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Investigations on the Effect of Silica Nanoparticles on Polyamide Coated PVDF Hollow FiberMembranes

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Abstract
Hollow fiber membranes (HFMs) find extensive applications in numerous separation fields for water desalination and treatment and recently for gas separation. It is mandatory to explore optional post-treatment modalities to come up with desirable membrane characteristics. Within this context, nanoparticles (NPs)are incorporated in HFMs membrane matrix either in the dope or as surface addition on coating by interfacial polymerization (IP) technique. In this study, silica NPs (20 nm) at different concentrations (0.05%, 0.075% and 0.1%) have been incorporated during polyamide film formation on Polyvinylidine fluoride/Polyacrylonitrile (PVDF/PAN) HFMs. Numerous post-treatment effects were monitored and analyzed for normally dried and Microwave (MW)post-treated PVDF/PAN HFMs. The observed characteristics included surface morphology, surface hydrophilicity, surface roughness, porosity and surface zeta potential at pH range from 4.6 to 8. Further, mechanical investigations centered on break strength, break strain and Young's modulus. Results revealed dimensional stability of the fabricated thin-film HFMs with varying changes of the surface roughness average (Ra) ranging from 28.5 nm to 54.3 nm. Assessment of relevant mechanical properties indicated minor to moderate effect on mechanical propertieswith maximum decrease manifested by MW post-treated samples. Interestingly, incorporation of silica NPs as well as MW post-treatment decreased contact angle. Also, minor alterations of porosity (75.7% to 84.5%) have been observed with all induced interventions. Finally, studies on the effect of silicaNPs and MW post-treatment revealed further increase of the zeta potential from -12.5 to -6 mV at pH=4.6 and from -16.5 to -7.5 mV at pH=8. On the other hand, the MW post-treatment showed marked decrease in zeta potential for as-spun, coated and incorporated silica NPs MW post-treated samples.

Keywords
Hollow fiber membranes, thin film nanocomposite, silica nanoparticles, microwave irradiation, PAN, PVDF

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I. Introduction

Polymeric hollow fiber membranes (HFMs) have been studied extensively and gained interest since 1960 due to their various advantages such as high packing density[1], high flux production, self supporting structure[2],as well as, possibility of hydraulic cleaning to mitigate membrane fouling[3]. These properties allow their usage in a wide spectrum of applications, ranging from water desalination[4], water treatment[5] to food industry, gas permeation[6], oil treatment[7], hemodialysis[8][9], as well as, pharmaceutical applications.

Several polymers have been used to produce HFMs, including Polyvinylidine fluoride (PVDF) which is hydrophobic in nature[5] and exhibits superior properties due to its semi-crystalline structure giving the membrane thermal stability as well as flexibility[10][11]. Also, PVDF has excellent chemical resistance in addition to ease of dissolving in organic solvents which makes it a favorable polymer for membrane fabrication.

Dope blendingwith additives or other polymers is a popular route to modify or enhance the membrane properties[12]. Several authors studied the effect ofblending Polyacrylonitrile (PAN) with PVDF membranes owing to PAN polymer‘s low cost, good biocomptability, hydrophilicity as well as good age resisting property[13].

Another modifying technique is interfacial polymerization (IP), which is usually carried out on membranes to form a thin-film composite membranes (TFC)to improve their surface properties and performance. Nanotechnology played a critical role in upscaling IP, where nanoparticles (NPs) are incorporated

into the selective thin coating layer to produce thin-film nanocomposite membranes (TFN), imparting further enhancement to membrane properties [14–16]. Different types (organic and inorganic NPs) such as Zinc Oxide[17, 18], CuO [19, 20], TiO_2[21],CNTs[22], Graphene and GO[23, 24] as well as different shapes (1 dimensional (D), 2D and 3D) NPshave been used [25].

Silica NPs are spherical inorganic NPs which are characterized by their high mechanical strength[26], outstanding hydrophilicity[27] as well as good thermal stability[6], which made them a popular choice in membrane modifications[28].

Mostafa et al.[29] synthesized TFN PVDF HFMs via incorporating silica NPs during IP. Results demonstrated increased hydrophilicity and surface roughness, while mechanical properties decreased. Safarina et al. [30], Abolfazli et al. [27], Abadikhah et al. [31]reported similar results for PVDF/Polydopamine flat sheet membrane, Polysulfone (PS) HFMs and Polyether sulfone (PES) membranes, respectively,upon incorporation of Silica NPs to produce TFN membrane. On the other hand, increased hydrophobicity was detected as well as significant increase in surface roughness and contact angle values for in-situ produced Silica NPs via sol-gel during PAN TFN flat sheet membrane production [32].

Numerous studies have been conducted to investigate surface modification using microwave(MW) irradiation as a clean, fast andsustainable post-treatment technique to alter membrane properties[29, 33–38].The findings of Abed et al. [34, 36, 37]demonstrated MW post-treatment as a superior tool to tailor membrane properties towards target application of PES HFMs in different media. Ahmed et al.[39][38] confirmed MW irradiation as a more effective post-treatment tool when compared to annealing technique, where hydrophilicity was enhanced and a decrease in pore size PES flat sheet and HFMswas observed.Yean et al. [40]compared hypochlorite post-treatment to corresponding MW irradiation for PES HFMs where MW irradiation caused noticeable improvement in membrane's rejection performance as well as altering morphological structure.The results of Fazullin et al. [35][41]revealed decreased surface roughness and increased membrane hydrophilicity for Nylon-Polytetrafluroethylene (PTFE) and Nylon-Polystyrene TFC membranes, again cofirming the ability of MW to fine tuneproperties and performance.

Membrane structural characteristics, such as roughness and porosity, and parameters defining the interaction of membranes with solutes in feed solutions, such as wettability, surface charge and zeta potential may be used to categorise factors affectingthe membrane's performance[42]. Measurement of the zeta potential gives an indication of the strength of electrostatic attraction or repulsion between particles[43][44][45].

Previous investigations have studied thoroughly the effect of NPs incorporation on TFN membranes properties and performance; however there is no reported study on their effect on PVDF/PAN TFN HFMs in addition to the lack of information on the effect of MW irradiation on their properties. The overall goal of this research is to fill this knowledge gap throughincorporating different ratios of silica NPs to produce PVDF/PAN TFN HFMs and subjecting these membranes to MW irradiation to study the effect on membrane morphology, surface roughness, mechanical properties, porosity, membrane's hydrophilicityin addition to surface zeta potential.

