

Probing the morphology and antiorganic fouling behaviour of the polyetherimide membrane modified with hydrophilic organic acids as additives

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Abstract

A facile approach for the preparation of organic antifouling polymer membrane has been developed by using low molecular weight organic acids as additives. The presence of these additives in the membrane was analysed by FTIR spectroscopy. The properties of the modified membranes were investigated in terms of contact angle, water uptake capacity, SEM and AFM analysis. These additives exerted a strong impact on rheological properties of casting solution, thereby altering the membrane morphology, surface roughness, water flux and hydrophilicity of the membranes, as compared to the pristine Polyetherimide (PEI) membrane. The organic antifouling property of the modified membrane was analysed by filtering both Bovine Serum Albumin (BSA) and humic acid solutions. Results showed that, additives exhibited remarkable improvement in the antifouling property (FRR of 72 %) and humic acid rejection up to 86 %. These outcomes offer new insight into the use of, cheaper and readily available organic acids as additives, compared to the traditional, synthetic polymer materials as additives in membrane preparation.

Key words : Organic acids, polyetherimide, humic acid, permeation, antifouling

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1. Introduction,

One of the most prevalent problems affecting the people throughout the globe is insufficient access to the clean water. Problems with water are probable to grow worse in the upcoming years because of the rapid growth of population, industrialization, global climate change and poor wastewater management.¹⁻² Since, it has gained much significance, the research work need to be concentrated on bringing forward a new and efficient water purifying method at lower cost with less energy. At the same time, it is necessary for minimizing the use of chemicals which impact on the environment.³ Membrane technology has gained vast application in the field of separation technology, especially in the water purification.⁴ As a result, preparation of hydrophilic, high flux and antifouling membranes is necessary to further expand the applications of membrane based separation process for water purification.

Polyetherimide (PEI) is a widely used membrane material due to its excellent mechanical and thermal properties. It has also a good film forming nature and chemically resistant to the wide range of pH.⁵⁻⁶ It has been noticed that, membrane prepared from the pristine PEI is hydrophobic in nature. Due to which, membranes suffering from severe fouling because of adsorption or deposition of foulants, which reduces the water transport across the membrane and deteriorates properties of the membrane surfaces.⁷ Since the efficiency of ultrafiltration (UF) membrane processes for drinking water production is majorly dependent on the adverse fouling effects caused by natural organic materials (NOM's) present in the surface water. It is well known that, NOM's present in the water could easily react with chlorine to form highly carcinogenic by-products such as, trihalomethanes (THMs), haloacetic acids (HAAs) and other halogenated organics.⁸ Without an appropriate treatment process, direct exposure to these carcinogenic by-products could cause cancers, miscarriages and nervous system complications. Hence, effective removal of NOM from water has become a stimulating research topic in contemporary development of water purification technologies.

A major fraction of NOM's present in the surface or ground water is comprised of humic substances.⁹ Generally, humic acid (HA) makes up the main component of humic substance (Figure 1) and has thus been studied by many researchers as a model compound for natural organic matter in water. In the earlier report, Fan et al. stated that hydrophobic membranes were more susceptible to NOM's fouling than hydrophilic membranes during the filtration of NOM's.¹¹ This was further substantiated by the work of Lee et al. in which by

using membranes of approximately the same molecular weight cut-off (MWCO), the regenerated cellulose membrane was appeared to have lower fouling propensity compared to PES membrane. This was primarily due to the higher surface hydrophilicity.¹³ Among the approaches used to augment hydrophilicity of membrane material, the addition of hydrophilic additive into the casting solution is generally considered as one of the most convenient methods to create the impact.

Figure-1

From the literature, it was observed that, the presence of low molecular weight organic additives offers an effective and convenient way to alter the membrane performance with enhanced hydrophilicity, high permeability, antifouling and rejection properties. This finding was in line with work of Kim et al. revealed the effect of addition of additive on the pore size of the Polysulfone (PSF) membrane by the phase inversion method. The results showed that, γ -butyrolactone additive increased the pore size of the membrane because of its higher miscibility with the water than NMP.¹¹ Kumar et al. prepared novel *N*-propylphosphonic chitosan derivative containing a terminal phosphonic acid functional group as an additive. The modified PSF membranes exhibited the improved hydrophilicity up to 58° and antifouling properties with flux recovery ratio of 79 % as compared to the pristine PSF membrane.¹² Also Zhang et al. investigated the influence of formamide (FM) as an additive on the morphology and performance of the PEI membrane. The results showed that, dense skin layer of the membrane, strongly depends on the extent of FM in the casting solution and performance of the membrane was significantly increased.¹³ Further Ghaemi et al. extensively studied the effect of organic acids such as ascorbic acid, citric acid and maleic acid on the morphology and removal of xenobiotics. The contact angle measurements showed that, hydrophilicity of the PSF membrane increased considerably after the addition of additives. Also membrane with these acids exhibited higher water flux, permeation and rejection compared to polysulfone membrane.¹⁵ Chuang et al. reported the role of acetic acid (AA) as an additive in the formation of poly (vinyl alcohol) (PVA) membranes. The experimental results described that, the AA additive exerts strong impact on the morphology and other properties of the membrane.¹⁴ Rahimpour et al. studied the influence of 2-hydroxyethylmethacrylate and acrylic acid additive on the structure and properties of the PSF membrane.¹⁶ The decreased surface roughness and pore size was observed for the modified

membranes. Also significant improvement in the hydrophilicity, pure water flux and protein rejection was observed compared to the pristine PSF membrane.

Based on these observations, our current work is to emphasize on the influence of low molecular weight organic additive in the dope solution on the membrane morphology, hydrophilicity, permeation and antifouling properties. Ascorbic acid, citric acid and maleic acid comprising of different structure and acidic strengths were used as hydrophilic additives and influence of these additives on the rheological properties of casting solutions were investigated by viscosity measurement. The presence of these additives in the membrane was examined by FT-IR spectroscopy. The characteristics of the resultant membranes were investigated in terms of water uptake capacity, water contact angle measurement, surface roughness, morphological features and permeation properties. Further, the organic antifouling behaviour of membranes was investigated in detail by using Bovine Serum Albumin (BSA) and humic acid (HA) as model foulants.

2. Materials and methods

2.1. Materials

Polyetherimide (PEI) ($M_w = 35,000$ Da) was purchased from Sigma Aldrich (India). The solvent N-methyl pyrrolidone (NMP) of analytical-grade purity was purchased from Merck, India. Bovine Serum Albumin (BSA) was obtained from Central Drug House (CDH), India. The humic acid was obtained from Himedia, India. The additives, ascorbic acid, citric acid and maleic acid were procured from Merck, India. The polyvinylpyrrolidone (PVP) was purchased from Sigma Aldrich, India.

2.2 Preparation of Membranes

The PEI membrane with various low molecular weight organic molecules as additives has been prepared according to the non-solvent induced Phase Separation method.¹⁷⁻¹⁸ For this purpose, desired ratio of PEI and PVP (pore forming agent) was dissolved in the desired volume of NMP at 60 °C. To this solution, calculated amount of different organic additives were separately added and magnetically stirred for 18 h at the same temperature. The obtained homogeneous solution was maintained for another 6 h in order to get rid of trapped air bubbles. The polymer solution was cast over a glass plate using a doctor's blade. Then it was gently immersed in the coagulation bath containing water as non-solvent. So obtained membrane was stored in deionised water for another 24 h, to ensure the complete phase

inversion. The obtained membrane was used for further analysis. Overviews of the experimental conditions were described in Table-1.

Table-1

2.3. Membrane characterization

2.3.1. FTIR analysis

The presence of low molecular weight organic additives in the membranes was analysed by FTIR studies. The FTIR spectra were recorded using Avatar 360 IR spectrophotometer in the range of 4000-400 cm^{-1} . The changes in the characteristic peaks of spectra were discussed in results and discussion.

