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PES-PANCMA Hollow Fiber Ultrafiltration Membranes with Long-lasting Antifouling Properties

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Abstract

In this study, functional modification of PES hollow fiber membrane has been carried out by incorporating highly hydrophilic polyethylene glycol (PEG) and silver nanoparticles (Ag) through thermal grafting. Poly(acrylonitrile-co-maleic acid) (PANCMA) was used as a linker to chemically attach PEG and silver to PES hollow fiber membrane. The successful functional modification of PES membrane was confirmed using different analytical techniques such as, Fourier transform infrared (FTIR) spectroscopy, Energy-Dispersive X-ray (EDX) studies, water contact angle (CA), Fourier Emission Scanning Electron Microscopy (FESEM), and the porometer. Further, the membranes were tested for the pure water flux and antifouling properties. From the contact angle data, it was identified that the new surface modification can increase the membrane hydrophilicity. The water contact angle of the PES UF membrane can be reduced by around 75.5% from 62.6 ± 3.7 to $15.3 \pm 1.2^\circ$ and the pure water flux increased by about 36% from 513LMH to 702LMH for the modified membrane. Antibacterial activity of the modified membranes was confirmed by the clear zone obtained in the zone of inhibition test. Based on the

experimental data, the prepared modified UF membranes seem promising for wastewater filtration.

Keywords

Ultrafiltration, Super hydrophilic, Surface modification, Photo grafting, Chemical attachment

1. Introduction

Water is a valuable resource to mankind. Over 3.6 million people around the world die each year from drinking unsafe water [1]. With the growing demand for high quality water, many new technologies of water purification are being developed to cater for potable and palatable water to humans. Waste water treatment facilities are also becoming popular in growing chemical and manufacturing industries to reduce pollution and protect the marine environment. Among these technologies are membrane-based processes that are inherently advantageous because of their high efficiency, ease of implementation, declining costs [2] and low environmental impact [3]. Their versatility to purify and recycle water renders them highly competitive candidates for use in water purification and water reclamation plants. However, one major drawback of this membrane technology is its depleting performance over time such as flux reduction, rejection impairment and membrane breakage, leading to high operational costs and short service life [4-6]. These performance deterioration problems originate from the accumulation of the organics that favors the attachment and growth of microorganisms onto the surface of the membrane. Low pressure UF membranes is the research focus of this work, since these membrane systems are suitable for rejection of pathogens and (in)organic micro pollutants and numerous reports indicate that biofouling is one of the most serious problems in these membrane systems [7-8]. To combat these issues, several strategies such as pre-treatment installation, ultrasonic entrenchment, chemical cleaning, backwashing and surface modification of the membranes have been introduced [9-10]. Among these, the most widely adapted method to increase the antifouling properties is surface modification of the membranes. In particular,

considerable efforts have been directed towards improving the hydrophilicity to reduce the membrane bio-fouling issue.

PES (Polyethersulfone), a popular membrane material have been studied for many the years for the synthesis of Microfiltration (MF), Ultrafiltration (UF) and Nanofiltration (NF) membranes due to its excellent chemical and mechanical properties [11-12]. However, its hydrophobic nature has limited its applications especially in membrane separation processes [13]. Thus, several techniques had been developed in order to solve this disadvantage. This includes hydrophilic modifications on the membrane surface to increase its permeability and reduce membrane fouling. Klaysom et al., introduced the surface modification of PES membrane by modifying the PES material through the sulphonation reaction [14]. Sulphonation is the best way of successfully bringing the negatively charged sulphonic acid group on to the PES membrane surface. PES membranes generated by sulphonation are proven to be more hydrophilic, better selective and more resistant to fouling [14-17]. However, during sulphonation (reaction with concentrated sulphuric acid) the physical and chemical property of the material may change (PES may degrade as phenol) [18]. Fig.1. shows the possible chemical degradation of PES during sulphonation.

