4.1. Membrane performances

4.1.1. Polyether sulfone/f-MWCNT mixed matrix membranes

4.1.1.1. Permeation studies of f-MWCNT/PES membranes

The effect of incorporation of functionalized multi walled carbon nanotubes on the performance of mixed matrix membrane is investigated by a comparative study of pure water flux of all the membranes. The measured value of pure water flux at two different pressures is summarized in Table 4.1. The pure water flux of mixed matrix membranes increased with increasing concentration of nanotubes up to 1 wt% as can be seen in the data. The pure water flux increased from 113.36 L/m^2h for pristine PES membrane to 431 L/m^2h for Ox-MWCNT membrane after 70 minutes of filtration which is because of the enhanced surface porosity and increased hydrophilicity of the membranes. In order to analyze the effect of pressure on the pure water flux of mixed matrix membranes we have performed the water permeation test at different pressures (Figure 4.1, 4.2, 4.3). The pure water flux ascended with the increase in trans-membrane pressure. This result is consistent with result reported by other group [244- 247].

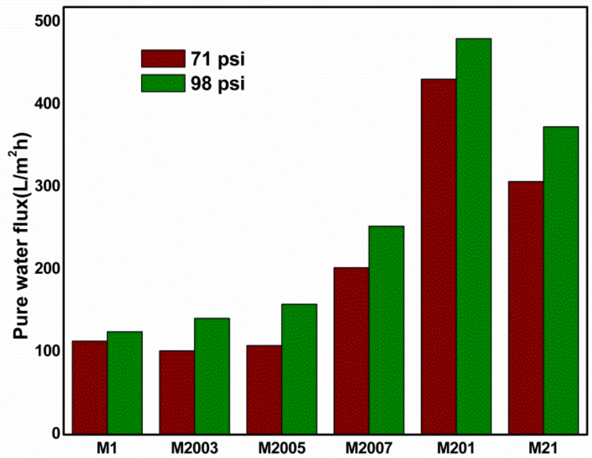

Figure 4.1 Pure water flux of pristine PES and mixed matrix membranes containing different weight percentages of Ox-MWCNT at different pressure

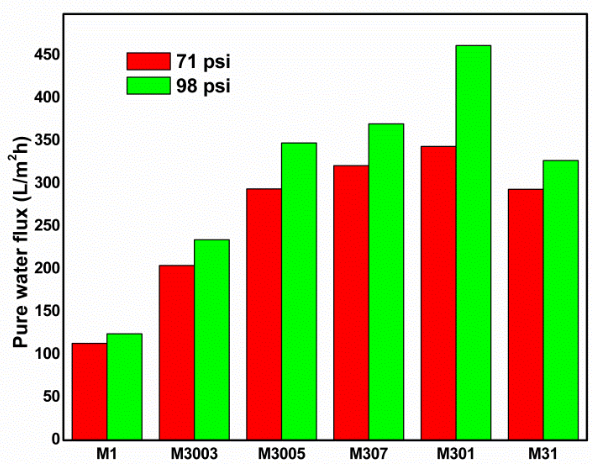

Figure 4.2 Pure water flux of pristine PES and mixed matrix membranes containing different weight percentages of Am-MWCNT at different pressure

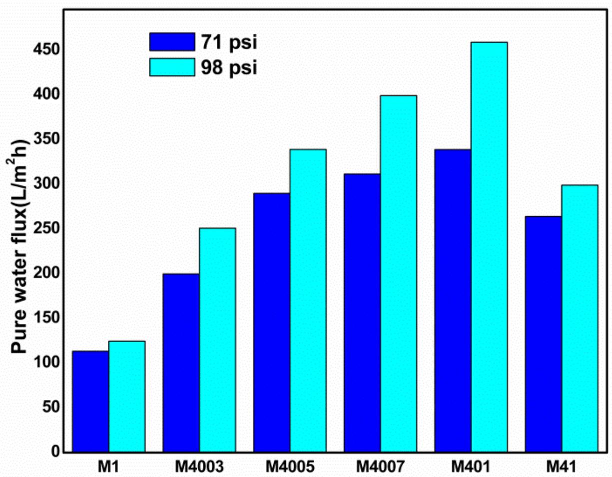

Figure 4.3 Pure water flux of pristine PES and mixed matrix membranes containing different weight percentages of Az-MWCNT at different pressure