2.3.2. Membrane morphology

The variations in the surface and cross-sectional morphology of the membranes was investigated by JEOL JSM-6380LA Scanning Electron Microscope. For this purpose, the prepared membranes were fractured cryogenically using liquid nitrogen and then smeared with gold in order to obtain conductance.

2.3.3. AFM analysis

Atomic force microscopy (AFM) was used to examine the changes in the topography and surface roughness of the prepared membranes after the addition of low molecular weight organic acid as additives. Images of the dry samples were taken using annova SPM Atomic Force Microscope. A small piece of the membranes (almost 1 cm^2) was cut and glued to a glass substrate. The image of membrane surfaces was obtained in a scan size of 10 $\mu\text{m} \times 10 \mu\text{m}$ and tapping mode was used to measure the surface roughness.

2.3.4. Viscosity measurement

The Brookfield DV-III Ultra (USA) instrument was used to measure the viscosity of the casting solution. The viscosity was determined by using a cup/cone geometry at 90/s shear rate, 22 rpm and 45 °C.

2.3.5 Porosity

Porosity of membrane was analysed by dry-wet weight method.¹⁹ The membrane soaked in distilled water was weighed after wiping the surface water with blotting paper. Then the wet membrane was placed in an air-circulating oven at 70° C for 24 h prior to

measure the dry mass. From the two weights (the dry sample weight and the wet sample weight), the porosity of the membrane was calculated using equation (1).

$$P(\%) = \frac{W_w - W_d}{\rho_w \times A \times \delta} \times 100 \quad (1)$$

Where ' P ' is the porosity of the membrane, W_w is the weight of wet sample (g), W_d is the weight of dry sample (g), ρ_w is the density of pure water (0.998 g/cm³), ' A ' is the area of membrane in wet state (cm²) and ' δ ' is the thickness of membrane in wet state (cm).

2.3.6. Water uptake and contact angle measurement

The water uptake study for the membrane was carried out according to the literature.¹⁹ Briefly, the membrane (1 cm²) was immersed in demineralized water for 24 h and weighed after wiping with blotting paper. Then the wet membrane was kept in a vacuum oven at 75° C for 25 h and the dry weight was measured. The percentage water content in the membrane was calculated using equation (2)

$$\% \text{ uptake} = \left(\frac{W_w - W_d}{W_w} \right) \times 100 \quad (2)$$

Where W_w and W_d are the weights of the membranes after swelling for 24 h under wet and dry conditions respectively.

The hydrophilic property of the membrane was analysed by the water contact angle (WCA) measurement. It was measured using FTA-200 Dynamic contact angle analyser according to the sessile droplet method. In order to minimize the experimental errors, the WCA measurement of each sample was measured three times and average value was reported.

2.3.7 Permeation properties

The pure water flux (PWF) of all membranes was analysed by a self-fabricated dead end filtration cell at room temperature. The membranes with an effective area of 5 cm² were dipped in distilled water for 24 h before commencing permeation experiment. Initially, each membrane was compacted at 0.4 MPa for about 1hr and then it was reduced to 0.3 MPa to obtain the pure water flux (J_{w1} , L/m² h). Then the flux was measured for every 10 min interval. The PWF, J_w was determined using equation (3)

$$J_w = \frac{Q}{\Delta t A} \quad (3)$$

Where J_w is expressed in L/m²h and 'Q' is the amount of water collected for Δt (h) time duration using a membrane of area 'A' (m²).

2.3.8 Antifouling properties

The antifouling behaviour of all prepared membranes was analysed using the reported procedure as in literature.²⁰ In brief, each membrane was subjected to compaction for an initial 30 min at 0.3 MPa. Then the pressure was reduced to 0.2 MPa and PWF of the membrane was determined J_{w1} (L/m²h) at 0.2 MPa TMP. The BSA solution was prepared with concentration of 0.8 g/L and passed through the membrane for 80 minutes. After BSA filtration, membrane was thoroughly washed with distilled water for 20 minutes and again PWF, J_{w2} (L/m²h) was measured. Finally, the antifouling performance of the membrane was calculated in terms of flux recovery ratio (FRR) using the equation (4).

$$FRR(\%) = \left(\frac{J_{w2}}{J_{w1}} \right) \times 100 \quad (4)$$

Generally, higher FRR signifies a better antifouling behaviour of the membranes. Also, in order to examine the fouling processes, the following studies were carried out. To estimate the total protein fouling (R_t) produced by the membrane after BSA filtration was calculated by the equation (5).

$$R_t(\%) = \left(\frac{J_{w1} - J_p}{J_{w1}} \right) \times 100 \quad (5)$$

The flux loss caused from both reversible and irreversible protein fouling (R_r and R_{ir}), which were calculated using equation (6) and (7)

$$R_r(\%) = \left(\frac{J_{w2} - J_p}{J_{w1}} \right) \times 100 \quad (6)$$

$$R_{ir}(\%) = \left(\frac{J_{w1} - J_{w2}}{J_{w1}} \right) \times 100 \quad (7)$$

2.3.9 Humic acid rejection study

The HA rejection behaviour of PEI membranes was carried out with the 5 mg/L HA solution in the feed tank. In order to study the relative flux of the membrane, the PWF was

evaluated before investigating the HA resistance behaviour of the membrane. The flux decline was measured in terms of relative fluxes.

The HA rejection efficiency of the membrane was tested by the filtration experiments. The concentration of HA solution in the feed tank and permeate solutions was measured by a UV-Vis spectrometer at a wavelength of 254 nm. The HA rejection efficiency of the membrane was determined by using equation (8)

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (8)$$

Where C_f and C_p (mg mL^{-1}) are the concentration of the HA in the feed and permeate respectively.

3. Results and discussion

3.1 ATR-IR spectroscopy

The incorporation of low molecular weight organic acids as additives in the PEI membrane was confirmed by IR spectrum. The Figure 2 represents the IR spectrum of the PEI and modified PEI membranes. It was observed that, intensity of the IR bands at 1725 cm^{-1} and 1782 cm^{-1} related to -C=O symmetric and asymmetric stretching respectively (characteristic imide group absorptions). The absorption peak at 1236 cm^{-1} corresponding to the aromatic ether linkage (C-O-C) of PEI. The membranes exhibited broad absorption peak around $3000\text{--}3600 \text{ cm}^{-1}$ corresponding to the stretching of hydroxyl functional groups (-O-H) was obtained after the addition of these additives. This was due to, some of the additives remains in the casted polymer structure after the fabrication process.

Figure-2

3.2 Water uptake capacity and contact angle

The hydrophilic nature of the membranes could be analysed by their water uptake capacity and water contact angle measurements. The water uptake capacity of any membrane, primarily depends on two parameters, firstly on the number of hydrophilic sites present in membrane matrix and secondly, on the morphology i.e., the presence of macrovoids in the membrane sub-layer.²¹ It can be noticed from the results presented in the Table-2, all the membranes having a higher water uptake capacity compared to PMA-0 membrane. The PMA-3 membrane exhibited a maximum of 76 %, since citric acid offers more hydrophilicity than other additives. Also, it has been observed from the SEM images that, the presence of these acids in the casting solution showed increased macrovoid in the membrane sublayer.

Due to this, the membrane can have more water molecules and thus increases the overall water uptake capacity.

The contact angle of the membranes was measured by the sessile drop method. The presence of these additive showed a decreasing trend of contact angle in the order of PMA-0 > PMA-1 > PMA-2 > PMA-3. In general, the smaller contact angle corresponding to the membrane surface with more hydrophilic nature. The pristine PEI membrane showed higher contact angle of 79°, whereas membrane with citric acid as an additive possessed contact angle of 68°. The significant change in the surface hydrophilicity of the membranes after the addition of these additives into the PEI casting solution can be attributed to the presence hydrophilic functional groups. The citric acid consists of three ionisable hydrogen atoms and it easily forms strong dipole interaction ($-\text{COO}^- \cdots \text{H}$) with water molecules. This mechanism helps to hold the water molecule on the surface of the membranes. However, maleic acid consists of two and ascorbic acid having one ionisable hydrogen atoms respectively.