Fig 1. Degradation of PES during sulphonation (reaction with strong sulphuric acid) [18]

In addition, methods such as coating [19], carboxylation [20], nitration [21], plasma treatment [22], and blending [23] etc, have been reported to enhance hydrophilicity and reduce the deposition of hydrophobic organics on the surface of the membrane. Among them, the blending method has been widely used since it is by far the simplest method [24]. Poly (N-vinyl pyrrolidinone) (PVP), a hydrophilic polymer having no hydroxide group or ionic charged group, has been widely used as a good additive for the modification of PES membrane through the blending method. Marchese et al. [25] observed that the anti-fouling property of the PES membranes blended with different PVPs was significantly increased without a significant reduction in selectivity. Similarly, Idris et al., observed that the polyethylene glycol (PEG) can also increase the membrane porosity and pure water permeability. Besides, PEG concentration in the casting solution was found to have significant effect towards the membrane solution flux and solute separation capability [26]. Several theories/both qualitative and quantitative/have been

proposed to explain the effectiveness of PEG as a component of antifouling (organic-resistant) surfaces [27]. However, it is well known that PVP and PEG are water soluble additives, and the elution of PVP and PEG from the blended membrane is unavoidable. To avoid the elution of PVP from the membrane surface, Moon et al, prepared highly hydrophilic microfiltration membranes by blending polysulfone with poly(vinyl pyrrolidinone acrylonitrile) copolymer via traditional phase inversion process without any process modification [28]. Incorporation of nanomaterials into polymeric matrices could also alter the hydrophilicity and the antimicrobial (anti-bio-fouling) properties of polymeric membranes. The nanoparticles such as silica [29], titanium dioxide [30], silver [31-33], zirconium dioxide, selenium and copper [34] (Akar et al., 2013) were used to modify the PES membrane surface. Still, research has been geared up again in search of a better membrane modification method to improve the PES-based membranes in the past few years [35].

In this work, a long lasting antifouling PES-PANCMA based ultrafiltration hollow fiber membrane was developed by grafting highly hydrophilic polyethylene glycol (PEG) and silver nanoparticle (Ag) on to the surface of the membrane. PANCMA was used as a linker to covalently attach the PEG and silver. The membranes were characterized using Fourier transform infrared (FTIR) spectroscopy, Energy-Dispersive X-ray (EDX), Contact angle (CA), Scanning electron microscopy (SEM), and the porometer. Both control and modified PES-PANCMA membranes were tested by zone of inhibition test and clean water flux test. Finally, the membranes were tested for their permeability and antifouling activity. The modified membranes seem promising to prevent fouling in UF application.

2. Experimental

2.1. Materials

Polyethersulphone (PES) powder was purchased from Sumitomo chemicals pte ltd, Japan. Acrylonitrile, Maleic anhydride, Potassium persulphate ($K_2S_2O_8$), anhydrous Sodium sulfite (Na_2SO_3), Silver nitrate ($AgNO_3$) and Polyethylene glycol (PEG) of molecular weight 400 were purchased from sigma Aldrich with 99% purity. High purity ethanol, NMP (N-methyl-2-pyrrolidone), PVPK30 (Polyvinyl pyrrolidone) and DEG (Diethylene glycol) were also purchased from sigma Aldrich and used as received. The water used was distilled and de-ionized (DI) with a Milli-Q plus system from Millipore, Bedford, MA, USA.

2.2. Synthesis of poly (acrylonitrile co maleic acid) (PANCMA)

Copolymerization of acrylonitrile and maleic anhydride was performed according to the previously reported precipitation polymerization process using $K_2S_2O_8$ and Na_2SO_3 as initiator [36]. After thorough drying, the synthesized PANCMA was used to prepare the dope solution.

2.2.1. 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, pore forming PVP and hydrophilic PANCMA 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, 5 wt% DEG, 59~69 wt% NMP and 0-10 wt% PANCMA, respectively. The composition of the dope solutions is shown in Table 1. The phase diagram for the used dope composition is shown in Fig. 2. PVP powder was first added into the NMP /DEG mixture in a RB flask and the solution was stirred by a mechanical stirrer for at least 1 hour. After complete dissolution of PVP, PANCMA and PES were added and allowed to stir at a constant speed of 250~350 rpm for at least 24 h at 80°C, to obtain a completely dissolved homogeneous polymeric solution. The solution (S5) with 10% PANCMA concentration was found to be heterogeneous. All other dope solutions from S0-S4 were used to fabricate the membranes. The dope solution was poured into the polymer tank and degassed at a vacuum pressure of -0.6bar for 20min. Nitrogen gas was purged into the dope tank to create inert atmosphere and to push the polymer to the polymer pump. NMP and water were mixed in 80:20 volume ratio (NMP: Water 80:20) and poured into the bore liquid tank. The polymer solution and the bore liquid were pumped to the spinneret (OD 1.2mm, ID 0.6mm). The air gap was fixed at 10mm. The hollow fiber membranes were fabricated at around 25°C and at around 65% relative humidity by means of a take up speed of 0.25m/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 h to washout the residual NMP, DEG and PVP that was not removed from the solution at the point of coagulation.

