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Responsive, self-cleaning membranes for fouling control in advanced agricultural wastewater treatment

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The main aim of the project was to explore novel ways with which to overcome fouling of nanofiltration (NF) membranes by inducing repulsion and responsiveness to the membrane surface, as well as an osmotic-induced flow reversal. Poly(NIPAM) brushes were grafted onto commercially available NF membranes. The temperature-induced conformational change was exploited to investigate the resistance to deposition of colloidal particles on the NF membrane. The overall project was mainly divided into 3 parts

1. To induce the responsiveness on the membrane surface
2. Characterize the surface to assure the proper incorporation of the responsiveness
3. Understanding the effect of reversible conformation change of poly(NIPAM) on the colloidal deposition on membrane surface.

The first two objectives were eth focus of the US team while the work on the third objective was conducted in Israel. Furthermore, the Israeli team conducted experiments aimed to assess the effectiveness of osmotic back-flushing for cleaning the NF membrane surface.

Polymer brushes were synthesized using ATRP, a controlled polymerization technique that consists of 2 steps: the initiator immobilization step, where the initiator was plugged on membrane surface and this is the site of polymer growth followed by ATRP, for the controlled growth of the PNIPAM at the sites of initiator immobilization. The duration of these two steps play a crucial role in membrane performance as the longer duration of first step induces highly dense elements of response, while longer duration of 2nd step generates a thicker brush. Therefore, to get the best performance, the experimental conditions were optimized. The surface characterization was done for the modified membranes and compared to the base membrane. IR spectroscopy was used to confirm grafting of poly(NIPAM). Further analysis of AFM images provided insights into membrane surface roughness. Modified membranes had a higher water contact angle than the bae membrane indicting that poly(NIPAM) is more hydrophobic than the surface of the base NF270 membrane. In addition, changes in zeta potential indicate changes in apparent surface charge as a result of the grafted nanostructure Finally, AFM imaging indicate that the modified membrane is rougher than the base membrane. Surface characterization not only confirmed surface modification it provides insights onto changes in membrane surface properties that could alter the performance of the modified membrane compared to the base membrane.

Direct microscopic observation of colloids deposition on PNIPAM modified NF membranes provided new insights into the antifouling characteristics. The brushes attached to the surface at optimized density expected to be stretched away from the surface. Cross-flow filtration experiments performed with confocal microscope indicates that this layer prevents foulants

from approaching the polyamide surface, thus improving the anti-fouling properties. Notably surface coverage of PNIPAM-modified membrane was lower, regardless of the particles surface charge. The non-specific mechanism acting to prevent deposition of colloids on the brushes is steric repulsion of the brushes. However, while successfully decreasing deposition in a significant way, the particles that deposit on the PNIPAM surface, were not removed with the NaCl cleaning protocol.

Backflushing experiments conducted using the NF membranes, as well as brackish reverse osmosis membranes, showed that the ability to induce an osmotic back flow through the membrane was strongly dependent on the osmotic agent used – sulphate-based salts provided the most prolonged backflush due to their high retention by the membrane. NaCl, on the other hand, leaked substantially through the membrane and the osmotic flux declined rapidly. Preliminary tests have shown that this osmotic flow reversal can successfully restore up to 80% of the flux lost after scaling by Calcium-Phosphate, a common problem and limitation in wastewater recovery for reuse.

Future extensions of this work should focus in the exact interactions between the polymer material used for the brush and the foulants to be removed, ensuring that a low binding energy exists. In this manner, even if some deposition should occur (since the primary function of the brush has been proven in the current study – the reduction of deposition propensity), such deposition will be weaker and more easily reversed. Successfully achieving both these functionalities, at a minimal reduction of membrane permeance, will greatly improve the robustness of nanofiltration membranes for wastewater reclamation.

Summary Sheet

Publication Summary

PubType	IS only	Joint	US only
Abstract - Poster	1	1	0
Abstract - Presentation	1	1	1
Reviewed	1	0	1
Submitted	1	1	0

Training Summary

Trainee Type	Last Name	First Name	Institution	Country
Ph.D. Student	Vu	Anh	U. of Arkansas	USA
M.Sc. Student	Hadas	Sagi	Technion	Israel
M.Sc. Student	Segev	Naama	Technion	Israel
M.Sc. Student	Ukrainsky	Ben	Technion	Israel
Ph.D. Student	Zhou	Fanglei	U of Ark	USA
M.Sc. Student	Fux	Gali	Technion	Israel
M.Sc. Student	Lerman	Sophia	Technion	Israel
M.Sc. Student	Segev	Naama	Technion	Israel
Ph.D. Student	Jacobi	Yuval	Technion	Israel
M.Sc. Student	Lahav	Yotam	Technion	Israel
M.Sc. Student	Lustig	David	Technion	Israel

The collaborative nature of this project was well reflected in the inherent synergy – the membranes were fabricated by the US team and were tested by the Israeli team. The project could not be realized without the combined capacity of the US team for advanced fabrication with the testing facilities of the Israeli group, particularly the microscopic visualization rig. Several presentations have been made at international conferences, and two joint publications are in preparation.

Fouling – the deposition of material separated by the membrane, on the membrane surface, is a major problem that increases the cost of wastewater reclamation using membrane technology.