Table-2

3.3 Rheological properties of the casting solutions

The rheology of the casting solution having major influence on the exchange rate of non-solvent and solvent during the phase inversion and thus, it can be utilized as an important parameter to change the precipitation kinetics and consequently, the formation of resulting membrane morphology.²² The additive showed an increase in the viscosity of the casting solution (Table-2). The PAM-0 casting solution has shown viscosity of 270 mPas and it was increased up to 650 mPas for the 1 wt % citric acid in the dope solution. Since the higher viscosity of the casting solution decreases the diffusional exchange rate of the non-solvent (water) and solvent (NMP) during the membrane formation process. This can contribute to delayed demixing and consequent formation of thinner skin layer and larger finger-like pores (or macrovoids) in the sub-layer.

3.4 porosity of the membranes

Table-2 indicates an effect of these hydrophilic additives on the porosity of the membranes. The results revealed that, all modified membranes exhibited higher porosity compared to the PAM-0 membrane. It can be found that, modified membrane exhibited enhanced porosity of 22- 34 % compared to the PAM-0 membrane. Moreover, membrane with 1 wt % citric acid has shown higher porosity (i.e higher pore density) among other two additives. The changes in the porosity of the membranes were explained by the following

reasons: 1. The addition of these additives showed an increase in the viscosity of the dope solution (table-2). Which delays the exchange between solvent and non-solvent during the phase inversion process. In highly viscous dope solution, solvent's (NMP) outward diffusion from the casting film is preferred over non-solvent's (water) inward diffusion because of its barrier effect against non-solvent. Since delayed demixing on the surface region of the casting film caused the formation of a dense top layer with higher porosity. 2. A portion of PVP (invariable additive) was leached out of the casting film during the phase separation and acted as pore forming agent. This could be another reason for enhanced porosity of the membranes.

3.5 Effect of additive on morphology of the membrane

The SEM was employed to study the morphological changes in the membranes, which play a significant role in the performance and selectivity of the membranes. During membrane preparation, casted polymer film was gently immersed in a coagulation bath containing water as non-solvent. Upon immersion, non-solvent (water) entused inward into the cast film from the coagulation bath. This enforced a remarkable change in the driving force across the cast film. At the same time, the polymer rich phase allowed water molecule (non -solvent) to equilibrate between the internal and external phases of polymer film before significant outward diffusion of NMP (solvent) molecules. Since, the influx of water molecule was predominantly high as compared to the out flux of NMP. This is because of the large diffusion coefficient of tiny water molecules compared to that of the much bulkier organic solvent molecule.²³⁻²⁴ On the other hand, the solvent (NMP) having strong affinity towards water molecule, so that they miscible each other instantaneously. These phenomena resulted in the formation of asymmetric membranes. From the Figure 3, it is clear that, all the prepared membranes have typical asymmetric structures, which consist of the thin skin layer and the porous sub layer. Further, we studied the effect of low molecular weight organic additives such as citric acid, ascorbic acid and maleic acid, which has a different structure and strength on PEI membrane morphology. Generally, these additives are used to act as a non-solvent against the base polymer because, skin and bottom layer morphology of the membranes are largely influenced by the rate of coagulation of the casting solution. The changes in the morphology with different additives discussed below.

3.5.1. Citric acid

The citric acid, which is a polycarboxylic acid was used as one of the additive in PEI membrane preparation. From the Figure 3 (d), it can be observed that, formation of

asymmetric structure with thinner skin layer thickness compared to neat PEI membranes. The induced changes in membrane morphology may be due to the interaction between components in the casting solution. The addition of citric acid into the casting solution may result in the formation of the secondary intermolecular force of interaction with the polymer chains (Figure 4). The different type of secondary forces such as hydrogen bonding, dipole interaction and dispersion forces reduced interaction among polymer chains. In addition, due to the hydrophilic nature of the citric acid there is a possibility for the formation of hydrogen bonds with solvent (NMP) molecule also.¹⁵ The both phenomena exhibited decreased outflow rate of solvent (NMP) and increased inflow rate of non-solvent (water), which resulted in delayed demixing in the coagulation bath. Therefore, the growth of the skin layer is reduced and formation of finger-like pores (or macrovoid) in the sub layer is improved.

Figure-3

Figure-4

3.5.2 Ascorbic acid

The ascorbic acid is a polyhydroxy acid used as another hydrophilic additive in the preparation of PEI casting solutions. The change in the morphological features like decline of skin layer thickness and formation of macrovoids in the sub-layer can be described in the same way as in the case of citric acid. (a) Decrease in the interactions between polymer chains due to the formation of the secondary intermolecular force of interaction between ascorbic acid and polymer chains. (b) Increase in the inflow of water molecule (non-solvent) and decrease in the solvent (NMP) outflow because of the hydrophilic nature of ascorbic acid (c). Also, there may be formation of hydrogen bonding between solvent and ascorbic acid.²⁵ Eventually, the rate of demixing affects the membrane formation with a thinner top-layer thickness and formation of macro-voids in the sub-layer compared to the pristine PEI membrane

3.5.3 Maleic acid

The maleic acid is a dicarboxylic acid employed as another additive in the preparation of PEI casting solutions. The change in the morphological features compared to the neat PEI membrane can be explained similarly as above. Since the addition of maleic acid produces instability in the thermodynamic equilibrium of the system.²⁵ Subsequently, the rate of demixing of solvent and non-solvent changes and resulting membrane with thinner top skin layer and formation of finger-like pores in the sub-layer.

3.6 AFM analyses of membrane

AFM analysis was carried out, to further explore the influence of these additives on surface topology and roughness parameters of the PEI membrane. Figure 5 illustrates the representative two and three dimensional topological images of all prepared membranes. From the images, the organic acids having a strong influence on the surface morphology of the membranes. The surface roughness is one of the most important parameter as it has a strong impact on fouling behaviour and also on the local mass transfer.²⁶ The results for roughness parameters, for PEI and modified membranes are presented in Table 3. All the membrane showed lower surface roughness as compared to the pristine PEI membrane i.e PAM-0. The maximum mean roughness (Ra) and route mean square roughness (Rq) value showed by PAM-0 membrane was 11.5 nm and 14.3 nm respectively. The membrane with citric acid as additive showed decrease in mean roughness around 48 % with the maximum feature heights (Rmax) of 61.5 nm compared to other membranes. This observation is particularly important since smoother surface shows the less adsorption of organic molecules to reduce the organic fouling.

Figure-5

Table-3

3.7 Water permeability

The filtration experiments have been conducted to investigate the permeability and antifouling property of the membranes. The important parameters like, water uptake capacity, hydrophilicity and morphological properties decide the performance of the membranes. Figure 6 represents the PWF of the membranes. The pristine PEI membrane showed a minimum of $133 \text{ L m}^{-2}\text{h}^{-1}$ and membranes with citric acid as additive showed maximum PWF of $242 \text{ L m}^{-2}\text{h}^{-1}$. The remarkable change in the performance of the membranes after the addition of organic acids as additives induced changes on the hydrophilicity and permeation properties of the membranes. The citric and malic acids having three and two carboxylic acid functional groups which impart the negative charge of the membranes. The carbonyl groups bonded to $-\text{OH}$ in carboxylic acid moieties has electrophilic character. Since carboxylic acids undergo dissociation easily and form the carboxylate anion. Ascorbic acid molecules are not able to properly ionize their $-\text{OH}$ functional groups because they do not have linked carbonyl groups. But it contains a number of hydroxyl groups and one ionisable hydrogen atom in its structure, which induce the hydrophilicity to the membranes.