Fig 2. Phase diagram for the dope composition

Table 1 Composition of the dope solutions for the hollow fiber membrane fabrications

Sample ID	PES (wt%)	PVP- K30 (wt%)	DEG (wt%)	NMP (wt%)	PANCMA (wt%)
S1	21	5	5	69	0
S2	21	5	5	66.5	2.5
S3	21	5	5	64	5
S4	21	5	5	61.5	7.5
S5	21	5	5	59	10

2.2.2. Membrane surface modification

Before surface modification, the prepared hollow fiber membranes were washed with water and ethanol to clean the surface of the membrane for about 15 min. The cleaned membranes were then immersed in 500ml of 2:1 PEG: AgNO₃ aqueous solution at 80°C for 2hrs for thermal grafting.

Fig 3. Schematic representation of stepwise modification of hollow fiber

Fig 3 shows the surface modification of PES-PANCMA membrane. The surface grafted membranes were then washed with excess water and dried at room temperature before characterization. The surface modified membranes were immersed into a post treatment solution of 40% ethanol and 60% glycerine before testing the clean water flux.

2.3. Membrane characterization

The unmodified as well as the surface modified hollow fiber membranes were investigated by Fourier transform infrared (FTIR) spectroscopy (FTIR8400, Shimadzu, Japan). The spectra were

measured in the transmittance mode from the wave number range 4000 – 450 cm^{-1} with 45 scans. A scanning electron microscope (SEM) Jeol Jsm-7600F coupled to a XmaxN detector for energy-dispersive X-ray (EDX) analysis was used to study the morphological appearance, the overall chemical composition and the distribution of the chemical elements of interest in the membrane. To obtain clear images, the surface modified PES hollow fiber membrane samples were sputter coated with platinum, using a JFC-1600 auto fine coater (JOEL, Tokyo, Japan) and then observed by using scanning electron microscopy. To obtain the cross-section images, membranes were immersed in liquid nitrogen and fractured before measurement. The effects of surface modification on the morphology were evaluated. The water contact angles (CAw) of the unmodified and modified hollow fibre membranes were determined using the Sigma 701 Tensiometer from KSV Instruments Limited to investigate the effect of surface modification on the hydrophilicity of the membrane. The liquid bowl was filled with DI water. The membrane samples were cut in to 15mm pieces and clamped to the sample holder. The hollow fibre was immersed into distilled water and the advancing contact angle was calculated with the aid of computer software. Five readings were measured for each sample and an average was obtained from the results. The pore sizes of the membranes are measured using the Porometer 3G instruments (equipped with 3GWin control software) from Quanta chrome. The control and the modified membrane samples of 100mm length were bended to 90° and potted in the sample holder using epoxy resin. The membrane samples were wetted in the Porofil liquid before analysis and then placed in the holder. The pore size was measured thrice to get the average pore size for each sample. The antibacterial activity of the control (S1) and the modified PES-PANCMMA membranes S2, S3 and S4 were determined qualitatively using the Zone Inhibition test. First, the nutrient agar is poured onto the disposable sterilized petri dishes and was allowed to solidify. 100 μL of 5×10^5 CFU/ml *E.coli* concentrations was streaked over the culture plate and was spread uniformly. The membrane samples were cut in to small pieces (10mm in length) and were placed gently over the solidified agar plate. The plate was incubated at 37°C for overnight and was observed. The antibacterial activity was identified and estimated by a clear zone of inhibition.