As part of this project, membranes were fabricated, such that they are more repellent towards fouling materials and, furthermore, could be cleaned on demand, therefore removing any unwanted accumulated material on the membrane surface. The resistance to deposition is achieved by coating the membrane with 'polymer brushes' – hair-like structures that prevent material from coming into direct contact with the membrane. Cleaning of these surfaces is achieved by inducing collapse of these brushes using a switch in the temperature and/or salinity of the feed stream, thus promoting release of the deposited material. Concurrently, the increased salinity induces an osmotic back-flush that further assists in lifting and removing deposited material.
The main achievements are the proof-of-concept that osmotic back-flushing can be induced and maintained with this type of membrane, using an appropriate salt, and illustrating the capacity for removal of deposited foulants. Furthermore, polymer-brush-coated membranes we fabricated and characterized, and subsequently tested for fouling resistance. Experiments showed that these membranes exhibited significantly lower deposition compared with the unmodified membrane.

The original plan was followed, for the most part. The main changes were as follows:

- The magnetic actuation of the polymer brush was not attempted. Instead, more time was spent on fine-tuning fabrication conditions of the brush-coatings and on deposition experiments using direct microscopic observation. In particular, this course of action was chosen due to early delays in achieving desired fabrication of the coated membranes with relatively small impact on the permeability. In addition, several early batches of membranes experienced 'aging' during transit, and arrived at the Israeli lab in an unusable state. This also caused significant delays and was eventually solved by improving the storage a protocol for shipping.

- The modeling of the brush response was abandoned, in light of the lack of success in experimentally reversing the fouling using brush conformation changes. Instead, modeling was focused on some estimates of brush repulsion capabilities. Primarily, modeling efforts were extended towards predicting the duration and magnitude of an applied osmotic backflush cycle, as affected by membrane and salt properties.

Publications for Project IS-4768-14R

Status	Type	Authors	Title	Journal	Vol:pg Year	Coun
Published	Reviewed	*Yachnin, Elina; Ramon, Guy*	Direct microscopic observation of macromolecular deposition on a nanofiltration membrane	***Separation Science and Technology***	: 2016	IS only
Published	Reviewed	*X. Qian, Q. Yang, A. Vu, S R. Wickramasinghe*	Localized Heat Generation from Magnetically Responsive Membranes	***Industrial & Engineering Chemistry Research***	55 : 9015-9027 2016	US only
Published	Abstract - Poster	*Yachnin, E., Segev, N., Ukrainsky, B, Ramon G.Z.*	Direct observation of macromolecular deposition and dynamics on a nano filtration membrane		:	IS only
Published	Abstract - Presentation	*Zhou, F., Yachnin, E., Ramon, G.Z., Qian, X., Wickramasinghe, S.R.*	Fouling Resistant Temperature and Magnetic Field Responsive Nanofiltration Membranes		:	Joint
Published	Abstract - Presentation	*Segev, N., Epstein, J.A., Ramon, G.Z.*	Reversibility of particle deposition as affected by the applied pressure and particle elasticity		:	IS only
Published	Abstract - Presentation	*A. Sengupta, A. Vu, S. R. Wickramasinghe*	Selective Modification of Membrane Pore and External Surfaces		:	US only
Published	Abstract - Poster	*Segev, N., Vu, A., Qian, X., Wickramasinghe, S.R., Ramon, G.Z.*	Colloidal deposition on polymer-brush-coated NF membranes		:	Joint
Submitted	Reviewed	*Naama Segev Mark, Anh Vu ,Ningyuan Chen, Xianghong Qian, S. Ranil Wickramasinghe and Guy Z. Ramon*	Colloidal deposition on polymer-brush-coated NF membranes		:	Joint
Submitted	Reviewed	*Asaf Dana, Sagi Hadas and Guy Z. Ramon*	Osmotic backwashing of brackish water membranes:Experiments and modelling		:	IS only

Effects of conformational changes of surface grafted polymer brushes during nanofiltration of oily wastewaters

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Abstract

Salt induced conformational changes below lower critical solution temperature from hydrophilic chain structure to hydrophobic coiled structure of grafted poly(NIPAM) on nanofiltration membrane has been employed to understand the interaction of oil/water with membrane surface. The grafting of poly(NIPAM) was evidenced by FTIR in terms of functionality. Poly(NIPAM) grafting was found to induce hydrophobicity and roughness on membrane surface, while reduction in surface charge was noticed. This conformational change influences the deposition of oil droplets on membrane surface and hence subsequent cleaning. The deposition of oil on poly(NIPAM) modified membrane was found to be more than the virgin membrane unlike the particle deposition. This can be attributed to the flexible nature of the oil droplets and favored mutual hydrophobic interactions between multiple droplets to for larger one and subsequent phase separation.

Keywords: Poly(NIPAM), oil deposition, hydrophobicity, controlled grafting, conformational change

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1. Introduction

Though membrane based technology provides efficient, clean, environmentally benign, energy intensive technology for variety of industries based on waste water treatment, generation of portable water, efficient biomedical separation; membrane fouling is one of the major issues required to be addressed to have long term separation scheme without deterioration of membrane performance. Membrane fouling can cause severe flux decline and affect the quality of the permeate compromising the efficiency as well as selectivity. Fouling can be divided into reversible and irreversible fouling based on the strength of interaction of foulant on the membrane surface. Reversible fouling can be removed by a strong shear force or backwashing. Formation of a strong matrix of fouling layer with the solute during a continuous filtration process will result in reversible fouling being transformed into an irreversible fouling layer. Irreversible fouling is the strong attachment of particles, that cannot be removed by physical cleaning. Recent investigations revealed that hydrodynamics, operating conditions, membrane properties, and foulant properties significantly influence the nature and strength of fouling. At low pressure, low feed concentration, and high feed velocity, concentration polarization effects are minimal and permeate flux is almost proportional to trans-membrane pressure difference. However, in the high pressure range, flux becomes almost independent of applied pressure. Deviation from linear flux-pressure relation is due to concentration polarization. At low feed flow rate or with high feed concentration, the limiting flux situation is observed even at relatively low pressures. Though physical cleaning, like

flushing with water is effective to remove reversibly bonded foulant from membrane surface, is not worth for irreversible fouling.