Figure-6

3.8 Antifouling performance against BSA

The most detrimental problem with membrane technology is fouling, which hampered the long term use of the membrane. The fouling is caused by the deposition or adsorption of particles, proteins, colloids, salts, macromolecules, etc., at the membrane surface or inside the pores.²⁶ It is well known that, an increase in hydrophilicity offers the enhanced fouling resistance of the membrane. Since strongly bound water molecules that prevent protein molecules from binding to surfaces. The contact angle and permeation results are direct evidences for the increased hydrophilicity of modified membrane as compared to the neat PEI membrane. As expected, the modified membranes showed the better antifouling property. BSA molecules have an isoelectric point of 4.9, therefore, BSA exhibit negative charge in the neutral solution.²⁷ The membrane surface is also negatively charged due to the presence of polycarboxylic acid or dicarboxylic acid or polyhydroxy acid of the additives on membrane surface. This resulted in a strong electrostatic repulsion force between negatively charged BSA molecules and membrane surface to reduce the fouling.

The antifouling properties of the membranes with and without additives (organic acids) were investigated by measuring the pure water flux recovery after membrane fouled by the 800 ppm of BSA solution. Figure 7 shows the pure water flux before, during and after BSA filtration. Water fluxes of the fouled membranes were measured after thorough washing with distilled water. The flux recovery ratio (FRR) of the prepared membranes is described in Table-4. The higher FRR value indicates a better antifouling property for the membrane. The pristine membrane exhibit lower flux recovery ratio of 21.4 % and membrane with citric acid as additive showed maximum FRR of 71.6 %. This specifies the high antifouling property of the modified membranes induced by the low molecular weight organic acids. The observed trend of FRR is matched by hydrophilicity of the membranes (Figure 8). Hydrophilic surface can adsorb water molecules and form a water layer, which retards the adsorption of protein and other fouling agents.²⁸

Figure-7

Figure-8

In general, the membrane fouling can be categorized as hydraulically irreversible and reversible. In hydraulically irreversible fouling, the fouling agents are strongly attached to the membrane and it can only be cleaned by chemical treatment. In case of hydraulically reversible fouling, the foulants are loosely bound to the membrane and it can easily be

removed by backwashing.²⁹⁻³⁰ The Table-4 represents the hydraulically reversible (R_r), hydraulically irreversible fouling ratio (R_{ir}) and total fouling ratio (R_t) for the membranes. From the results, it was clear that, all the modified membranes exhibited higher hydraulic reversibility in the order of PMA-3 > PMA-1> PMA-2> PMA-0. The hydraulic reversible fouling ratio of the membrane was considerably increased from 14.5 % for the pristine membrane to 65.7 % for the membrane with citric acid as the additive. These results demonstrate that, membrane with organic acids as additives show a remarkable change in the pure water flux, hydrophilicity and antifouling property.

Table-4

3.9 Antifouling performances against HA

To further investigate the HA rejection and antifouling property of the prepared membranes, the filtration experiments were carried out at 0.2 MPa TMP with 5 mg/L initial concentration in the feed tank. The Figure 9 represents the relative fluxes of the membranes. It clearly showed that, the rate and extent of is fouling reduced significantly after the addition of additives (Figure 10). The rapid flux declined was observed at the beginning of each filtration experiment. The adsorption of HA is considered as the first step in membrane fouling and is strongly be influenced by on the physico-chemical properties of both membranes and foulants, especially the affinity of foulants towards the membrane material.³¹ A maximum in the resistance against fouling was observed for the PAM-3 membrane with HA rejection up to 84.7 % (Figure 11). This is corresponding to the low contact angle (higher hydrophilicity) and other surface parameters. Considering that, here fouling is dominated by the adsorption of HA on the membrane surface. Since these additives impart the negative charge to the membrane, reduce adsorption of HA on the membrane surface due to the electrostatic repulsion between HA molecules and the membrane surface.³² Therefore, it is important to prepare the membrane with improved hydrophilicity and less roughness to improve antifouling ability and performance of the membrane.

Figure-9

Figure-10

Figure-11

4. Conclusion

The presence of a small quantity of low molecular weight organic acids in the casting solution imparts a strong influence on the morphology and antifouling properties of

polyetherimide membrane. The rheology of the casting solution was changed dramatically after addition of additive and highly influenced membrane morphological features. The modified membrane showed significantly thinner skin-layer, formation of macro-voids in the sublayer and smoother surface compared to the pristine polyetherimide membrane. The water uptake capacity and water contact angle measurements confirmed the enhanced hydrophilicity of the membranes for all of the organic acid additives. The permeation experiments showed enhanced water flux of $242.3 \text{ L m}^{-2}\text{h}^{-1}$ with flux recovery ratio up to 72 % for PAM-3 membrane. The humic acid rejection study showed that modified membrane having rejection efficacy up to 86 %. Overall, the performance of the membranes revealed that, prepared membranes with citric acid offered a higher efficiency compared to maleic acid and ascorbic acid.

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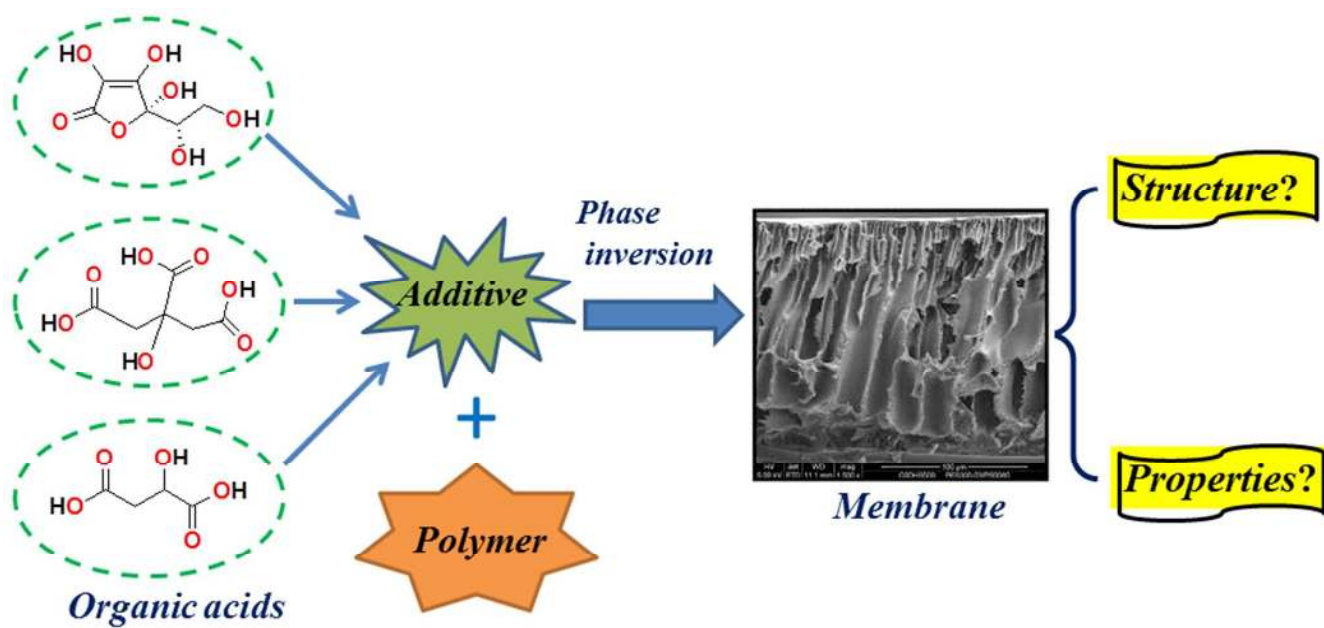
Tables