The clean water flux of the control PES (S1) and the modified PES-PANCMMA membranes S2, S3 and S4 were measured by using the filtration system shown in Fig.4. The fibres with the total effective membrane area of 0.03 m^2 were used to fabricate the membrane module. The two

edges of the membrane module were sealed by using epoxy glue while keeping the lumen open on one side to collect the permeate water. The developed membrane module was mounted into the filtration system. Cross-flow ultrafiltration experiments were carried out at 1bar feed pressure.

Fig 4. Filtration set up used to study the clean water flux

Filtration occurred from the outside to the inside of the fiber. The permeation was collected in a beaker mounted on an electronic balance. After compaction, the pure water flux (J_w) was determined. The pure water weight at four different time intervals (interval between each sampling point was 15 min) was measured to get the average water flux for each sample. The pure water flux and permeability were calculated by the following equations:

$$\text{Water flux } (J_w) = \frac{\text{Permeate volume (L)}}{\text{Area (m}^2) \times \text{Time (h)}}$$

Pure water permeability = $J_w/\Delta P$

ΔP is the pressure drop through the membrane (bar).

A long term (4200min) filtration test was carried out by using waste water. Cross-flow ultrafiltration experiments under constant pressure mode were carried out on the control (S1) hollow-fiber membrane module and the best performing modified PES-PANCMA membrane (S3) module by using the same filtration apparatus shown in Figure.5. The waste water was stirred using electrical stirrer to get homogenous feed water and was then pumped through the hollow-fiber membrane at 0.4 bar pressure. The permeation was collected in a vessel mounted on an electronic balance. Flux drop was calculated by using the following equation:

$$\text{Flux drop } (\Delta J_w, \%) = 100 - \left(\frac{J_w(\text{time-x})}{J_w(\text{initial})} \times 100 \right)$$

In order to study the filtration efficiency of the membrane, Total organic carbon (TOC) and turbidity of the feed and permeate were measured and the rejection percentage was calculated according to following equation:

$$\text{Rejection (R, \%)} = \left[1 - \frac{C_p}{C_f} \right] \times 100$$

Where C_p and C_f are permeate and feed concentrations of TOC and turbidity respectively.

3. Results and Discussion

3.1 Membrane Characterization

3.1.1 Fourier Transform infra-red analysis

PES and PES/PANCMA hybrid hollow fibers were successfully fabricated by using the dry-wet spinning process. The fabricated hollow fiber surfaces were then modified with PEG and Ag by a standard thermal grafting process. FTIR analysis was used to investigate the interaction of PEG and Ag to the PANCMA/PES hollow fiber membrane. The FTIR spectrum is shown in Fig 5. Fig.5 represents the FTIR spectra for neat PES membrane S1 as well as for PES/PANCMA

membranes S2, S3 and S4 (blended with 2.5 wt %, 5 wt % and 7.5 wt% of PANCMA respectively) and grafted with PEG and silver. It is confirmed from the spectra that the PEG and silver is successfully grafted to the PES/PANCMA membrane. The band at 2247cm^{-1} is due to the C-N stretching of the nitrile group and the band at 1710cm^{-1} is the C = O stretching vibration of the acid carbonyl group present in the PANCMA. The absorption band at 1169cm^{-1} is attributed to the C-O-C stretching vibration of repeated $-\text{O}-\text{CH}_2-\text{CH}_2-$ units of polyethylene glycol. The broad band at 3558 cm^{-1} is due to the stretching vibration of hydroxyl group present in the PEG. It is also observed that, as the PANCMA concentration increases, the intensity of the PANCMA and PEG vibrational bands increases.

Fig 5. FTIR spectra of S1) PES S2) PES/PANCMA (2.5 wt%)/PEG/Ag S3) PES/PANCMA (5wt%)/PEG/Ag S4) PES/PANCMA (7.5wt%)/PEG/Ag

A schematic representation of the grafting of PEG/Ag to PANCMA and their bonding interaction is shown in Fig 6.

Fig 6. Schematic representation of possible grafting of PEG/Ag to PANCMA

3.1.2 Morphology of Hollow fibers

The hollow fiber membranes fabricated through dry-wet spinning process had an average inner diameter of 0.6mm and an outer diameter of 1.0mm. The surface morphology and cross section of the hollow fiber membranes were examined using SEM and the micrographs were shown in Fig.7 and Fig.8. The Micrographs of the modified hollow fibers show a smooth PEG surface together with uniform distribution of silver particles.