Table 4.1 Pure water flux values of the membranes at different pressure

Membrane	Pure water flux(L/m^2h)	
	71 psi	98 psi
M1	113.36	124.62
M2003	101.60	140.93
M2005	108.00	158.14
M2007	202.31	252.59
M201	431.00	480.00
M21	306.80	373.22

M3003	204.52	234.59
M3005	294.15	347.92
M3007	321.39	370.21
M301	343.81	461.79
M31	293.71	327.36
M4003	199.85	251.10
M4005	290.00	339.10
M4007	311.70	399.30
M401	339.00	459.00
M41	264.10	299.20

The pure water flux has also been measured on acidic and neutral conditions. The data is plotted in the Figure 4.4, 4.5. In all the cases i.e. membranes having the oxidized, amide and azide functionalized multiwalled carbon nanotubes showed the same nature of plot. On decreasing the pH value from 7 to 3, the pure water flux value declined for all the mixed matrix membranes. In our work we observed enhancement in flux on variation from acidic to neutral condition, the result is in agreement with the result reported by Agboola et al using NF membrane [248]. According to Hilal et al swelling behaviour of membrane in different environment might be reason for flux enhancement [249]. The increased membrane flux at higher pH is due to charged functional group at membrane matrix which forces adjacent polymers apart at high pH value. While at lower pH membrane polymers come closer since the charge of the membrane matrix is shielded which resulted in lower flux.

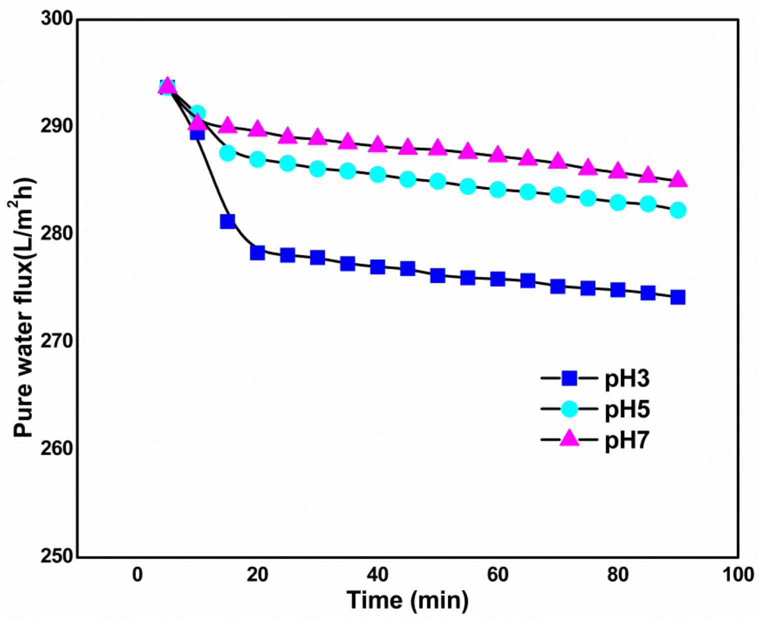

Figure 4.4 Pure water flux versus time of 1%Am-MWCNT/PES (M31) membrane for different pH