Table-1 Composition of casting solution

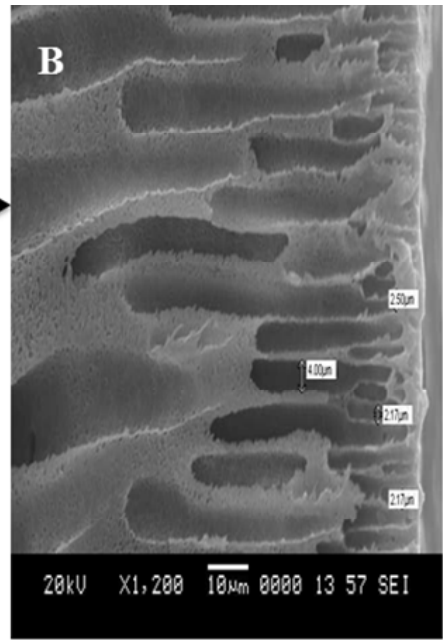
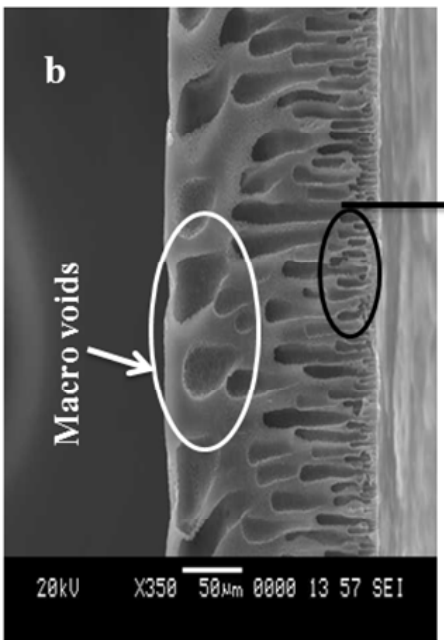
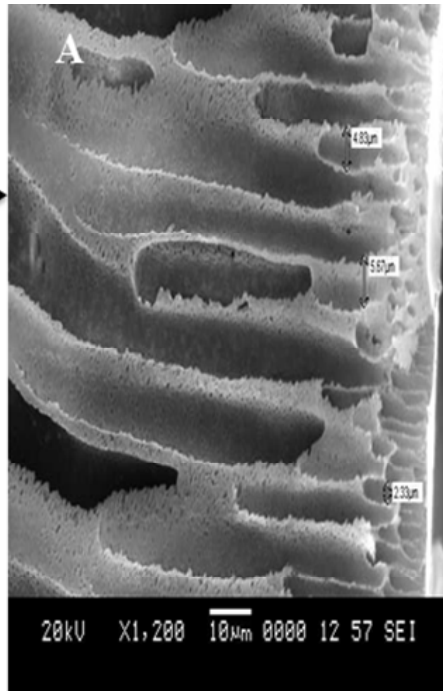
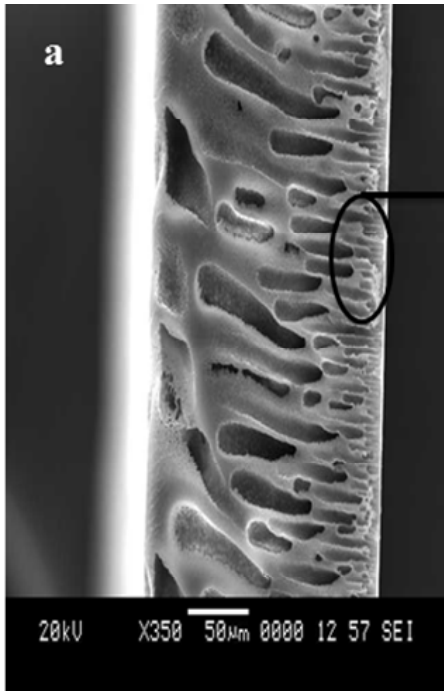
Table-2 The properties of the membranes

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Polyetherimide based membrane was modified with various hydrophilic organic acids as additives. The results showed that the additives exhibited remarkable improvement in the antifouling property (FRR of 72 %) and humic acid rejection up to 86%.