II. Experimental Investigations

2.1 Materials

Polyvinylidene fluoride (PVDF) andPolyacrylonitrile (PAN)were used as base polymers, supplied from Alfa Aesarand Sigma Aldrich, respectively. Solventused in this study, namely, Dimethyl formamide (DMF) waspurchased from Carl-Roth.Distilled water (DW) was used as the bore fluid and in coagulation, washing baths and for preservation. Isopropyl alcohol used for membrane activation was supplied from TEDIA. Silicon (IV) oxide, nano powder (20 nm), used for TFN fabrication, was purchased from Alfa Aesar. Trimesoyl chloride (TMC), m-phenylene diamine (MPD) and Piperazine (PIP),which were used to prepare Polyamide active layer,were purchased from Siga-Aldrich and Fine Chemicals.Adipoyl chloride and Triethylamine (TEA) were supplied from ACROS and Fisher Chemicals, respectively. Cyclohexane, purchased from El Nasr Pharmaceutical Chemicals Co., was used as the organic solvent. Magnesium chloride ($MgCl_2$) used to preserve as spun and coated PVDF/PAN fiber, was purchased from El Nasr Pharmaceutical chemicals. Sodium chloride (NaCl) supplied from Chemika was used in MW post-treatment. For membrane porosity measurements, Kerosene oil was purchased from Misr Petroleum Co. Potassium Chloride (KCl) purchased from Sigma-Aldrich was used to prepare zeta potential measurements of electrolyte solutions. Hydrochloric acid (HCl) and Sodium hydroxide (NaOH), supplied from ADWIC and Sigma-Aldrich, respectively, were used for preparing pH titration solutions for zeta potential measurements.

2.2 Dope Preparation

PVDF/PAN/DMF HFMs of dope composition ~~of~~ (18/1/81 wt%) were spun by dry-wet phase inversion techniqueusing a single orifice spinneret, according to the method used by Mostafa et al.[29]. After spinning, the as-spun HFMs were soaked and rinsed with DW for 24 hours to ensure complete phase inversion as well as

removing excess solvent. Then, samples were soaked in three consecutive isopropanol solutions of different concentrations (2%, 4%, and 0.5%) for 40 minutes each, for surface activation. Isopropanol supports rapid removal of residual solventand additives, and minimizes possibilities of pore dimensional changes. Fibers were washed with DW before any characterization or coating took place.

2.3 Thin-film Nanocomposite Preparation

SpunPVDF/PANHFMs were thin-film dip-coated horizontally in a rectangular dish. Fibers were washed very well with DW before starting the coating process to guarantee a clean surface. HFMs of 30 cm length were fixed separately on a wooden frame to ensure the formation of an intact coating on the fibers. The coating procedure was described in details previously in Mostafa et al. work [29]. Two coating solutions were prepared for IP, aqueous Amine solution (using MPD, PIP and TEA) and organic phase (using Cyclohexane, TMC and Adipoyl chloride). Different concentrations of silica NPs were added separately to the Amine solution (0.05, 0.075 and 0.1 wt%) and sonicated for an additional 40 minutes to prevent agglomeration of NPs and to ensure homogeneous solution formation.Finally, fibers were stored in 1% $MgCl_2$ solution until further investigations.

2.4 Microwave Post-treatment

As spun, TFC and TFN HFM samples were subjected to MW irradiationusing a 900 Watts microwave oven (DAEWOO Electron KOR-1A 6A, Korea) attached to an on-off temperature controller. MW post-treatment procedures were carried out according to Abed et al.[36]operating conditions (2% NaCl solution at 55°C and 10 minutes) where fibers were washed with DW, soaked in 2% NaCl solution in a ceramic dish placed inside the microwave, and post-treated for 10 minutes at 55°C.Sample codes of as spun, TFC, TFN and their MW post-treated PVDF/PAN HFMs are presented in **Table 1**.

Table 1: Sample codes of PVDF/PAN HFMs at different conditions

Sample code	Membrane description
P	As-spun fiber
P/MW	MW post-treatment ofP sample
TFC	Thin film coated P sample
TFC/MW	MW post-treatment ofTFCsample
TFN 0.05	0.05% Silica NPs thin film nanocomposite P sample
TFN 0.05/MW	MW post-treatment ofTFN 0.05 sample
TFN 0.075	0.075% Silica NPs thin film nanocomposite P sample
TFN 0.075/MW	MW post-treatment ofTFN 0.075 sample
TFN 0.1	0.1% Silica NPs thin film nanocomposite P sample
TFN 0.1/MW	MW post-treatment of TFN 0.1 sample

2.5 Characterization

2.5.1. Membrane Morphology

Morphological characteristics of the fibers were studied using bench-top scanning electron microscope (SEM) model JEOL JCM-6000 Neoscope apparatus. SEM images were acquired at high voltage of 15 kV and standard probe current. Fibers were washed thoroughly and dried before testing, then cut with a sharp razor, set on sample holder using carbon double face tape followed by gold sputtering for 1 minute to enhance sample conductivity.

2.5.2. Surface Roughness

Fibers surface topography was measured using "TT-AFM workshop" atomic force microscope device (AFM) having 1.5 μm resolution, attached to a 400X optical microscope. Fibers were thoroughly washed, dried and 1 cm lengths were cut and set on a double face tapefixed on a magnetic coin. Testing conditions were set on vibrating mode with a scan area of 5μm×5μm. Roughness parameters as well as 3D topography images were acquired from the AFM images using "Gwidyyon" software. An average of five samples was calculated for each condition.

2.5.3. Mechanical Properties

Mechanical properties of fibers were measured using H5kS Tinius Olsen bench-top universal tensile testing machine, equipped with small sample holder and a 5N load cell. Testing conditions were set at 50 mm/min test speed and 100 mm gauge length. An average of five sample repetitionswas calculated for each condition.

2.5.4. Water Contact Angle (CA)

The OCA 15EC Contact angle model, made by the company of Data Physics Instrument GmbH, was used to measure HFMs contact angles while altering the morphology of water droplets on the samples. For each HFM condition, five fibers were assessed, and the average values were computed.