Modification of the surface properties of the membranes in terms of surface charge, functionalities or morphologies including roughness have been widely utilized to enhance the antifouling properties of the membranes. Grafting hydrophilic monomers either ionic: zwitterionic, ionic liquid or non-ionic: poly(2-hydroxyethyl methacrylate), poly(ethylene diamine) was demonstrated to highly effective for organic foulant, while grafting of ionic polymer provides effective resistance over biofouling due to their intrinsic antimicrobial characteristics. Grafting polymers, that response in presence external stimuli was also demonstrated to be highly effective in order to improve the antifouling properties of the membrane. Magnetic responsive membranes exhibit efficient capability of breaking concentration polarization by micromixing due to magnetic interaction of magnetically responsive polymer brush with applied oscillating magnetic field.

Grafting poly(NIPAM) (N-isopropyl acrylamide) is associated with polymer-bound water in addition to the bulk water acting as the solvent. Intermolecular hydrogen bonding interaction with the amide moieties of poly(NIPAM) was found to be one of the dominating interactions. Poly(NIPAM) possesses a sharp demixing transition in an aqueous environment having a lower critical solution temperature (LCST) at 32 °C. Below LCST, the poly(NIPAM) predominately exists in hydrated form with chain structure, while above LCST, the polymer possesses conformational change to coiled structure being hydrophobic by dehydrating the associated water molecules. This temperature induced response have been utilized as thermos-responsive membranes. However, this hydration/dehydration associated conformational change can also be induced at a temperature lower than LCST by different means. Enhancement of the ionic strength of the feed by addition of salt can induce electrostatic interaction between the ions and the water

molecules. In order to generate solvated ions, the poly(NIPAM) brush dehydrates resulting conformational change to coiled form. In the present investigation, such salt induced conformational changes have been utilized for the application of treatment of oil-water by nanofiltration. The effect of this conformational changes on the interaction of the membrane materials and the oil vis-à-vis water has been investigate to understand the adsorptive fouling of the membrane and the subsequent cleaning by inducing the conformational change.

2. Experimental

2.1 Materials

The reagents used in the present investigation are of ACS reagent grade unless it is otherwise specified. Acetonitrile and methanol were procured from EMD Millipore, Billerica, MA, while ethanol was procured from VWR International, Radnor, PA. N-isopropylacrylamide (>98%) was purchased from TCI America, Boston, MA. α-bromoisobutyryl bromide (98%) was procured from Alfa-Aesar, Ward Hill, MA. Rest of the other chemicals used in present study including Triethylamine, 4-dimethylaminopyridine, N,N,N',N",N"-pentamethyl diethylenetriamine (99%), sodium chloride (ACS reagent grade), CuBr and $CuBr_2$ were purchased from Sigma-Aldrich, Munich, Germany. The deionized water used throughout the investigation was obtained from Thermo Fisher 18 MΩ Barnstead Smart2Pure system, Schwerte, Germany. NF 270 membrane was procured from Dow Filmtec, Edina, Minnesota. The membranes were cut into circle with a diameter of 25 mm and used for the experiments.

2.2 Grafting of poly(NIPAMP) responsive brush on NF270 membrane

A two-step surface modification method was adopted to graft the poly(NIPAM) responsive polymer brush on the surface of commercially available NF 270 membrane in a controlled manner. The first step was initiator immobilization to control the location of grafting, whereas the second step was atom transfer radical polymerization to control the length of the grafted polymers. All the membrane samples were washed thoroughly with 1:1(v/v) ethanol-water mixture for a duration of 2 hous in order to remove the preservatives, followed by overnight drying in vacuum oven at 40°C for. The initiator immobilization was carried out in acetonitrile solvent. The reaction mixture was prepared by dissolving 100 mM triethylamine, 5 mM 4-dimethylaminopyridine. Then 1% by volume of α-bromoisobutyryl bromide was added to the reaction mixture to which the washed NF270 membrane was already dipped. Due to very high reactivity of the initiator, α-bromoisobutyryl bromide, the transfer process was done very quickly. The initiator immobilization was carried out for a duration of 15 min at ambient temperature followed by quenching the reaction with water. Subsequently, the membrane was washed with ethanol-water mixture to remove unreacted precursors and finally dried overnight to make it ready for the ATRP step.

The ATRP was carried out in a three necked round bottom flask. A homogeneous reaction mixture containing NIPAM:CuBr: N,N,N',N",N"-pentamethyl diethylenetriamine in a molar ratio of 100:1:3 in molar ratio in 9:1, v/v water/methanol solvent was prepared. Initially, the homogeneous solution of NIPAM in water-methanol was prepared by mixing them for a duration of 30 min in argon atmosphere, followed by addition of N,N,N',N",N"-pentamethyl diethylenetriamine with continuous stirring for additional 15 min. Finally, the membrane was dipped inside the flask with the addition of CuBr in argon atmosphere and the reaction was allowed to continue for designated 1 hour of ATRP time. The stringent condition of oxidant free environment is a prerequisite for the ATRP process to maintain appropriate ratio of Cu ions in +1

and +2 states to be suitable for forward reaction towards controlled polymer growth. Finally, the membranes were washed thoroughly with water/methanol 1:1 (v/v) mixture for removal of unreacted species and stored in water/ethanol 1:1 (v/v) mixture. **Figure 1** schematically presents the modification process.