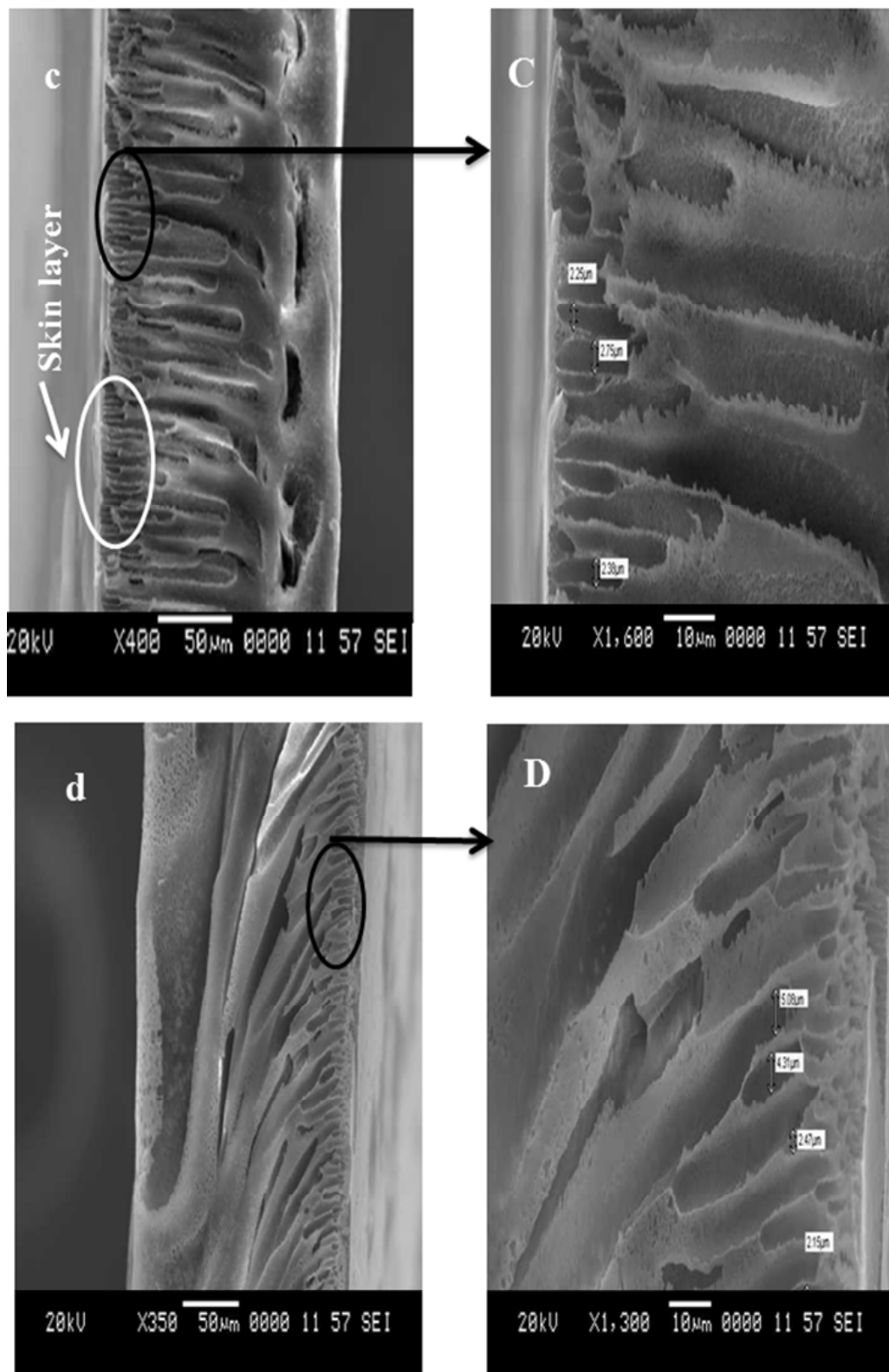


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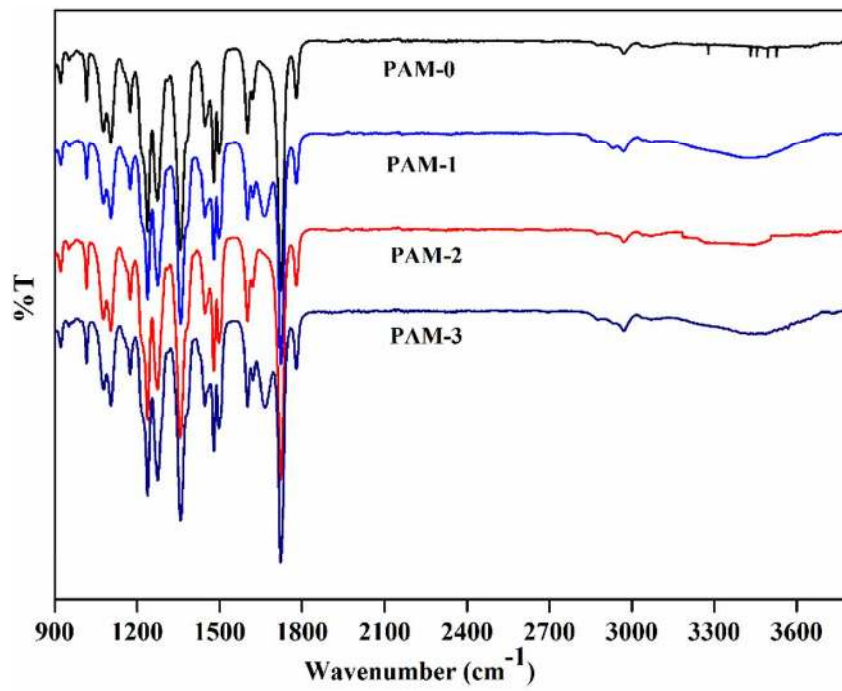


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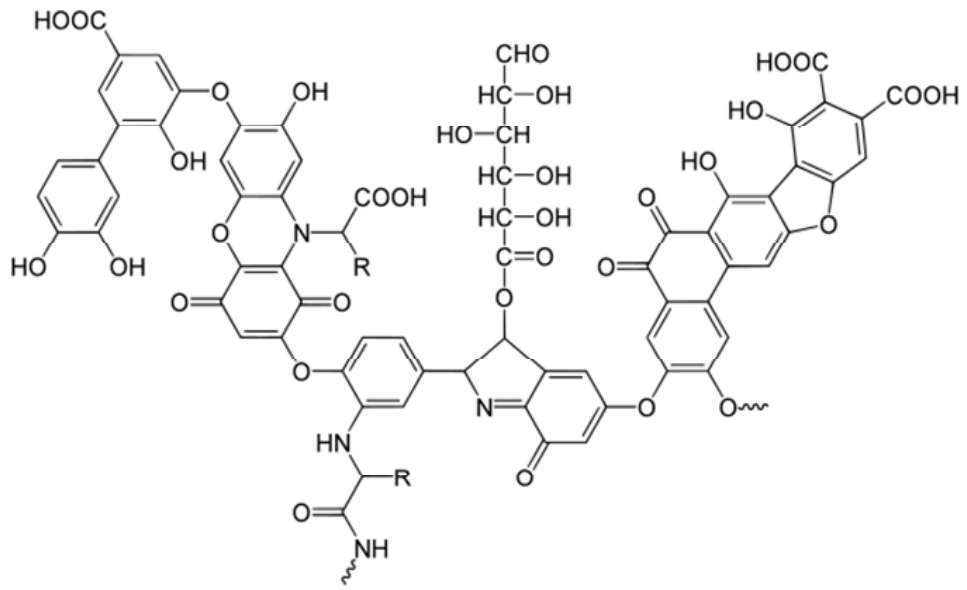


Figure 1 : Structural model of humic acid [10]

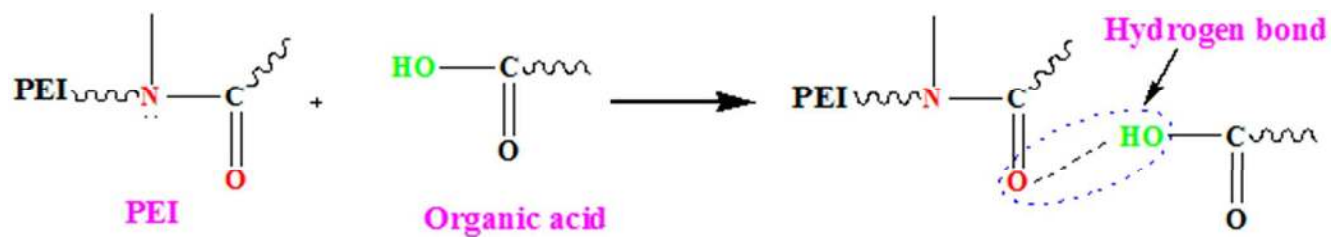
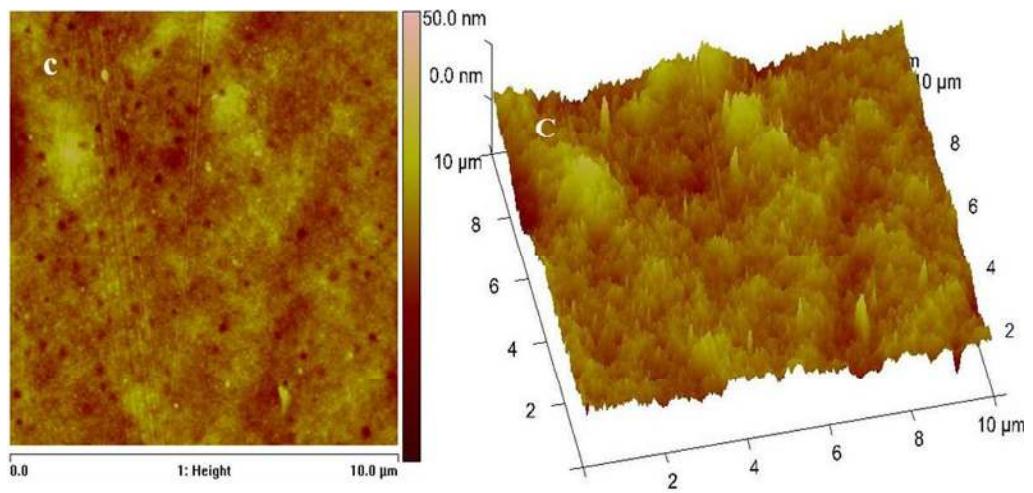
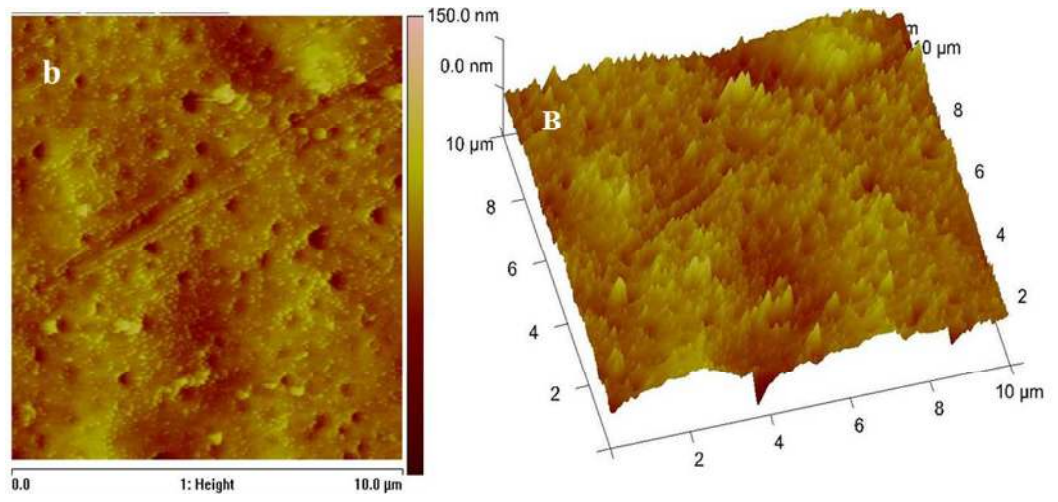
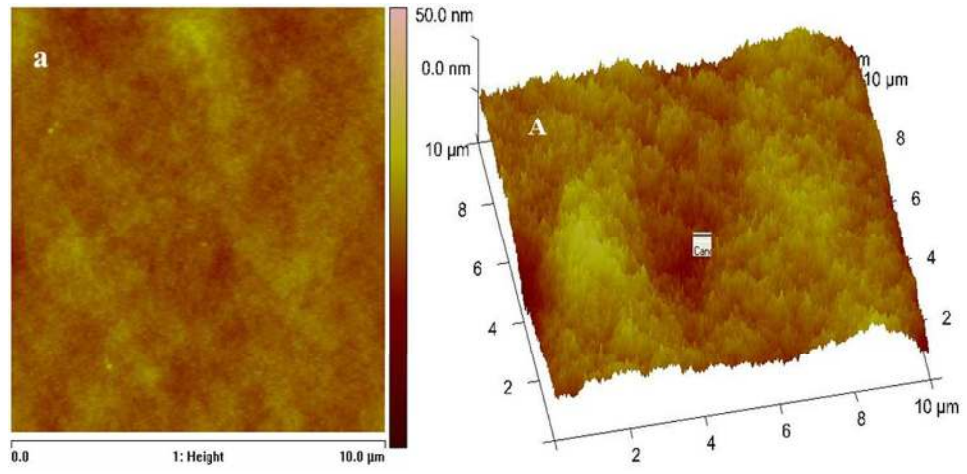