2.5.5. Membrane Porosity

Gravimetric method was used to measure HFMs porosity [5]. HFMs were dried in an oven at 60°C for one hour then weighed, followed by soaking in Kerosene oil for 24 hours, drained and wiped with filter paper to ensure

removal of excess oil and finally they were weighed. Membrane porosity was calculated according to the following equation (1)

$$\boldsymbol{\varepsilon} = \frac{\frac{\boldsymbol{w1-w2}}{\boldsymbol{\rho k}}}{\frac{\boldsymbol{w1-w2}}{\boldsymbol{\rho k}}+\frac{\boldsymbol{w2}}{\boldsymbol{\rho p}}} \times \mathbf{100} (1)$$

Where,
w_1: weight of wet membrane (g)
w_2: weight of dry membrane (g)
ρ_k: density of kerosene (g/cm^3)
ρ_p: density of polymer (g/cm^3)

2.5.6. Zeta Potential

Zeta potential measurements of HFMs were carried out using Surpass Electrokinetic analyzer for solid surface analysis (Anton Paar GmbH, Austria) equipped with two titration units, 0.05 mol/L HCl and 0.05 mol/L NaOH,to adjust testing electrolyte pH automatically and connected to PC software to automatically calculate and graph results.Adjustable gap cell was used to measuresurface zeta potential equipped with twosample holders of 20x10 mmdimensions, where the distance between them was adjusted to have a gap height of 100 μm. HFMs were cut and fixed on the sample holders using double face tape beside each other and in a perpendicular direction to the testing solution flow direction.Sample holders were then inserted in the adjustable gap cell. The cell was rinsed and filled with 0.001 mol/L KCl as the electrolyte solution. Testing was performed at pH range of 4.6-8 and pressure limit of 400 mbar. Streaming current was converted to zeta potential using Helmholtz-Smoluchowski[46] equation (2). Values of at least 4 runs for each condition were measured and their averages were calculated.

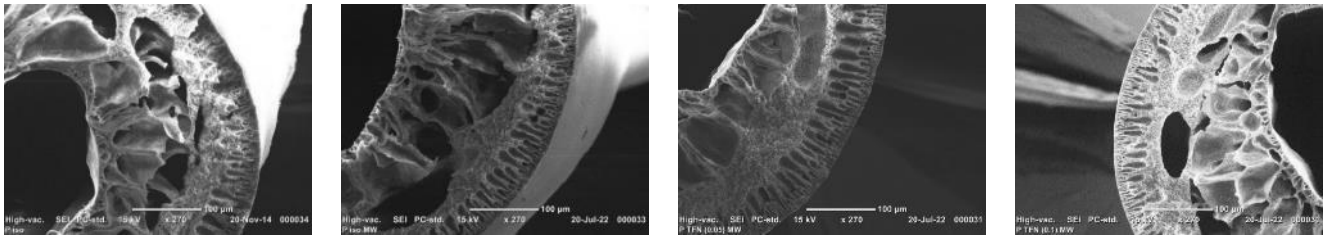
$$\boldsymbol{\zeta} = \frac{\mathbf{dU}}{\mathbf{dp}} \times \frac{\boldsymbol{\eta o}}{\boldsymbol{\varepsilon \times \varepsilon o}} \times \frac{\mathbf{L}}{\mathbf{A \times R}} \quad \mathbf{(2)}$$

Where,
dU/dp: streaming potential vs. pressure slope (mV/mbar),
ηo: viscoisty of electrolyte (mPa.s)
ε: electrolyte dielectric constant (V/m)
εo: permittivity of vacuum (F/m)
L: length of streaming channel (mm)
A: cross-section are of the streaming channel (mm^2)
R: resistance inside the measuring channel cell (Ω).

III. Results and Discussions

3.1. Scanning Electron Microscopy (SEM)

Cross-sectional and surface images of some PVDF/PAN HFMs and MW post-treated samples are shown in **Figure 1** and **Figure 2**. Cross-sectional images present a typical asymmetricstructure exhibiting inner and outer finger-like structures, due to penetration of bore and coagulation non-solvents causing phase inversion process during spinning, with a dense spongy layer in between and a dense outer layer, agreeing with Preaneeth et al.[47] findings.SEM cross-sectional images confirm intact morphological characteristics not affected by neither thin film coating or MW post-treatment. **Figure 2** shows the surface morphology of HFMs, where all images demonstrate a fine porous surface. Surface pores are noticeably tighter upon coating, as shown in TFC sample, while their smoothness was slightly affected upon adding Silica NPs to the coating to form TFN. The formation of a highly rough surface upon increasing the Silica NPs content, reaching a maximum at 0.1 Silica NPs loading, is apparent, which could be attributed to Silica NPs agglomoration on the membrane surface at higher ratios.



P **P/ MW** **TFN 0.05/ MW** **TFN 0.1/ MW**

Figure 1: Cross-sectional SEM images of P, P/MW, TFN 0.05/MW and TFN 0.1/MW samples