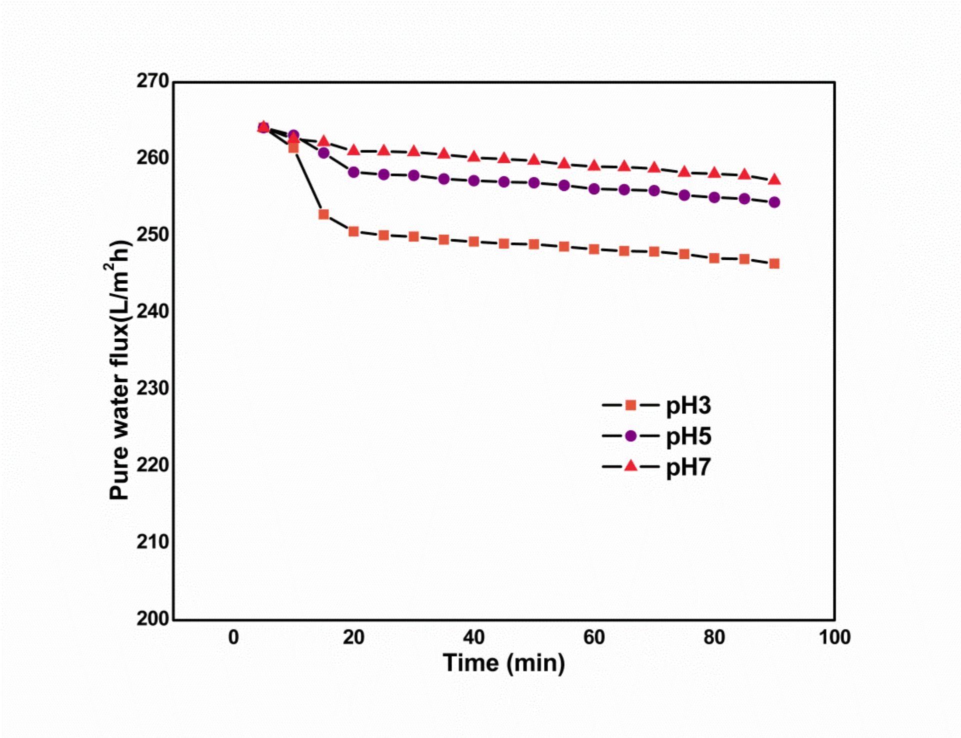

Figure 4.5 Pure water flux versus time of 1%Az-MWCNT/PES (M41) membrane for different pH

4.1.1.2. Heavy metal removal studies

Feed solutions were prepared by dissolving the appropriate amount of compound to the DI water. We have prepared feed solution of 1 ppm concentration. Stock solution of chromium and lead are prepared by dissolving 2.84 g of $K_2Cr_2O_7$ and 1.59 g of $Pb(NO_3)_2$ in 1000 ml of DI water. Cadmium solution was prepared by dissolving 1 g of cadmium salt in minimum volume of HCl and then making it up to 1000 ml with DI water. Feed solution of copper and arsenic were prepared of 1000 mg/L concentration with the respective metal salts. The pH of the feed solution is varied acidic (pH 2.5) to neutral environment (pH 7) for the rejection experiment. The effect of applied trans membrane pressure is also studied for Cr(VI) metal and at optimized conditions for rest of the metals. The rejection was calculated as given below:

$$\boldsymbol{R}(\%) = \frac{C_f - C_p}{C_f} \times \mathbf{100} \qquad \textbf{(1)}$$

Here C_f and C_p are concentration of metal ions in feed and permeate respectively and were measured by Atomic absorption spectroscopy (AAS) and also by conductivity bridge analyzer.