Fig 7. SEM pictures of unmodified and modified hollow fiber membranes

As seen in Fig 8, the hollow fibers exhibit different internal structures depending on their composition. S1 is the neat PES membrane which shows the presence of large number of macro voids in its internal structure. Whereas, as the PANCMA concentration increases from 2.5 wt% to 7.5wt%, the void structure diminishes gradually and formation of uniform sponge like structures over the entire membrane cross section is observed. According to Khayet et al [37], macro voids and cavity structures are formed when the rate of coagulation is fast and sponge like structures are formed when the coagulation process is slow. From the micrographs, it is observed that, the addition of PANCMA reduced the macro voids in the membrane. This can be explained by the increase in viscosity of the polymer solution with increase in polymer concentration. The increase in solution viscosity slows down the diffusion of non-solvent into the membrane which in turn decreases the rate of coagulation.

Fig 8. Cross section morphology of unmodified and modified hollow fiber membranes

3.1.3 EDX analysis of the hollow fiber membranes

The presence of silver particles was further confirmed by EDX analysis and the spectra are shown in Fig 9. The EDX spectra show a peak at 3KeV which corresponds to the silver and the peak around 2.5 KeV belongs to sulphur which comes from PES. It is also observed that, the grafted silver concentration increases with the increase in PANCMA concentration. This fact is further evidenced from the elemental mapping shown as an inset in Fig 9. The EDX mapping also confirms the uniform distribution of silver all over the membrane surface.

Fig 9. EDX results of unmodified and modified hollow fiber membranes

3.1.4 Contact angle

The hydrophilicity of the PES-PANCMA membranes was measured by their contact angle and the results are tabulated in Table 3. With S1 being the control, the rest of the samples shows a decrease in water contact angle with an increase in PANCMA concentration and reached the lowest at S4 with $15.3 \pm 1.2^\circ$. This test has proven the effectiveness of PEG grafting with PANCMA in generating a more hydrophilic membrane with S4 having at least a 75.5% decrease in the contact angle from the control membrane. From the analytical data it is identified that the hydrophilic PEG grafting with PANCMA can be used to reduce the surface CAw of the PES membrane.

3.1.5 Pore Size Analysis

The average pore size of the control PES membrane (S1) and the modified PES-PANCMA membrane samples S2, S3 and S4 are presented in Table 3. The experimental data indicates that the mean pore size of the membranes decrease with the PANCMA concentration. This may be due to the increase in viscosity of the dope solution. The lowest average pore size achieved is $0.05 \pm 0.02 \mu\text{m}$ for membrane sample S4 whereas the control membrane exhibited a mean pore size of $0.09 \pm 0.025 \mu\text{m}$.

Table 3 Pore size, contact angle and the clean water flux of the control PES membrane and the modified PES-PANCMA membrane samples.

Sample ID	Pore size (μm)	CAw ($^\circ$)	Clean water flux (LMH)
S1	0.09 ± 0.025	62.6 ± 3.7	513 ± 21
S2	0.08 ± 0.03	48.1 ± 1.8	567 ± 18
S3	0.07 ± 0.015	24.7 ± 2.3	702 ± 27
S4	0.05 ± 0.02	15.3 ± 1.5	581 ± 14

3.1.6 Zone inhibition test

The antibacterial activity of the control (S1) and the modified PES-PANCMA membranes S2, S3 and S4 were determined qualitatively using the zone inhibition test. Here, the membranes S2, S3 and S4 exhibited positive results with S1 as the control, which do not show any inhibition zone.