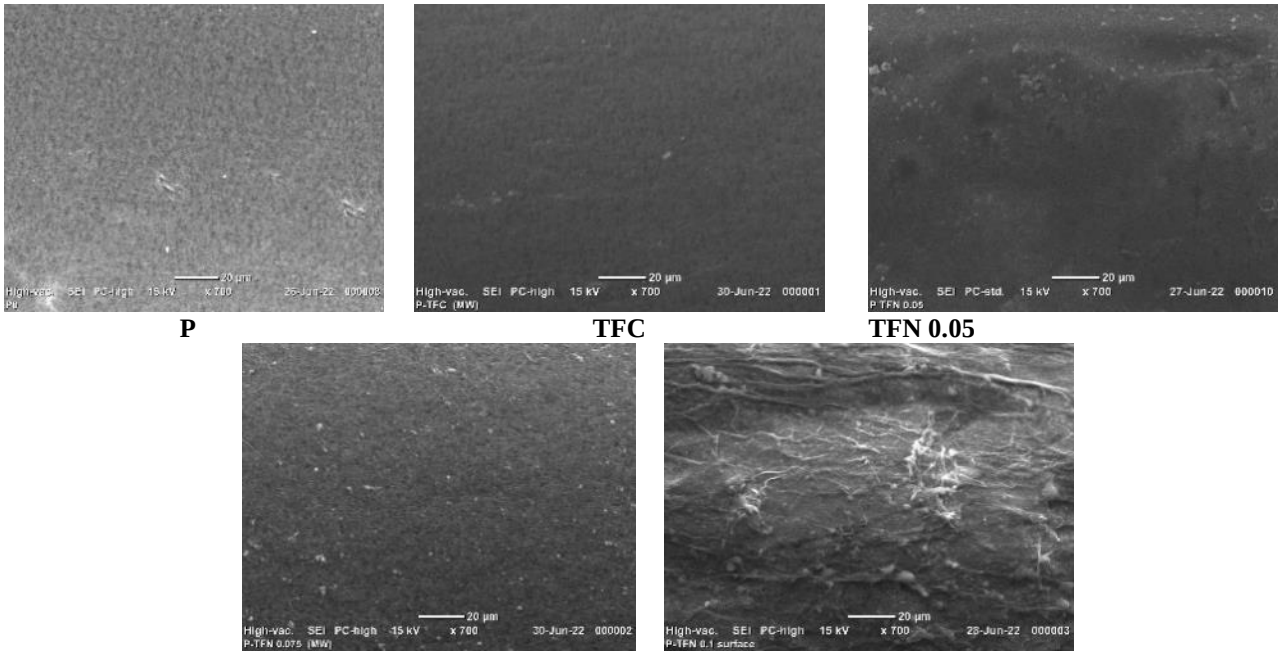


Figure 2: Surface SEM images of P, TFC and TFN PVDF/PAN HFMs

3.2. Mechanical Properties

Table 2 shows break strength, break strain and Young's modulus of as spun, TFC, TFN PVDF/PAN HFMs and their MW post-treated samples. All break strength values decreased slightly after silica NPs incorporation to form TFN membranes, whilebreak strength increased significantly after TFC without silica NPs incorporation which could be due to NPs acting as stress concentrations in the TFN surface leading to strength decrease. A similar decreasing trend was depicted for break strain, where it decreased after coating with and without silica NPs, which is expected as composites usually sacrifice the membrane's strain as a result of combined strain of membrane and the coating layer[29][48]. On the other hand, coating with and without silica NPs enhanced Young's Modulus, while MW irradiation decreased the break strength and modulus slightly causing moderate alterations on break strain.

Table 2: Mechanical properties of as spun, TFC, TFN PVDF/PAN HFMs and their MW post-treated samples

Sample code	Break strength (MPa)		Break strain(%)		Young's modulus(MPa)	
	Control	MW post-treated	Control	MW post-treated	Control	MW post-treated
P	2.84	2.58	42.2	42.3	71.3	63.5
TFC	3.29	2.63	33	34.6	99.1	77.2
TFN 0.05	2.85	2.82	36	31.1	79.5	81.8
TFN 0.075	2.5	2.33	39.3	43.1	70.2	65.3
TFN 0.1	2.79	2.69	37.3	30.1	96.2	81.6

3.3. Surface Roughness

Figure 3shows topographical 3D images of some PVDF/PAN HFMs and MW post-treated samples where they exhibit characteristic peaks and valleys of the membrane surface, becoming rougher or smoother according to the condition to which they were subjected.**Figure 4**shows average surface roughness (Ra) values of HFMs in this study, where all roughness Ra values increased upon coating, whether thin film coating or after incorporating silica NPs in the thin film coating, with the highest value of 52.3 nm for TFN 0.05 silica NPs loading.These findings are in accordance with Mostafa et al. [29], Guzman et al. [32] and Abadikhah et al. [31] where surface roughness values increased for PVDF-TFN HFMs, PAN-TFN FS membranes and PES-TFN FS membranes, respectively, after coating. This increase in surface roughness Ra was attributed to the nature and shape of the coating layer, having a leaf like structure. It is worth mentioning that all average surface rouhghness values decreased upon MW irradiation which may be attributed to surface smoothening and conditioning due to dipoles created by microwaves causing significant altering surface peaks and valleys,

agreeing with Mostafa et al.[29] findings.MW irradiation showed maximum smoothening effect for TFN 0.075 sample, where roughness decreased 32.8 % (from 50 nm to 33.6 nm) after MW post-treatment.

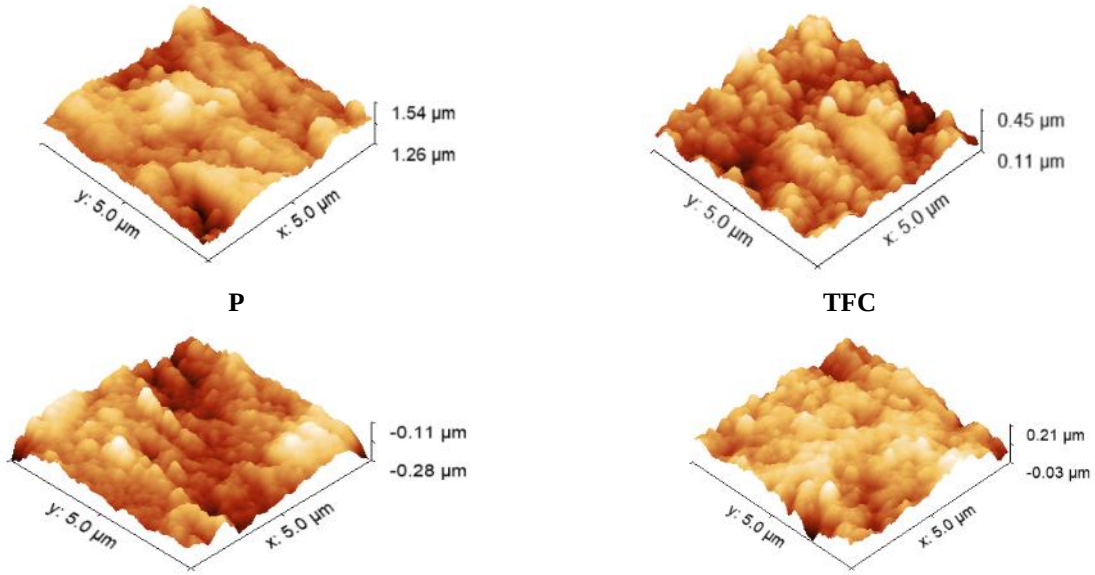


Figure 3: Surface roughness Ra 3D images of P, TFC, TFN 0.075 and TFN 0.075/MW PVDF/PAN HFMs samples

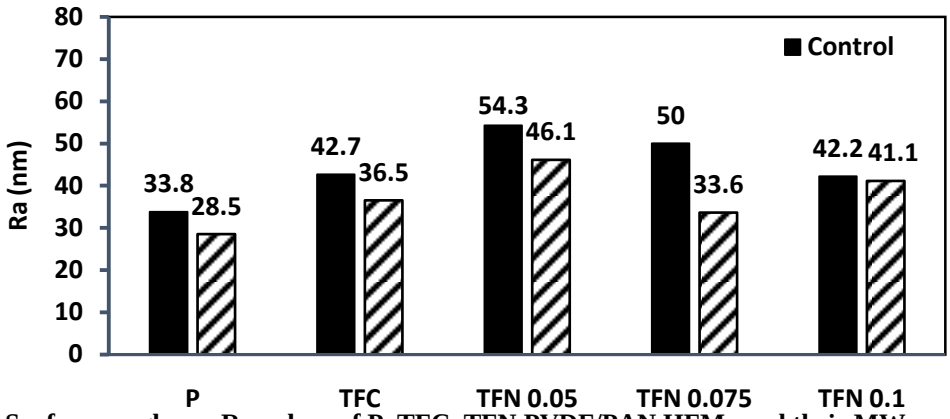


Figure 4: Surface roughness Ra values of P, TFC, TFN PVDF/PAN HFMs and their MW post-treated samples