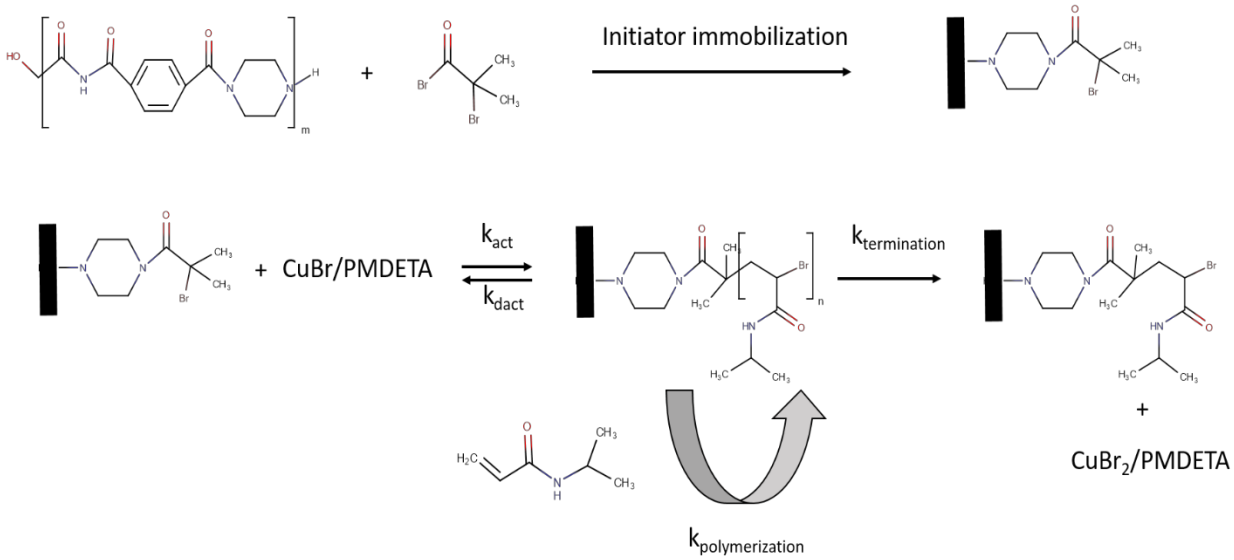


Figure 1: Schematic presentation of the modification process

2.3 Characterization of the modified membrane

Atomic force microscopic (AFM) investigation was carried out using an atomic force microscopy (AFM) equipped with Dimention Icon AFM from Bruker, from Bruker, Santa Barbara, CA. Nanoscope V815R3sr1 software with NanoScope Analysis program was employed in order to analyze the collected data. The membrane samples were dried overnight prior to the investigation by AFM. Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopic (ATR-FTIR) analysis was carried out using a Shimadzu IRAffinity-1 spectrometer equipped with a PIKE single-reflection horizontal ATR accessory procured from Shimadzu, Columbia, MD, USA. A wide

spectral range of 600-4000 cm^{-1} was investigated with 1000 to achieve optimum signal to noise ratio. Air contact angle on the membrane surface was measured in static mode using captive bubble method at room temperature and pressure (OCA 20, Future Digital Scientific Corp., Garden City, NY, USA). Using the circle fitting method, the angle between the air bubble and the membrane surface was measured in every 0.1 second at 5 different locations on the surface. Highly hydrophilic nature of the membrane surface decides the air contact angle measurement to be appropriate compared to water contact angle. The surface charge on membrane was measured in terms of zeta potential using Delsa Nano HC particle analyzer procured from Beckman Coulter, Brea, CA.

Degree of grafting is a basic and simple method to measure the amount of polymer which is grafted from the surface of the membrane. The base membrane was rinsed and dried overnight in a vacuum oven at 40°C. The dried weight of the unmodified membrane was recorded. After modification, the membrane was washed in DI water and then dried overnight in a vacuum oven at 40°C. The membrane was then weighted again. The degree of grafting, DG (mg/cm2), was calculated using the following equation:

$$DG = (W1 - W0)/Am$$

where, W0 is the mass of the unmodified membrane and W1 is the mass of the membrane after modification and drying. Am represents the area of the membrane and is 13.4 cm2 in this study.

2.4 Performance of modified membranes

The aqueous solution of 0.01M sodium chloride was used as a background electrolyte to achieve the conformational change of poly(NIPAM) grafted on membrane surface. A custom-made crossflow filtration cell with channel dimensions (0.6 mm x 6 mm x 36 mm) having effective

surface area of membrane 216 mm^2 was used in the present investigation. The feed was subjected to an applied pressure of 3 bars and with continuous stirring. A gear pump (Micropump, Cole Parmer, Vernon Hills, IL, USA) was employed to achieve and maintain a constant cross-flow velocity of 0.07 m/s. Changes to the trans-membrane pressure (TMP), occurring during the experiment, were monitored by a differential pressure transducer (PX409, omega engineering, UK). Electrical conductivity and temperature were continuously monitored with a probe (M200 easy line, METTLER TOLEDO, USA) placed into the feed solution, while the electrical conductivity of the permeate was measured at the end of experiment by a probe, cyerscan PC 300, Eutech instruments, Singapore. The feed solution was pumped into the flow cell for 40 minutes of deposition, during which five random images of the membrane surface at different locations were acquired every 5 minutes. Deposition was followed by a cleaning protocol composed of 5 steps. First, the feed pressure was reduced to zero (designated as TMP=0) to eliminate the permeation. Then, feed solution was replaced with a concentrated salt solution containing 1.5M NaCl (designated as salt), after which the feed was replaced again to MilliQ water (water). The last two steps were repeated twice. Each of the cleaning steps lasted 20 min. After the 'cleaning cycles' were completed, the flux recovery was tested with DI water only.