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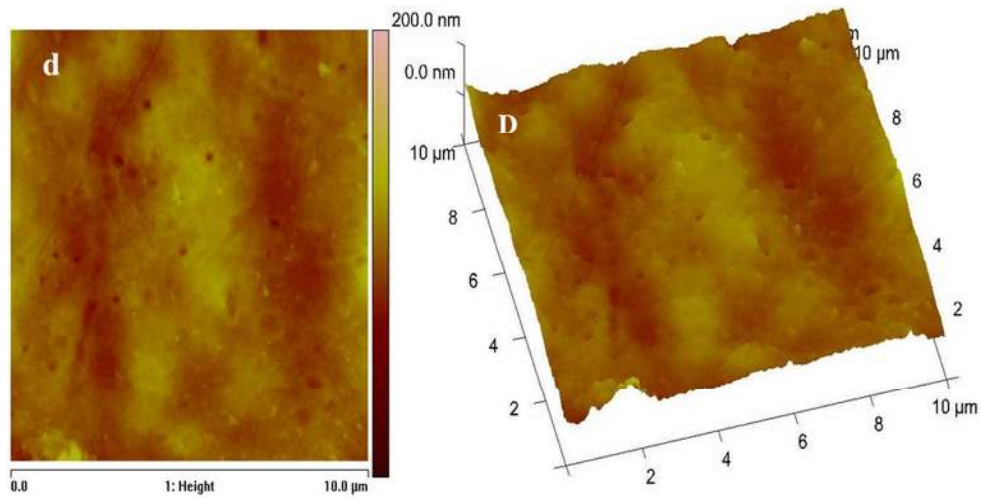


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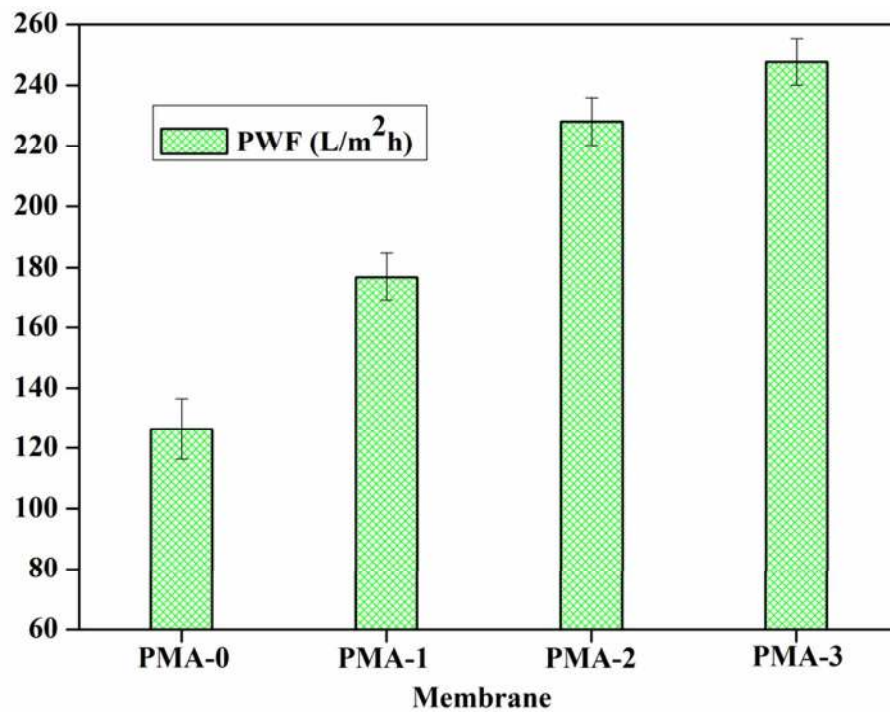


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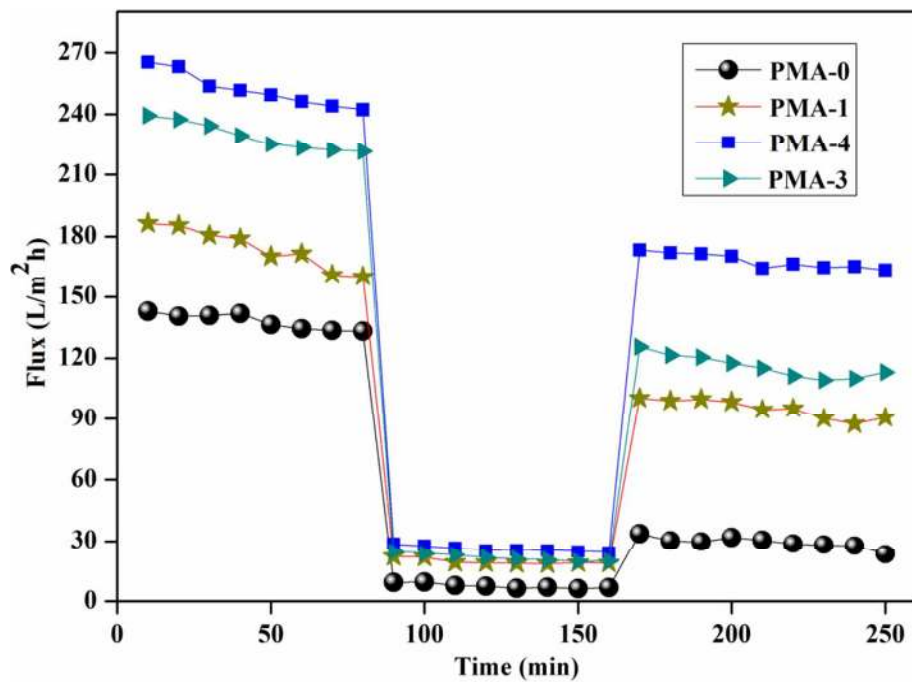