Fig.10. shows the zone of inhibition for all different samples from S1 to S4. From the figure, it shows that all the membranes with silver cleared the *E.coli* bacteria around them and we observed distinct zones of inhibition (clear areas with no bacterial growth) around the membranes. The width of the zone around the S1, S2, S3 and S4 was about 0 mm, 1 mm, 2 mm and 2.5 mm respectively. This attributes to the bactericidal property of silver nanoparticles in the composite membranes. It was found that, as the concentration of PANCMA in the membrane increases, the zone of inhibition increases gradually, which is due to the increased attachment of the silver particles onto the membrane via chemical bonding with the acid functional group in PANCMA. In contrast, the control exhibits no zone of inhibition under the same conditions and high bacterial growth near the membrane was detected. These results indicated that the hollow fiber membranes with silver had a broad

Fig 10. Zone of inhibition of modified and unmodified membranes

3.2. Membrane performance

3.2.1 Clean water flux

The membranes S1-S4 were tested to evaluate the clean water flux of the membrane by using a cross flow filtration setup. Table 3 shows the clean water flux of all the four membranes at a constant feed water pressure of 1bar. All membranes were run in the system under similar

conditions with S1 as the control. A trend of increasing flux is shown for the first three membranes with the increase in PANCMA concentration. S3 has highest flux as compared to S1, S2 and S4. Initially the clean water flux increased as PANCMA concentration increased and after S3 the flux dropped gradually. The initial flux increase is due to the increase in hydrophilicity of the membrane and the flux drop is due to the decrease in pore size of the PES-PANCMA (S4) membranes.

3.2.2. Long time performance and the fouling evaluation

A long time (4200min/72hrs) separation test was carried out for the control membrane (S1) and the best performing membrane (S3), and the results are summarized in Fig 11a. It should be noted that the flux drop for the control membrane is higher (45.3% of the initial flux) compared to the PES-PANCMA membrane (19.4% of the initial flux). The flux drop of the membranes is shown in Fig 11b. It is also observed that the modified PES-PANCMA membrane (S3) gives comparatively stable flux. It indicates that there is not much decrease in the flux with respect to time for the hybrid membrane. This stable flux indicates that the PEG-AG grafted PES-PANCMA membrane repel the organic matters from the surface of the membrane (antifouling surface).

Fig 11. Pure water flux (a) and Flux drop (b) for the control and the best performing membrane in long time run

In order to study the filtration efficiency of the membrane, the total organic carbon (TOC) and turbidity of the feed water (reservoir water) and permeate water were measured (6 samples were collected every 60mins once and measured the TOC and Turbidity in order to get the average TOC and Turbidity removal efficiency). Percentage of rejection was calculated and plotted in Fig.12. From the experimental data it was found that the TOC removal of the control (S1) and the modified membrane (S3) were almost same for the first 1000min. However, after 1000min

the modified sample S3 is slightly better than the control sample S1. This is due to the selectivity of the membrane surface. Similarly, the turbidity removal also found to be better for the sample S3 compared to unmodified sample S1.

Fig12. Contaminant removal efficiency for the control and the best performing membrane in long time run with wastewater: TOC rejection (a) Turbidity rejection (b)

4. Conclusions

In the current work, PES-PANCMA hollow fiber membranes were fabricated by dry wet spinning. Highly hydrophilic polyethylene glycol (PEG) and silver nanoparticles (Ag) were covalently attached to the acid group in the Poly (acrylonitrile-comaleic acid) (PANCMA). The prepared membranes were characterized thoroughly. The EDX and the FTIR data confirmed the covalent attachment of silver (Ag) and polyethylene glycol (PEG) with PANCMA. From the contact angle data, it was identified that the new surface modification can increase the membrane hydrophilicity. The water contact angle of the PES UF membrane can be reduced by around 75.5% from 62.6 ± 3.7 to 15.3 ± 1.2 and the pure water flux increased by about 36% from 513LMH to 702LMH for the modified membrane. Antibacterial study was performed for the prepared membrane using the zone of inhibition test and the clear zone for the modified membranes indicate the antibacterial properties of the membrane. During long time test with reservoir water, it was found that the modified membrane exhibited a lower flux drop giving a stable flux compared to the control membrane. Based on the experimental data, the prepared modified UF membranes seem promising for wastewater filtration.

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Research Highlights

- PES-PANCMA hollow fiber UF membranes were fabricated by dry wet spinning
- PEG and Ag were chemically attached to PES-PANCMA membranes by thermal grafting
- The membranes were tested for the pure water flux and zone of inhibition test
- Antifouling properties of the membranes were studied in a long time experiment
- The surface modification helps to reduce the water contact angle drastically

Graphical Abstract