3.4. Water Contact Angle

Table 3 shows contact angle (CA) values of as spun, TFC, TFN PVDF/PAN HFMs and their MW post-treated samples. All CA values decreased after coating whether with TFC or after incorporating silica NPs indicating increased membrane hydrophilicity. Results agree with most published research on silica NPs incorporation to fabricate thin film nanocomposite membranes[27][29][31][49].TFN 0.075 sample showed a maximum decrease of 31.4%, while, TFN 0.05 sample showed minimum decrease of 9.55%, which agrees with its increased roughness value. After MW irradiation, CA of all samples decreased except for TFN 0.075 and TFN 0.1 samples which may be attributed to higher silica NPs loading causing a reverse effect on surface hydrophilicity.

Table 3: Water contact anglesand membrane porosity values of as spun, TFC, TFN PVDF/PAN HFMsand their MW post-treated samples

Sample	Contact Angle (°)		Porosity (%)	
	Control	MW post-treated	Control	MW post-treated
P	89	68.5	80.26	84.56
TFC	72	68.6	78.27	80.52
TFN 0.05	80.5	72.3	78.42	82.35
TFN 0.075	61.9	75.4	75.71	79.68

TFN 0.1	75.4	78.5	79.78	80.86

3.5. Membrane Porosity

As shown in **Table 3**, it is apparent that porosity of HFMs decreased after coating, where TFN 0.1 sample, having 0.1% Silica NPs,showed lowest porosity. It is worth mentioning that porosity of all HFMs increased upon subjecting them to MW irradiation. As expected, interfacial polymerization manifested moderate decrease of porosity due to intrinsic self-healing property of coating process. On the other hand, MW post-treated samples manifested opposite trend leading to increasing porosity by 5% for P/MW and TFN 0.075/MW samples which may be due to intrinsic heating of MW irradiation in saline solution causing water dipoles and salt ions leading to magnified vibrations inside membrane pores aiding in pores widening [36].

3.6. Zeta Potential

Zeta potential is an important characteristic of different types of membranes. It serves both characterization and screening issues for intended application. It is of prime importance to address the possible interventions that might influence membrane zeta potential and the required application direction. With identification of the zeta potential of the medium to be treated by specific membrane, the membrane fabrication scheme may be selected for improving separation and minimizing fouling[45]. In this work, incorporation of silica NPs has been selected as the principal intervention during interfacial polymerization of PVDF/PAN HFMs. Also, MW irradiation of thin film PVDF/PAN HFMs was also tried to explore the combined effect of silica NPs loading and MW. Results of these investigations are shown in **Figure 5** and **Figure 6**. Results of as-spun P sample agrees with Regoršek findings[50] for PVDF/PAN HFMs in 0.001 mM KCl electrolyte solution. Zeta potential curve shifted towards less negative values upon coating where TFC sample manifested maximum decrease of 50% at pH=8. The effect of silica NPs loading shifted zeta potential curve to an intermediate state between coated and uncoated potentials, which is in accordance with Bauman et al. [51] findings. On the other hand, some endeavors reported fabrication of membranes with moderate positive zeta potential using chemical or physical treatments [52].The immediate outcome of our findings is that interfacial polymerization with inclusion of silica NPs represents an effective intervention to shift zeta potential towards less negative situation. It opens windows for selection of the appropriate membrane for low pressure separation schemes and also biomedical applications. For instance, agricultural drainage water contain numerous negatively charged organic pollutants which manifest negative potential, so trials could be tailored to define the required membrane possessing similar negative potential to minimize absorption of foulants.MW also proved effective for reducing negative zeta potential to different degrees enabling wider choice for membrane applicants as shown in**Figure 6**. This trend merits additional investigations to include different MW heating medium other than NaCl and also for different processing times and temperatures.

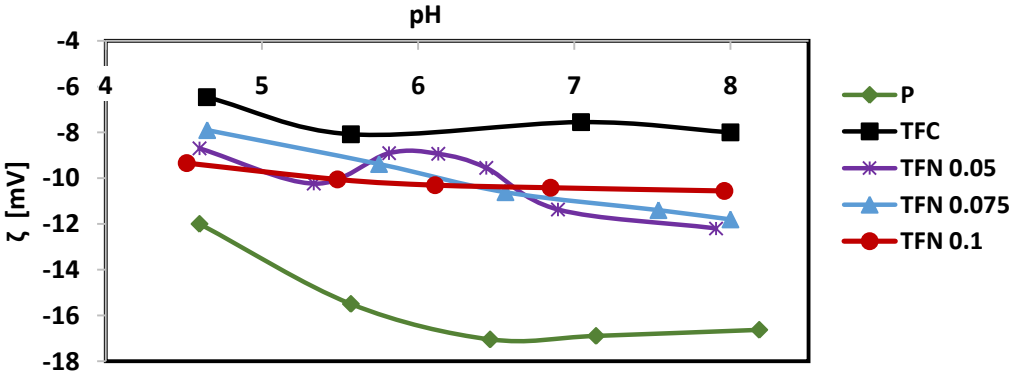


Figure 5: Zeta potential vs. pH of P, TFC and TFN PVDF/PAN HFMs samples

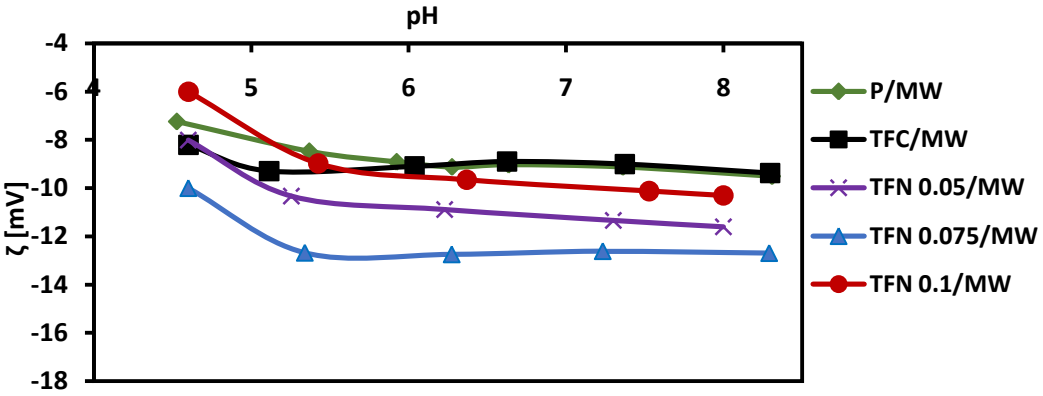


Figure 6: Zeta potential vs. pH of MW post-treated P, TFC and TFN PVDF/PAN HFMs samples

