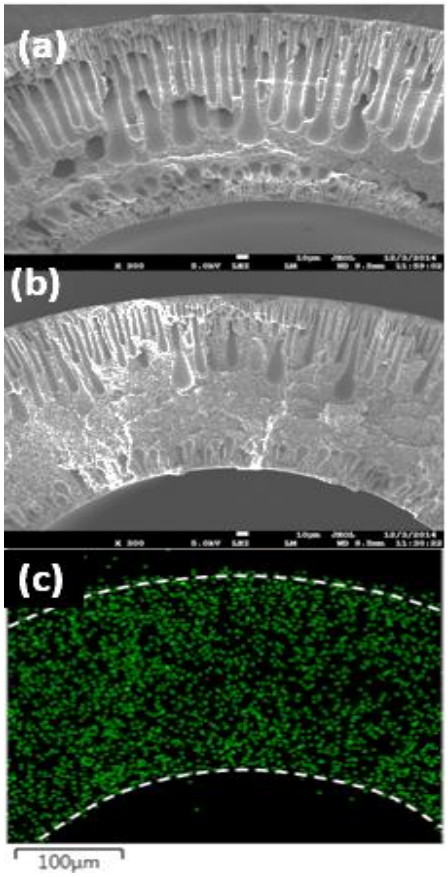

Fig. 5. SEM image (cross section) of control membrane M1 (a) and modified (best performing) hollow fiber membranes sample M4 (b) Elemental mapping of modified (best performing) hollow fiber membranes sample M4 (c).

With M1 being the control, the rest of the samples showed a decrease in water contact angle with an increase in PANCMACDAMN concentration. The lowest water contact angle was exhibited by M5 with 14.2 ± 2.3^{o}, which is 78.1% lower than that of the control membrane (contact angle of control membrane was 64.6 ± 3.2^{o}). This significant drop in contact angle was achieved mainly because of the incorporation of hydrophilic PANCMACDAMN grafted PEG-Ag to PES matrix.

The hydrophilic groups in the copolymer additive attracts water more effectively and hence a drop in Contact angle was achieved. This is similar to Zhu et al., who has reported a 25% reduction in contact angle of PES membrane by blending 2% of Styrene –co- maleic acid [**21**].

Pore size analysis

The average pore size of the control PES membrane (M1) and the PEG-Ag grafted PANCMACDAMN modified PES membrane samples M2, M3, M4 and M5 are presented in **Table 1.** The experimental data indicates that the mean pore size of the membranes decreases gradually with increase in the PANCMACDAMN concentration. This may be due to the increase in viscosity and coagulation of the dope solution. Generally, pores in the

membranes are formed by diffusion of non-solvent from coagulation bath into the membrane matrix and the de-solvation of casting solvent. If the solution viscosity increases, the diffusion of coagulant into the casting solution will be reduced and hence the macro voids can be reduced. The dense surface generally forms when a high ratio of the solvent out flow occurs compared to the non-solvent inflow.The lowest average pore size achieved was 0.04 ± 0.02µm for membrane sample M5 whereas the control membrane exhibited a mean pore size of 0.07 ± 0.02µm.

Membrane performance analysis

Clean water flux

The membranes M1-M5 were tested to evaluate the clean water flux of the membrane by using a cross flow filtration setup at a constant feed pressure of 1bar and the results are presented in **Table 1**. All membranes were tested in the system under similar conditions with M1 as the control. The pure water flux of the membrane increased with increasing PEG-Ag functionalized PANCMACDAMN concentration. The highest flux achieved in this study was 1050.2 ± 24 LMH for the membrane sample M4 which is around 120% higher than the control membrane M1 (477.6 ± 18.2 LMH). This improvement is mainly due to the increase in the membrane hydrophilicity provided by the incorporation of polymer additive. The copolymer additive contains hydrophilic hydroxyl (-OH), amine (-NH_2) and acid (-COOH) groups. This observation replicates the previous results reported in literature on the flux improvement achieved by the incorporation of hydrophilic additives. When a water molecule comes in contact with these functional groups, they from hydrogen bonding with water and thereby they increase the permeability of a membrane. However, when compared to M4, sample M5 gives slightly lower flux due to the slight reduction in membrane pore size or pore compression.

Fouling evaluation using Bovine Serum Albumin (BSA) solution

In order to evaluate the effect of the PEG-Ag grafted PANCMACDAMN on the membrane, the control M1 and the best performing membrane sample M4 were chosen on the basis of pure water flux permeability tests (**Table 1**). A 12hrs filtration test was conducted using 10ppm BSA in DI water as a feed solution. For this filtration test, three membrane modules for each membrane (Control and modified) were subjected for testing under same conditions simultaneously and the average permeability was taken and reported here. The results are summarized in **Fig. 6 (b).** It is observed that the PEG-Ag grafted PANCMACDAMN modified membrane sample M4 gives a more stable flux compared to the control membrane sample M1. **Fig.6 (c)** shows the normalized permeability (*J*/*J0*) or flux drop over time for the BSA filtration test. The flux drop for the membrane M4 is only 14.29% of the initial flux after 9hrs protein separation whereas the flux drop for control membrane M1is 60% for the same duration of operation. The obtained results highlight that the presence of negatively charged –OH, and –COOH functional groups on the PEG-Ag grafted PANCMACDAMN can best repel the protein from the surface of the membrane. In order to evaluate the selectivity and the filtration efficiency of the membrane, the total organic carbon (TOC) of the feed BSA solution and permeate water were measured (4 samples were collected every 60mins with 15mins frequency and the TOC was measured in order to get the average TOC removal over time). The percentage of TOC rejection was calculated and presented in **Fig. 6(d).**