The average permeation rate at a pressure of 3 bar is 17.7 μm/s and 3.6 μm/s for NF270 and PNIPAM-coated NF270, respectively. To overcome this difference in conditions, two sets of experiments were performed. Long-term deposition at the same water flux (5.5μm/s) and a deposition-release protocol (deposition stage followed by the cleaning protocol outlined above), with a fixed particle flux towards the membrane. In the latter case, to maintain a similar particle flux (or a larger particle flux for PNIPAM, so as to be conservative), the particle concentration in the PNIPAM experiments was 5 times bigger than that for the base NF270.

3. Results and discussions

3.1 Characterization

The modified membranes were characterized for their surface charge, morphologies and functionalities. The appearance of a peak at 1635 cm^{-1} for the modified membrane was assigned to the amide functionality obtained during grafting of NIPAM on membrane surface through the initiator. The poly(NIPAM) grafting was found to enhance the contact angle on the membrane surface indicating the induction of hydrophobicity on membrane surface. This fact was also corroborated by the measurement of surface charge in terms of zeta potential. At pH 7, the zeta potential of NF 270 virgin membrane was measured as -15 mV, which was reduced to -10 mV on grafting of poly(NIPAM) brush. The grafting of poly(NIPAM) was also found to enhance the overall roughness of the membrane surface as obtained from microscopic imaging. Figure 2 is showing the surface characterization of the modified membrane compared to the virgin membrane.

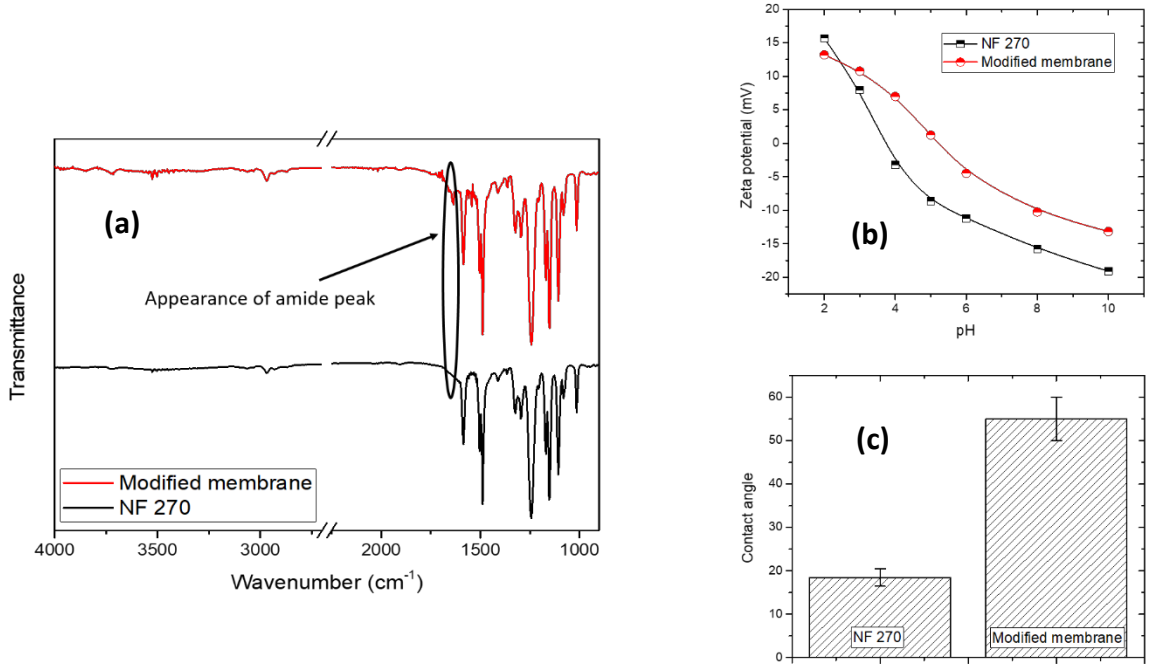


Figure 2: The characterization of modified membrane (a) FTIR; (b) zeta potential; (c) contact angle

Figure 3 is showing the AFM images for modified membranes in 2D, 3D and 3D in 2D angles. The figure suggested the clear change in surface morphology on grafting poly(NIPAM) on NF270 surface. Almost 1.5 to 2 times enhancement in the membrane surface was observed on grafting the polymer. The surface roughness for virgin membrane was evaluated as 3.42 nm and became 6.20 nm on modified membrane surface. This observation is quite similar to other literature reports and also very significant in membrane performance mainly fouling as the rougher surface provides more surface area of the membrane to interacts with the feed component including foulants.