4.1.1.2.1. Effect of pressure and pH:

The rejection percentage of Cr(VI), Pb(II) and Cu(II) is 74.0, 69.2, 92.5 respectively at 71 psi (2.5 pH) for azide membrane having 1wt% MWCNT concentration which was decreased to 52.3, 31.2 and 80.5 at higher pressure. At similar conditions the rejection percentage of Cr(VI), Pb(II) and Cu(II) were 63.1, 55.3, 86.7 and 46.1, 42.7, 52.3 for 0.1% & 0.05% concentration, which was reduced to 42.3, 35.7, 70.1 and 36.2, 30.4, 34.3 respectively, on increasing the pressure applied to the membranes. All the values are summarized in Table 4.2. As shown in Table 4.1, the pure water flux for mixed matrix membrane having MWCNT percentage 0.05 is higher than 1, however the rejection capacity of membrane having higher nanotube concentration was more (Figure 4.6). The higher flux accounts for the lesser hindrance at the surface of the membranes due to lesser percentage of nanotubes as well as bigger pores compared to membranes containing higher weight percentage nanotubes and thus results lesser rejection comparatively. Our mixed matrix membranes were giving very high pure water flux (around 450 LMH) which clearly showed that the water preferentially goes through the nanotubes present in the pore and because of the hydrophobic walls of nanotubes the flow was much smoother which was not in case of pristine PES membrane. As shown in the Figure 4.7 at acidic pH the rejection is higher this may be due to the proton also competes with heavy metal at acidic pH which is not in case of neutral pH. From the experiments we have found the optimum condition for rejection studies is at pH 2.5 and 71 psi pressure.

Table 4.2 Rejection studies of metal ions at pH 2.5 for azide functionalized MWCNT/PES membranes at pressure 71 psi and 98 psi

Membrane	**Removal capacity (%)**					
	Cr(VI)		**Pb(II)**		**Cu(II)**	
	71 psi	**98 psi**	**71 psi**	**98 psi**	**71 psi**	**98 psi**
M1	20.0	17.1	19.0	16.3	22.9	21.3
M4005	46.1	36.2	42.7	30.4	52.3	34.3
M401	63.1	42.3	55.3	35.7	86.7	70.1
M41	74.0	52.3	69.2	31.2	92.5	80.5

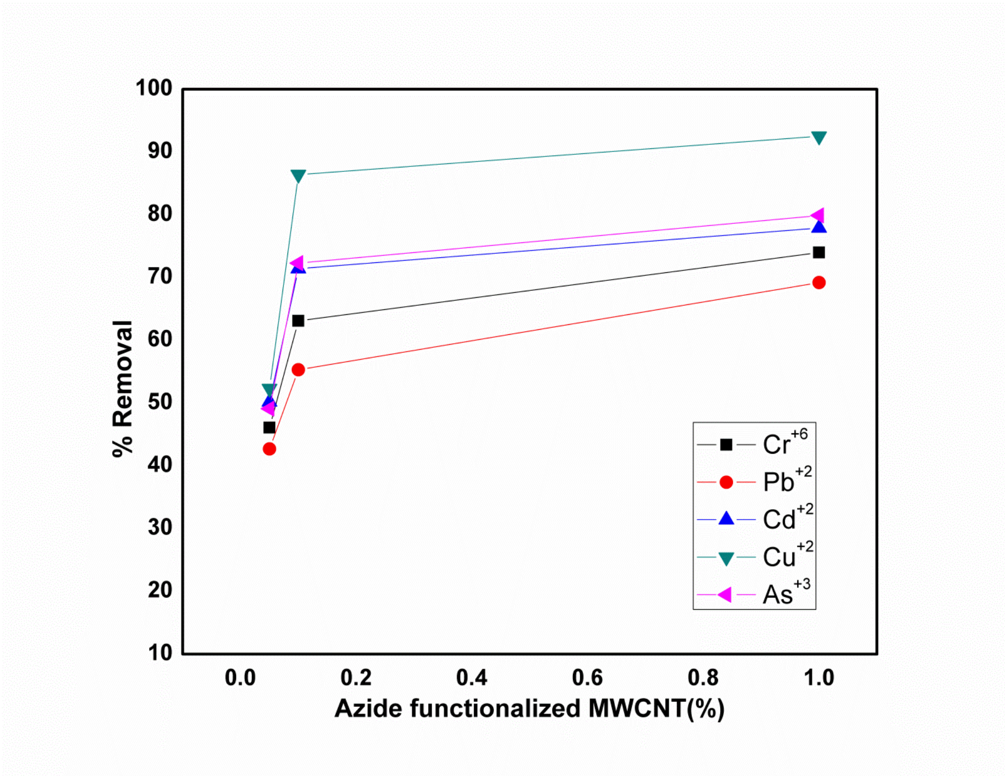

Figure 4.6 Percentage rejection of metal ions at pH 2.5 for mixed matrix azide functionalized MWCNT/PES membranes containing different % of nanotubes at 71 psi pressure