IV. Conclusions

In this study, the effects of incorporating Silica NPs on morphological and mechanical characteristics of thin-film PVDF/PAN HFMs have been investigated. Also, the effects of MW irradiation on the resulting membranes properties have been investigated. The Silica NPs were incorporated during the interfacial polymerization stage with Silica NPs concentration ranging from (0.05 to 0.1%). The effects of different NPs concentration on membranes characteristics were evaluated including morphological characteristics (SEM), surface roughness Ra, break strength, break strain and Young's modulus. The effects on contact angle, porosity and zeta potential were evaluated as well. Results showed that the process has the capacity to regulate HFMs mechanical properties. Also, Results showed good capacity to regulate porosity though range from 75.7% to 84.5% and to regulate contact angle though range from 62° to 89°. Also, MW post-treatment showed capacity to decrease negative zeta potential for all samples incorporating silica NPs as well as the control sample. The result of this study enables a flexible process for preparation of HFMs that have tailored properties, which would enable it to properly cope with a wider range of intended applications while minimizing potential fouling effects.

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References

[1] Peng, N.; Widjojo, N.; Sukitpaneenit, P.; Teoh, M. M.; Lipscomb, G. G.; Chung, T. S.; Lai, J. Y. Evolution of Polymeric Hollow Fibers as Sustainable Technologies: Past, Present, and Future. *Prog. Polym. Sci.*, **2012**, *37* (10), 1401–1424. https://doi.org/10.1016/j.progpolymsci.2012.01.001.

[2] Feng, C. Y.; Khulbe, K. C.; Matsuura, T.; Ismail, A. F. Recent Progresses in Polymeric Hollow Fiber Membrane Preparation, Characterization and Applications. *Sep. Purif. Technol.*, **2013**, *111*, 43–71. https://doi.org/10.1016/j.seppur.2013.03.017.

[3] Moch, I. Membranes, Hollow-Fiber. *Kirk-Othmer Encycl. Chem. Technol.*, **2005**, No. 4, 1–31. https://doi.org/10.1002/0471238961.0815121213150308.a01.pub2.

[4] Liang, C. Z.; Askari, M.; Choong, L. T. (Simon); Chung, T. S. Ultra-Strong Polymeric Hollow Fiber Membranes for Saline Dewatering and Desalination. *Nat. Commun.*, **2021**, *12* (1). https://doi.org/10.1038/s41467-021-22684-1.

[5] Ahmad, H.; Zahid, M.; Rehan, Z. A.; Rashid, A.; Akram, S.; Aljohani, M. M. H.; Mustafa, S. K.; Khalid, T.; Abdelsalam, N. R.; Ghareeb, R. Y.; et al. Preparation of Polyvinylidene Fluoride Nano-Filtration Membranes Modified with Functionalized Graphene Oxide for Textile Dye Removal. *Membranes (Basel).*, **2022**, *12* (2), 224. https://doi.org/10.3390/membranes12020224.

[6] Chang, P. T.; Paranthaman, S.; Rosli, A.; Low, S. C. Manipulating Membrane Hydrophobicity By Integrating Polythylene-Coated Fume Silica in PVDF Membrane. *ASEAN Eng. J.*, **2022**, *12* (1), 157–164. https://doi.org/10.11113/aej.v12.17336.

[7] da Silva Barbosa Ferreira, R.; Dias, R. A.; Araújo, E. M.; Oliveira, S. S. L.; da Nóbrega Medeiros, V.; de Lucena Lira, H. Hollow Fiber Membranes of Polysulfone/Attapulgite for Oil Removal in Wastewater. *Polym. Bull.*, **2022**, No. 0123456789. https://doi.org/10.1007/s00289-022-04142-0.

[8] Zhang, Q.; Lu, X.; Liu, J.; Zhao, L. Preparation and Preliminary Dialysis Performance Research of Polyvinylidene Fluoride Hollow Fiber Membranes. *Membranes (Basel).*, **2015**, *5* (1), 120–135. https://doi.org/10.3390/membranes5010120.

[9] Verma, S. K.; Modi, A.; Singh, A. K.; Teotia, R.; Bellare, J. High Flux Nanocomposite Hollow Fiber Membrane for Hemodialysis. *Adv. Mater. TechConnect Briefs*, **2017**, 291–294.

[10] Sun, D.; Yue, D.; Li, B.; Zheng, Z.; Meng, X. Preparation and Performance of the Novel PVDF Ultrafiltration Membranes Blending with PVA Modified SiO2 Hydrophilic Nanoparticles. *Polym. Eng. Sci.*, **2019**, *59*, E412–E421. https://doi.org/10.1002/pen.25002.

[11] Abed, M. R. M. Poly (Vinylidene Fluoride) (PVDF) Based Hydrophilic Hollow Fibre Membranes - Prospects for Wastewater