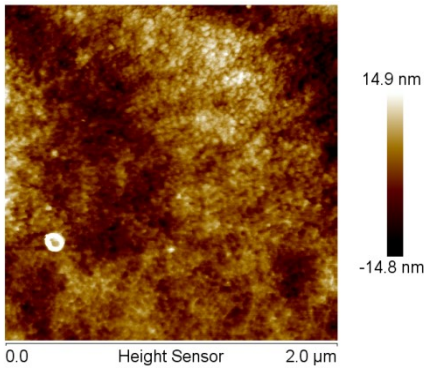
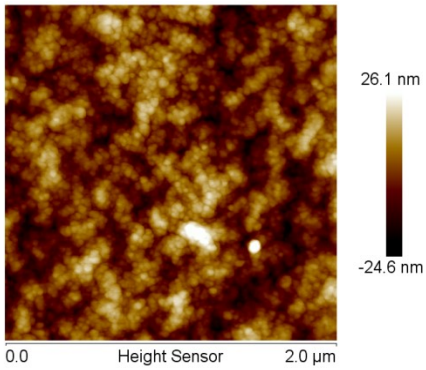
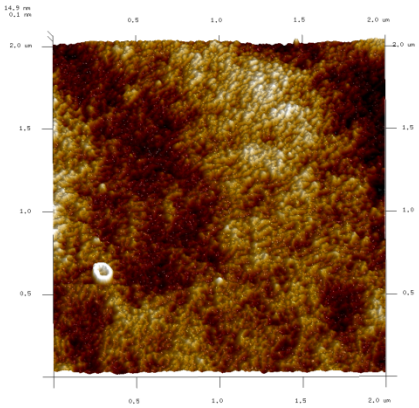
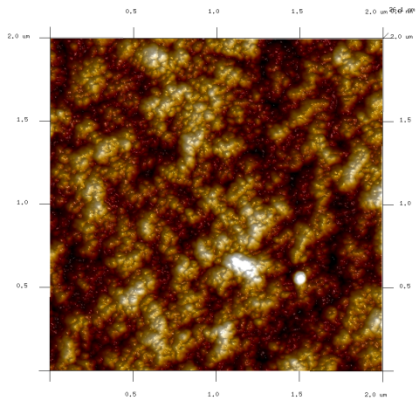
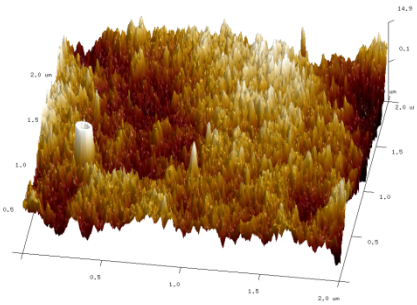
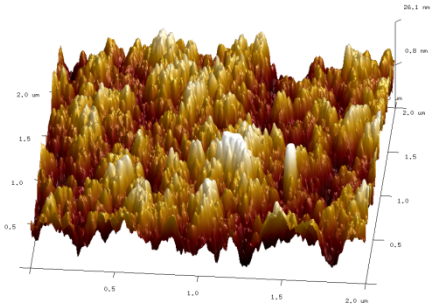
	Base NF270	Modified NF 270 with PNIPAM
2D		
3D n 2D angle		
3D		

Figure 3: The AFM images in 2D, 3D in 2D angle and 2D for modified and virgin membranes

Figure 4 represents the variation in degree of grafting over the duration of ATRP time for same duration of (0.5 h) initiator immobilization. As mentioned earlier, the ATRP is a controlled grafting method propagates through the dynamic equilibrium between Cu(1)/Cu(2) ratio, the longer duration of ATRP time slowly generates longer poly(NIPAM) brush on the NF270 surface, hence degree of grafting should enhance. Figure 4 is showing an almost linear enhancement in degree of grafting from ~ 6 ug/cm2 at 1 h of ATRP to ~ 28 ug/cm2 for 4 h of ATRP.

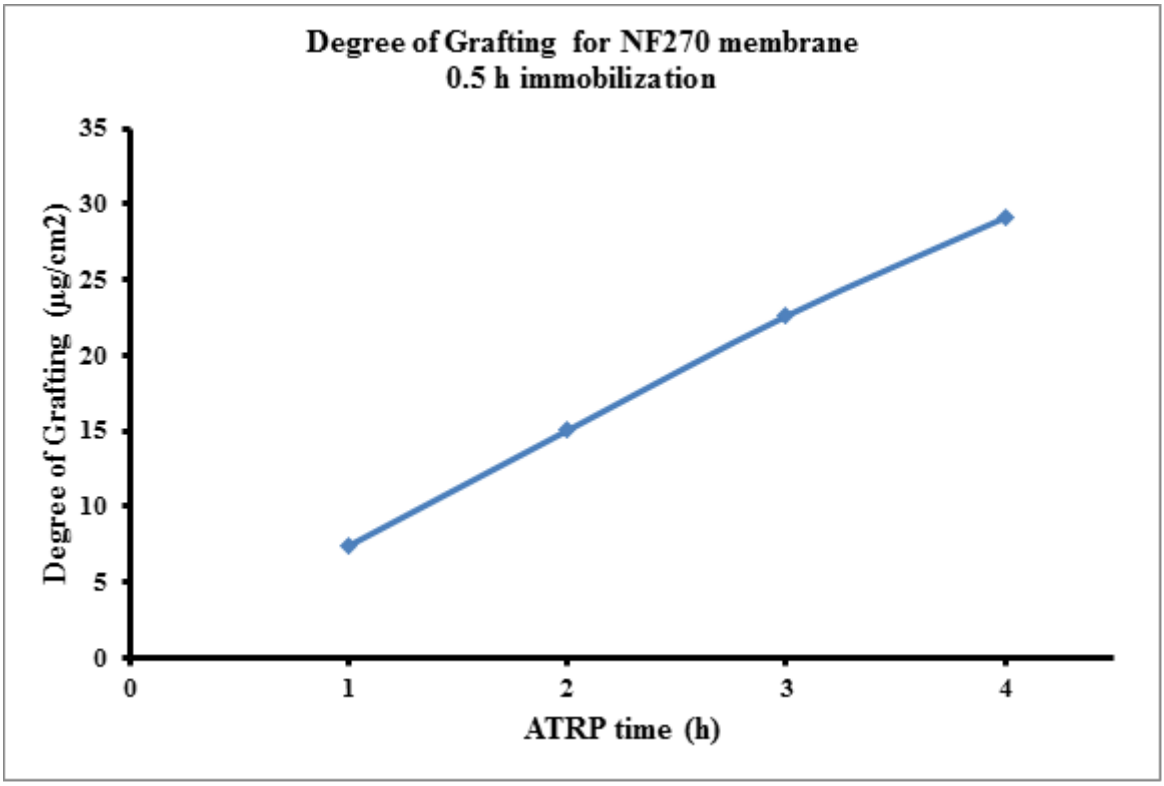


Figure 4: The degree of grafting of poly(NIPAM) on Nf270 as a function of duration of ATRP