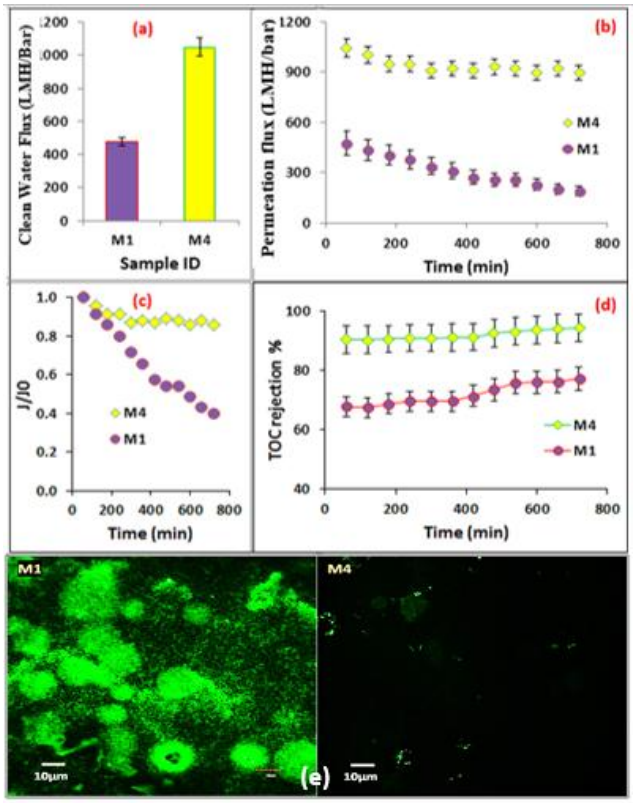

Fig. 6. Clean water flux for the control membrane sample M1 and the best performing membrane sample M4 at 1bar feed pressure (a), Permeation flux during long time run with 10ppm BSA solution at 1bar feed pressure for the samples (b), normalized water permeability for the BSA solution separation during long time run (c) and BSA protein (TOC) removal efficiency / selectivity of the membranes in % (d) Confocal lacer scanning (CLSM) image of control (M1) and best performing membrane sample (M4) after protein filtration (e).

From the experimental data, it is found that, the TOC removal of the membrane M4 is higher and more stable compared to membrane M1. This result also confirms the increased hydrophilicity of the PEG-Ag grafted PANCMACDAMN blended membrane. Recent studies have also shown that the negative surface charge of the membrane prevents the deposition of the negatively charged colloidal particles such as proteins, lipids and

amino acids etc., on the membrane surface by electrostatic repulsion, which could slow down or reduce the membrane fouling [**22,23**]. On a related note, it is interesting to see from **Fig. 6(d)** that the increase in TOC removal efficiency of the control membrane M1 with time may be due to the pore constriction/pore blocking or development of fouling on the membrane surface [**24**]. Finally, a confocal lacer scanning microscope (CLSM) analysis was conducted on the membrane samples to evaluate the protein absorption on the membrane surface and the images are presented in **Fig. 6(e)**. From the images it can be further confirmed that the protein absorption on the membrane M4 surface can be negligible however, the protein absorption on the control membrane M1 is high.

Conclusion

Bio-fouling is a major issue in all membrane-based water treatment systems. In this study, we demonstrate a new method to impart bio-fouling resistance to a membrane surface by developing a highly hydrophilic water insoluble unique copolymer additive, namely poly (acrylonitrile co maleic acid co di-amino maleio-nitrile) (PANCMACDAMN) with electronegative carboxylic functional groups. In addition, another highly hydrophilic polyethylene glycol (PEG) and positively charged antibacterial compound silver (Ag) were covalently attached to the copolymer additive by a thermal grafting method. The final additive PEG-Ag attached PANCMACDAMN was used to modify polyethersulfone (PES) ultrafiltration (UF) membrane. Characterization tests indicate that the innovative surface chemistry increases the hydrophilicity of the membrane by reducing the water contact angle (CA_w) by 78.1% and increases its permeability by 120% compared to the control membrane. More importantly, the innovative surface chemistry prevents protein attachment to it and continuously exhibit inhibition to microbes even after a 12hrs continuous filtration of protein solution. Based on the findings, it can be concluded that the novel PEG-Ag attached PANCMACDAMN will be an ideal additive to prevent biofouling on the membrane surface.

Acknowledgements

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