Treatment, Faculty of Engineering, Imperial College London, 2012.
[12] Gugliuzza, A. Blending Modification of Membranes. *Encyclopedia of Membranes*; 2020; Vol. 2, pp 2008–2010. https://doi.org/10.1007/978-3-642-40872-4.
[13] Ghadiri, M. A.; Beyranvand, A.; Morsali, S. Investigating the Effects of Nonsolvent Additive and Spinning Conditions on Morphology and Permeation of PAN Hollow Fiber Membranes. *Adv. Polym. Technol.*, **2022**, *2022*, 16. https://doi.org/10.1155/2022/8988568.
[14] Zargar, M. Novel Thin Film Nanocomposite Membranes with Improved Properties for Enhanced Desalination Performance, The University of Adelaide, Australia, 2016.
[15] Yang, Z.; Yin, J.; Deng, B. Enhancing Water Flux of Thin-Film Nanocomposite (TFN) Membrane by Incorporation of Bimodal Silica Nanoparticles. *AIMS Environ. Sci.*, **2016**, *3* (2), 185–198. https://doi.org/10.3934/environsci.2016.2.185.
[16] Khulbe, K. C.; Matsuura, T. Thin Film Composite and/or Thin Film Nanocomposite Hollow Fiber Membrane for Water Treatment, Pervaporation, and Gas/Vapor Separation. *Polymers (Basel).*, **2018**, *10*, 1–22. https://doi.org/10.3390/polym10101051.
[17] Li, J.; Ren, L. F.; Zhou, H. S.; Yang, J.; Shao, J.; He, Y. Fabrication of Superhydrophobic PDTS-ZnO-PVDF Membrane and Its Anti-Wetting Analysis in Direct Contact Membrane Distillation (DCMD) Applications. *J. Memb. Sci.*, **2021**, *620*. https://doi.org/10.1016/j.memsci.2020.118924.
[18] Ardeshiri, F.; Salehi, S.; Peyravi, M.; Jahanshahi, M.; Amiri, A.; Rad, A. S. PVDF Membrane Assisted by Modified Hydrophobic ZnO Nanoparticle for Membrane Distillation. *Asia-Pacific J. Chem. Eng.*, **2018**, *13* (3). https://doi.org/10.1002/apj.2196.
[19] Saldías, C.; Terraza, C. A.; Leiva, A.; Koschikowski, J.; Winter, D.; Tundidor-Camba, A.; Martin-Trasanco, R. PVDF Composite Membranes with Hydrophobically-Capped CuONPs for Direct-Contact Membrane Distillation. *Nanomaterials*, **2021**, *11* (6), 1497. https://doi.org/10.3390/nano11061497.
[20] Liu, Y.; Guo, R.; Shen, G.; Li, Y.; Li, Y.; Gou, J.; Cheng, X. Construction of CuO@CuS/PVDF Composite Membrane and Its Superiority for Degradation of Antibiotics by Activation of Persulfate. *Chem. Eng. J.*, **2021**, *405*, 126990. https://doi.org/https://doi.org/10.1016/j.cej.2020.126990.
[21] Farahani, M. H. D. A.; Rabiee, H.; Vatanpour, V. Comparing the Effect of Incorporation of Various Nanoparticulate on the Performance and Antifouling Properties of Polyethersulfone Nanocomposite Membranes. *J. Water Process Eng.*, **2019**, *27*, 47–57. https://doi.org/10.1016/j.jwpe.2018.11.012.
[22] Punetha, V. D.; Rana, S.; Yoo, H. J.; Chaurasia, A.; McLeskey, J. T.; Ramasamy, M. S.; Sahoo, N. G.; Cho, J. W. Functionalization of Carbon Nanomaterials for Advanced Polymer Nanocomposites: A Comparison Study between CNT and Graphene. *Prog. Polym. Sci.*, **2017**, *67*, 1–47. https://doi.org/10.1016/j.progpolymsci.2016.12.010.
[23] Zinadini, S.; Vatanpour, V.; Zinatizadeh, A. A.; Rahimi, M.; Rahimi, Z.; Kian, M. Preparation and Characterization of Antifouling Graphene Oxide/Polyethersulfone Ultrafiltration Membrane: Application in MBR for Dairy Wastewater Treatment. *J. Water Process Eng.*, **2015**, *7*, 280–294. https://doi.org/10.1016/j.jwpe.2015.07.005.
[24] Ionita, M.; Pandele, A. M.; Crica, L.; Pilan, L. Improving the Thermal and Mechanical Properties of Polysulfone by Incorporation of Graphene Oxide. *Compos. Part B Eng.*, **2014**, *59*, 133–139. https://doi.org/10.1016/j.compositesb.2013.11.018.
[25] Chew, Y. T.; Yong, W. F. Recent Advances of Thin Film Nanocomposite Membranes: Effects of Shape/Structure of Nanomaterials and Interfacial Polymerization Methods. *Chem. Eng. Res. Des.*, **2021**, *172*, 135–158. https://doi.org/10.1016/j.cherd.2021.06.003.
[26] Zhang, H.; Li, B.; Sun, D.; Miao, X.; Gu, Y. SiO2-PDMS-PVDF Hollow Fiber Membrane with High Flux for Vacuum Membrane Distillation. *Desalination*, **2018**, *429*, 33–43. https://doi.org/10.1016/j.desal.2017.12.004.
[27] Abolfazli, Z.; Rahimpour, A. Fabrication and Modification of Thin-Film Composite Hollow Fiber NF Membranes. *J. Membr. Sci. Res.*, **2017**, *3* (1), 42–49. https://doi.org/10.22079/jmsr.2017.23347.
[28] Yu, L. Y.; Xu, Z. L.; Shen, H. M.; Yang, H. Preparation and Characterization of PVDF-SiO2 Composite Hollow Fiber UF Membrane by Sol-Gel Method. *J. Memb. Sci.*, **2009**, *337* (1–2), 257–265. https://doi.org/10.1016/j.memsci.2009.03.054.
[29] Mostafa, Y. O.; Abed, K. A.; El Mahallawy, N. A. H.; Sorour, M.; El Bayoumi, M. The Effect of Microwave Irradiation on Morphological and Mechanical Characteristics of Nano Silica Loaded PVDF Hollow Fiber Membranes. *Egypt. J. Chem.*, **2022**. https://doi.org/10.21608/ejchem.2022.145444.6338.
[30] Safarnia, M.; Pakizeh, M.; Namvar-Mahboub, M. Assessment of Structural and Separation Properties of a PVDF/PD Composite Membrane Incorporated with TiO2 Nanotubes and SiO2Particles. *Ind. Eng. Chem. Res.*, **2021**, *60* (1), 659–669. https://doi.org/10.1021/acs.iecr.0c06045.
[31] Abadikhah, H.; Kalali, E. N.; Behzadi, S.; Khan, S. A.; Xu, X.; Agathopoulos, S. Amino Functionalized Silica Nanoparticles Incorporated Thin Film Nanocomposite Membrane with Suppressed Aggregation and High Desalination Performance. *Polymer (Guildf).*, **2018**, *154*, 200–209. https://doi.org/10.1016/j.polymer.2018.09.007.
[32] De Guzman, M. R.; Ang, M. B. M. Y.; Hsu, K.-T.; Chu, M.-Y.; Millare, J. C.; Huang, S.-H.; Tsai, H.-A.; Lee, K.-R. Enhancing Performance of Thin-Film Nanocomposite Membranes by Embedding in Situ Silica Nanoparticles. *Membranes (Basel).*, **2022**, *12* (6), 607. https://doi.org/10.3390/membranes12060607.
[33] Sze Yean, L. Effect of Bore Fluid and Post Treatment on Polyethersulfone Ultrafiltration Hollow Fiber Membrane, Universiti Teknologi Malaysia, 2008.
[34] Abed, K. A.; Mahallawy, N. A. El; Sorour, M. H.; El-bayoumi, M. A.; Mostafa, Y. O. Experimental Investigation on Polyethersulfone (PES) Hollow Fiber Membranes Post-Treatment Using Microwave Heating. In *1st International Joint Symposia on "Product Development and Innovation" and "Industrial Systems and Operations Management"*; 2016.
[35] Fazullin, D. D.; Mavrin, G. V.; Shaikhiev, I. G. Effect of MW Radiation on Thin-Film Polymer Membranes. *Surf. Eng. Appl. Electrochem.*, **2020**, *56* (1), 105–111. https://doi.org/10.3103/S1068375520010044.
[36] Abed, K. A.; Mahallawy, N. A. El; Sorour, M. H.; El-bayoumi, M. A.; Mostafa, Y. O. Microwave Post-Treatment of PES Hollow Fiber Membranes Immersed in NaCl Solution. *J. Sci. Eng. Res.*, **2017**, *4* (9), 520–527.
[37] Abed, K. A.; Mahallawy, N. A. El; Sorour, M. H.; El-bayoumi, M. A.; Mostafa, Y. O. Effect of Microwave Post-Treatment on PES Hollow Fiber Membranes. In *Arab International Industrial Conference*; 2018.
[38] Ahmed, I.; Idris, A.; Noordin, M. Y.; Rajput, R. High Performance Ultrafiltration Membranes Prepared by the Application of Modified Microwave Irradiation Technique. *Ind. Eng. Chem. Res.*, **2011**, *50* (4), 2272–2283. https://doi.org/10.1021/ie1017223.
[39] Idris, A.; Ahmed, I.; Misran, M. Novel High Performance Hollow Fiber Ultrafiltration Membranes Spun from LiBr Doped Solutions. *Desalination*, **2009**, *249* (2), 541–548. https://doi.org/10.1016/j.desal.2008.07.031.
[40] Sze Yean, L.; Idris, A. Effect of Bore Fluid and Post Treatment on Polyethersulfone Ultrafiltration Hollow Fiber Membranes, Universiti Teknologi Malaysia, 2008.
[41] D. Fazullin, D.; A. Kharitonova, E.; V. Mavrin, G. Modification of Thin-Film Polymer Membranes by Microwave Radiation in Ammonia Medium. *Int. J. Eng. Technol.*, **2018**, *7* (4.36), 1050–1053. https://doi.org/10.14419/ijet.v7i4.36.24951.
[42] Deshmukh, S. S.; Childress, A. E. Zeta Potential of Commercial RO Membranes: Influence of Source Water Type and Chemistry.