3.2 Performance of the modified membrane

Figure 5 shows the variation in water flux as a function of duration of filtration for the modified membrane in presence of hot as well as cold feed. The temperature of the feed is chosen such a way that one is below the LCST and another is above LCST to achieve hydrophilic or hydrophobic conformation during filtration operation. Below LCST, the poly(NIPAM) brush exists as chain structure with extensive hydrophilic interaction with the water molecules present in boundary layer. Therefore, the permeability of water through this conformation is not hampered resulting almost consistent flux value over a duration of almost 1 h of operation. However, at a temperature higher than LCST, the polymers attain hydrophobic coiled conformation generating additional hydrophobic barrier for the water molecules to pass. Consequently, significant reduction in water flux was observed over the duration of filtration operation. No such response was observed for virgin membrane. This conformational change has been induced at ambient temperature by the application of NaCl to enhance ionic strength. In order to make the salt hydrated, the water molecules interacting with poly(NIPAM) would release resulting conformational change on the polymer at room temperature. This process is energetically favourable because the ionic species induce stronger electrostatic interaction with water molecules, resulting the release of high solvation energy compared to the energetics associated with the electrostatic interaction of polar groups of poly(NIPAM) with the water molecules.

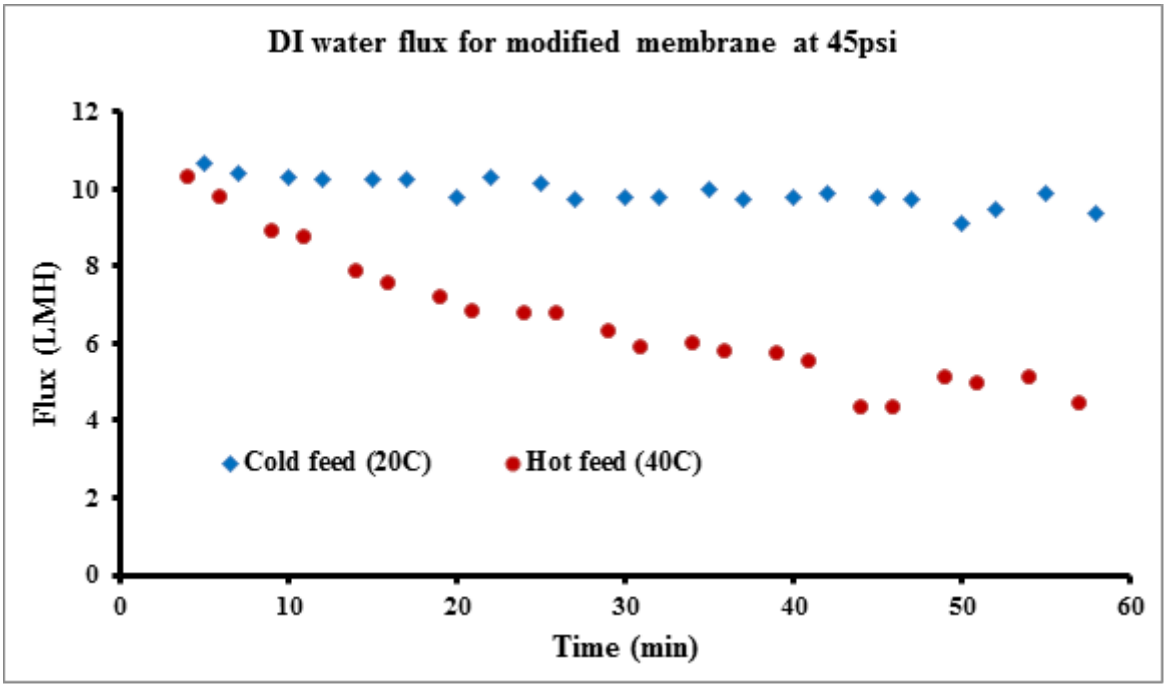


Figure 5: The variation of water flux as a function of duration of filtration through modified membrane using hot and cold feed