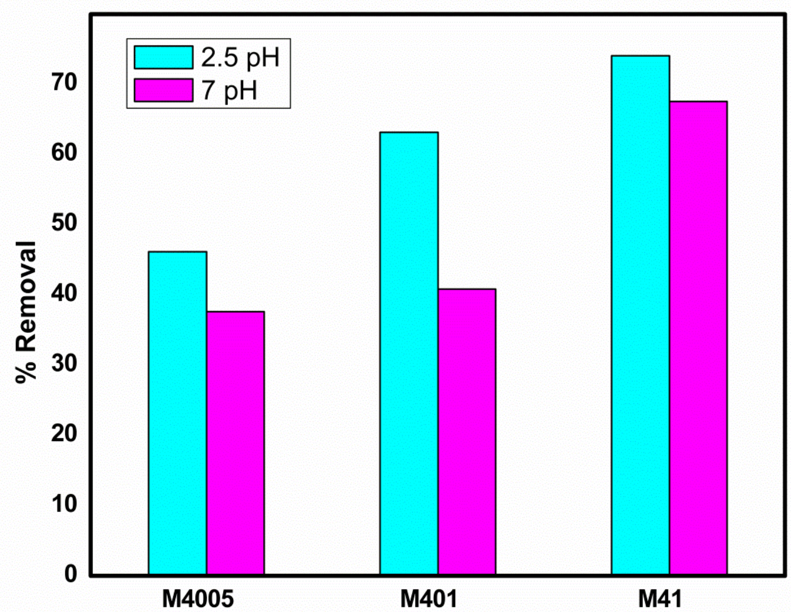

Figure 4.7 Percentage removal of Cr(VI) metal ion at acidic and neutral pH for different mixed matrix azide functionalized MWCNT/PES membranes at 71psi pressure

The rejection experiments were performed at the above mentioned optimum condition (pH 2.5 and pressure 71 psi) for pristine PES, oxidized, azide and amide functionalized MWCNT incorporated mixed matrix membranes. It is observed from the data shown in Table 4.3, 4.4, 4.5 that nanotube incorporated membranes are having better rejection than pristine PES membrane which is because of the presence of functionalized nanotube they not only reduce the pore size of the membranes but also smoothens the path of water inside the pores, hence results better rejection. The attached functionalities –COOH, $–CONHCH_2CH_2NH_2$, –

CON_3 enables the complexation ability of the membranes with heavy metal ions. Among all the three functionality azide functionalized membranes are giving the best rejection which is due to higher metal binding capacity of azide functional group. The maximum rejection was obtained at acidic pH because protons also compete with the heavy metal ions.

Table 4.3 Rejection studies of heavy metal ions at pH 2.5 for oxidized MWCNT/PES membranes at pressure of 71 psi

Membrane	Removal capacity (%)				
	Cr(VI)	**Pb(II)**	**Cd(II)**	**Cu(II)**	**As(III)**
M1	20.0	19.0	20.5	22.9	18.3
M2005	31.1	22.3	49.7	45.5	51.2
M201	49.3	29.1	54.3	48.2	55.3
M21	58.5	35.5	68.1	78.3	75.7

Table 4.4 Rejection studies of heavy metal ions at pH 2.5 for amide functionalized MWCNT/PES membranes at pressure of 71 psi

Membrane	Removal capacity (%)				
	Cr(VI)	**Pb(II)**	**Cd(II)**	**Cu(II)**	**As(III)**
M1	20.0	19.0	20.5	22.9	18.3
M3005	45.3	43.2	49.2	50.3	51.2
M301	62.2	54.7	75.1	85.1	74.9
M31	73.5	68.7	79.5	92.1	80.3