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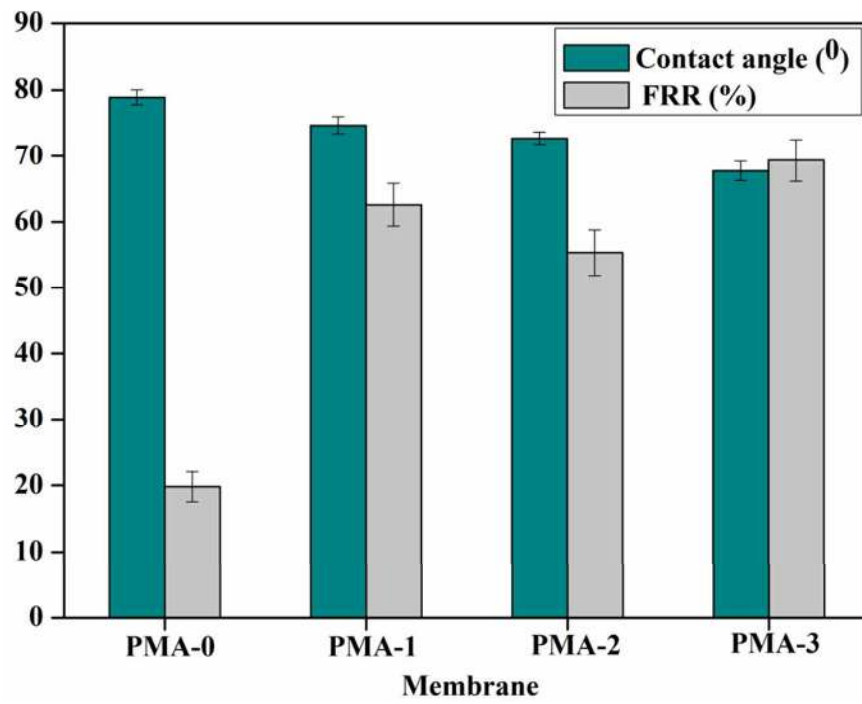


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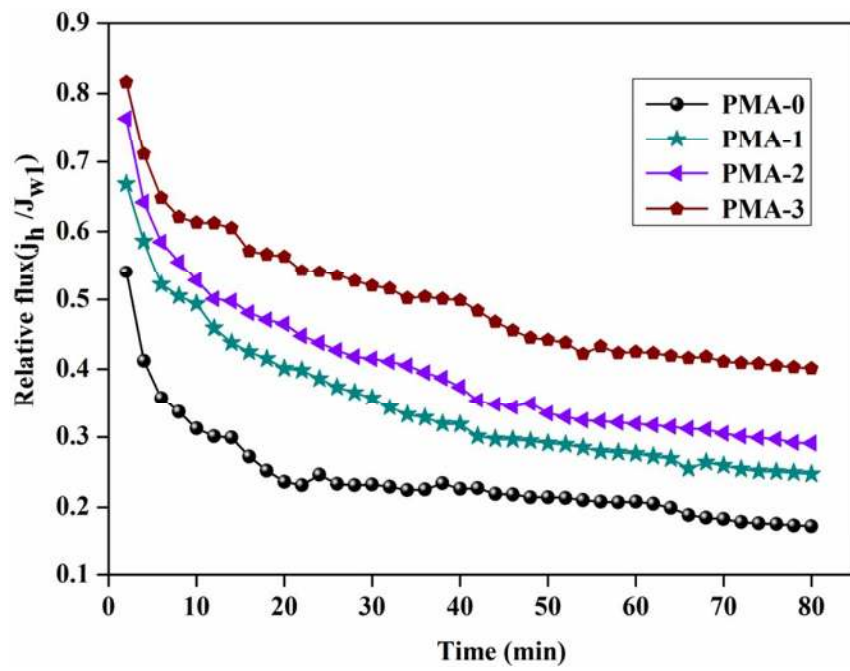


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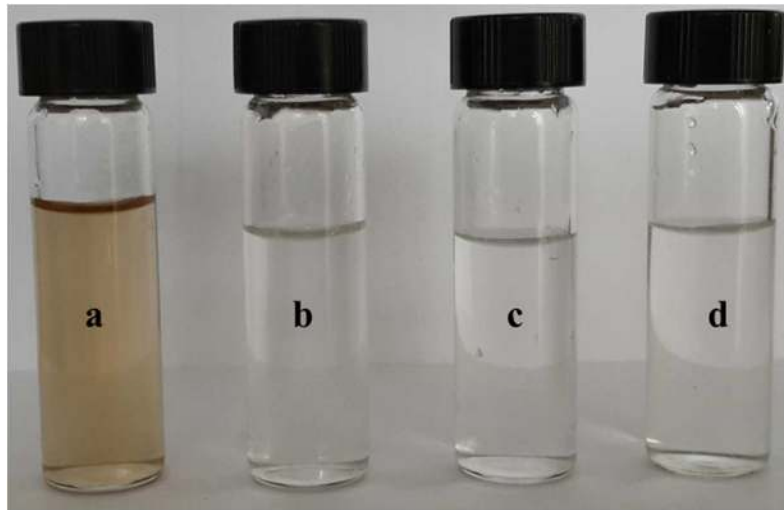


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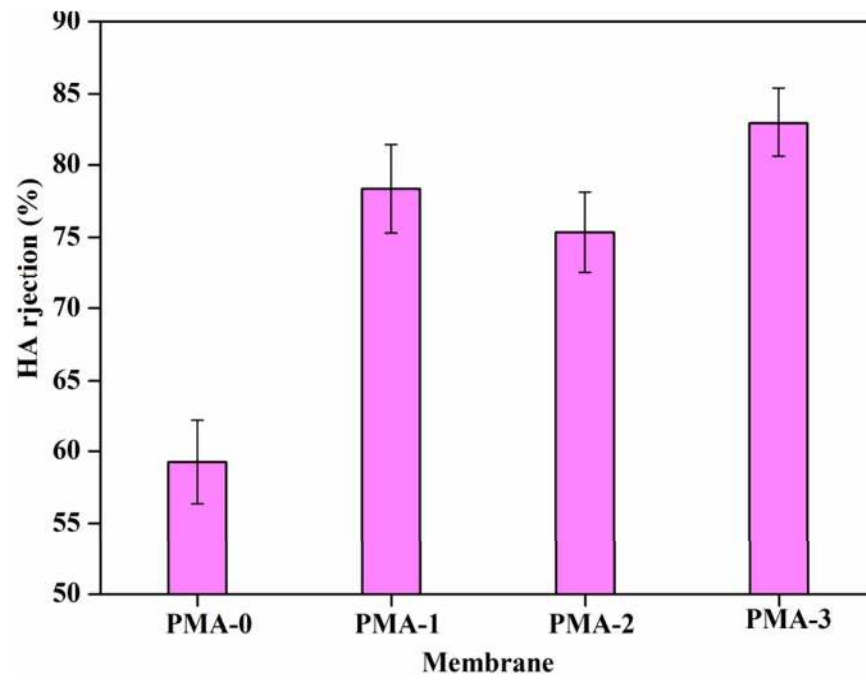


Figure 11 : The HA rejection by prepared membranes

Table-1: Composition of casting solution

Membrane	Additive	PEI (wt.%)	NMP (wt.%)	PVP (wt.%)	Additive (wt.%)
PMA-0	-	18	80	2.0	-
PMA-1	Ascorbic acid	18	79	2.0	1.0
PMA-2	Maleic acid	18	79	2.0	1.0
PMA-3	Citric acid	18	79	2.0	1.0

Table-2 : The properties of the membranes

Membrane	Membrane thickness (μm)	Water uptake (%)	Viscosity (mPas)	Porosity (%)	Contact angle ($^{\circ}$)
PMA-0	121	58	270	38.1	79
PMA-1	123	72	490	53.5	75
PMA-2	120	69	382	49.4	73
PMA-3	122	76	650	58.6	68

Table-3 : The roughness parameters of the membranes

Membrane	Image surface area (μm^2)	Surface area Difference (%)	Roughness		
			Ra (nm)	Rq (nm)	Rmax (nm)
PMA-0	101	0.53	11.5	14.3	108
PMA-1	101	1.45	10.4	14.0	177
PMA-2	100	0.91	6.05	7.93	102
PMA-3	101	0.58	5.55	7.0	61.5

Table-04 : Filtration and antifouling performance of the membranes

Membrane code	Permeate Flux ($L\ m^{-2}h^{-1}$)			FRR and Fouling recovery (%)			
	J_{w1}	J_p	J_{w2}	FRR	R_t	R_r	R_{ir}
PMA-0	133.1	9.2	28.6	21.4	93.0	14.5	78.6
PMA-1	160.5	11.5	96.8	60.3	92.5	53.1	39.7
PMA-2	223.8	12.1	118.5	52.9	85.0	47.5	47.1
PMA-3	242.3	14.2	173.5	71.6	94.1	65.7	28.4