Figure 6 is showing the performance of grafted membrane in comparison with the virgin membrane in order to understand the interaction of oil particles during nanofiltration of oil-water. The initial 40 min of operation deals with the deposition of oil droplets at a constant flow and applied pressure of 3 bars for five different locations of the membrane. The % surface coverage for NF270 membrane is marginally more at any instant, though the behaviour of NIPAM modified membrane is little steeper with time indicating greater interaction of oil with the membrane surface. This fact is quite easily understood based on the higher surface charge and hydrophilic nature of the base membrane compared to the modified membrane. During 45 to 60 min of operation, when the trans membrane pressure reached zero, the surface coverage of unmodified surface was reduced to ~ 2 %, while the modified membrane it decreased up to ~ 12.5 %. Then the

membrane is subjected to two repetitive cycles of cleaning with 1.5 M NaCl for 15 min of duration followed by water for 15 min of duration. The transmembrane pressure was kept 0 during this cycles. As proposed, the NaCl induces the conformational change on poly(NIPAM) brushes even at room temperature. This local perturbation would lead to cleaning of the membrane surface for subsequent recovery of the flux. This process led to no surface coverage of oil droplet for virgin membrane, while for modified membrane deviation in surface coverage was observed. A reduction in surface coverage was achieved on these consecutive application of NaCl followed by water. However, the cleaning performance of modified membrane was not satisfactory compared to the virgin membrane. This observation was completely opposite compared to our previous investigation on deposition of polystyrene particles. Unlike polystyrene particles, the flexible nature of oil droplets with respect to size and shape is believed to be responsible for their difference in behaviour. Moreover, the mutual coaleases between oil drops is predominating due to high mutual hydrophobic interaction and large viscosity. Such extensive agglomeration can lead to separation of oil phase from water and deposited as a separate layer on membrane surface. More hydrophobic surface would provide stronger hydrophobic interaction leading to stronger affinity for such oil deposition.

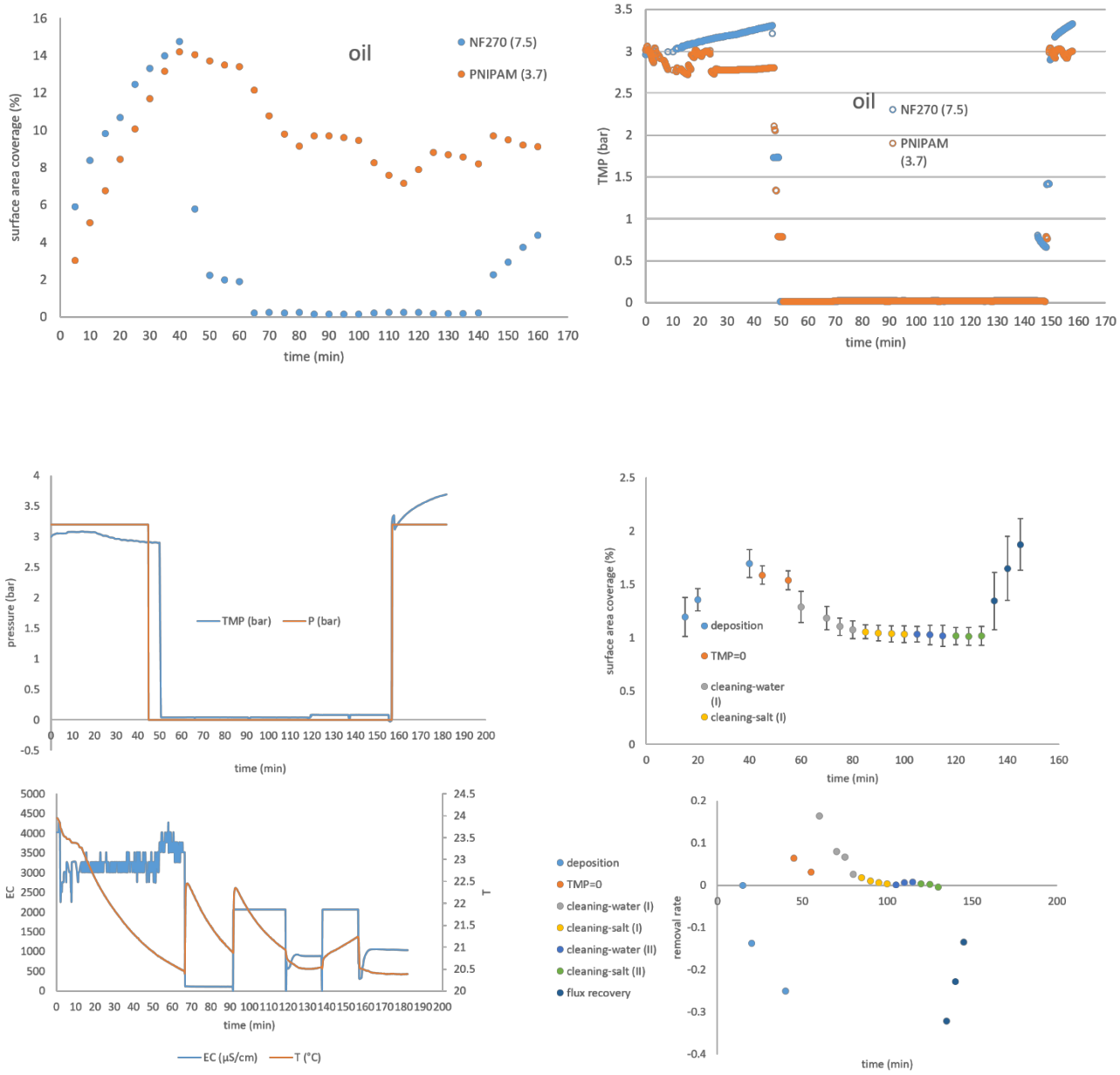


Figure 6: The performance of modified membrane on salt induced conformational change during oil-water nanofiltration

Conclusion

Ionic strength induced ambient temperature conformational change from hydrophilic to hydrophobic and vise versa of poly(NIPAM) brush grafted on NF270 was found to investigate the

interaction of oil droplets with modified membrane surface and subsequent membrane performance and cleaning. The behaviour of oil droplets are unique and unlike to the particle behaviour due to the flexibility in their size and shape. Mutual hydrophobic interaction and high viscosity are responsible for such unique behaviour of mutual aggregation and subsequent phase separation for deposition.