Desalination, **2001**, *140* (1), 87–95. https://doi.org/10.1016/S0011-9164(01)00357-5.
[43] Breite, D.; Went, M.; Prager, A.; Schulze, A. The Critical Zeta Potential of Polymer Membranes: How Electrolytes Impact Membrane Fouling. *RSC Adv.*, **2016**, *6* (100), 98180–98189. https://doi.org/10.1039/c6ra19239d.
[44] Fievet, P.; Szymczyk, A.; Labbez, C.; Aoubiza, B.; Simon, C.; Foissy, A.; Pagetti, J. Determining the Zeta Potential of Porous Membranes Using Electrolyte Conductivity inside Pores. *J. Colloid Interface Sci.*, **2001**, *235* (2), 383–390. https://doi.org/10.1006/jcis.2000.7331.
[45] Jun, B. M.; Cho, J.; Jang, A.; Chon, K.; Westerhoff, P.; Yoon, Y.; Rho, H. Charge Characteristics (Surface Charge vs. Zeta Potential) of Membrane Surfaces to Assess the Salt Rejection Behavior of Nanofiltration Membranes. *Sep. Purif. Technol.*, **2020**, *247* (April). https://doi.org/10.1016/j.seppur.2020.117026.
[46] Belfort, G.; Davis, R. H.; Zydney, A. L. The Behavior of Suspensions and Macromolecular Solutions in Crossflow Microfiltration. *J. Memb. Sci.*, **1994**, *96* (1), 1–58. https://doi.org/https://doi.org/10.1016/0376-7388(94)00119-7.
[47] Praneeth, K.; Tardio, J.; Bhargava, S. K.; Sridhar, S. Synthesis and Characterization of PVDF/PAN Hollow Fiber Blend Membranes for Purification of Surface Water Treatment. *Chem. Bioprocess Eng. Trends Dev.*, **2015**, 257–268. https://doi.org/10.1201/b18402.
[48] Wongchitphimon, S.; Wang, R.; Jiraratananon, R. Surface Modification of Polyvinylidene Fluoride-Co-Hexafluoropropylene (PVDF–HFP) Hollow Fiber Membrane for Membrane Gas Absorption. *J. Memb. Sci.*, **2011**, *381* (1–2), 183–191. https://doi.org/http://dx.doi.org/10.1016/j.memsci.2011.07.022.
[49] Urper-Bayram, G. M.; Bossa, N.; Warsinger, D. M.; Koyuncu, I.; Wiesner, M. Comparative Impact of SiO2 and TiO2 Nanofillers on the Performance of Thin-Film Nanocomposite Membranes. *J. Appl. Polym. Sci.*, **2020**, *137* (44). https://doi.org/10.1002/app.49382.
[50] Regoršek, V. P. Zeta Potential Characterization of Hollow Fiber Membranes, Maribor, 2018.
[51] Bauman, M.; Košak, A.; Lobnik, A.; Petrinić, I.; Luxbacher, T. Nanofiltration Membranes Modified with Alkoxysilanes: Surface Characterization Using Zeta-Potential. *Colloids Surfaces A Physicochem. Eng. Asp.*, **2013**, *422*, 110–117. https://doi.org/10.1016/j.colsurfa.2013.01.005.
[52] Breite, D.; Went, M.; Prager, A.; Schulze, A. Tailoring Membrane Surface Charges: A Novel Study on Electrostatic Interactions during Membrane Fouling. *Polymers (Basel).*, **2015**, *7* (10), 2017–2030. https://doi.org/10.3390/polym7101497.