Table 4.5 Rejection studies of heavy metal ions at pH 2.5 for azide functionalized MWCNT/PES membranes at pressure of 71 psi

Membrane	**Removal capacity (%)**				
	Cr(VI)	**Pb(II)**	**Cd(II)**	**Cu(II)**	**As(III)**
M1	20.0	19.0	20.5	22.9	18.3
M4005	46.1	42.7	50.2	52.3	49.1
M401	63.1	55.3	71.4	86.4	72.3
M41	74.0	69.2	77.9	92.5	79.9

4.1.1.3. Tertiary wastewater treatment

The secondary effluents used in this study were collected from municipal wastewater treatment plant located in Tarsali (Vadodara, India). The water samples were stored at 25 ^{o}C until use. The major effluent quality parameters are presented in Table 4.6.

Table 4.6 Typical quality parameters of selected quality effluent

COD (mg/L)	50.3±1.7
UV_{254}(cm^{-1})	0.32±0.02
TOC (mg/L)	15.9±0.5
Turbidity (NTU)	3.1±0.2
pH	8.1±0.1
Total nitrogen (mg L^{-1})	61.1±3.2
Total phosphorus (mg L^{-1})	0.51±0.04

The filtration experiment was performed on Laboratory membrane filtration setup fabricated in-house. The membrane had an effective area of 50 cm^2. The experiment was performed on neutral pH of the effluent i.e. approximately 8. The experiment was performed in batch concentration mode: that is collecting the permeate stream separately and recycling the retentate stream to the feed tank. A standard pathway including 2 steps was followed: in the first step new membrane was washed with DI water and pure water flux was measured in order to determine the membrane water permeability. In second step the filtration of secondary effluent was performed. The feed tank was filled with effluent (3000 ml) and at regular time interval the permeate volume was measured which provides the permeate flux. The water sample of feed and permeate is collected to analyzed the water quality parameters.

4.1.1.3.1. Membranes

The membrane used for the effluent filtration was pristine poly ether sulfone (M1), 1% Azide functionalized MWCNT incorporated polyether sulfone (M41) and 1 % Amide functionalized MWCNT incorporated polyether sulfone (M31) mixed matrix membrane. The details of the membranes were summarized in Table 3.1 in Chapter 3.

4.1.1.3.2. Rejection for several water quality parameters

The removal of the organic matter which were present in the municipal secondary effluent gives the efficiency of the filtration processes and was measured in terms of rejection percentages, which were referred to several water quality parameters. As summarized in the Table 4.6, the water quality parameters chosen in this work were chemical oxygen demand (COD), Total organic carbon (TOC), turbidity (turb), total nitrogen (N) and total phosphorous (N). The rejection percentage for the case of TOC was defined by Eq 2.

$$\boldsymbol{R_{TOC} = \frac{TOC_F - TOC_P}{TOC_F} \times 100} \qquad \textbf{(2)}$$

Where TOC_F and TOC_P are total organic carbon present in the feed and permeate solution respectively. Similarly the rejection percentages was measured for remaining water quality parameters and is represented by R_{COD} for COD, R_{turb} for turbidity, R_N for total nitrogen and R_P for total phosphorous content. The values of rejection percentage for all parameters are summarized in Table 4.7.

Table 4.7 Rejection percentage of water quality parameters

Membrane	R_{COD} (%)	R_{UVA} (%)	R_{TOC} (%)	R_{turb} (%)	R_N (%)	R_P (%)
M1	58.3	59.0	55.6	75.5	20.1	54.3
M31	75.7	80.1	73.7	76.2	56.5	62.2
M41	84.0	85.7	89.4	83.1	65.5	67.9

The pristine membrane gives comparatively less rejection percentage to the mixed matrix membranes. The membrane containing amide f-MWCNT gave the rejection in the range of 50-80% however the azide f-MWCNT has given 65-90 % rejection. In summary the mixed matrix azide f-MWCNT membrane gave elimination of the organic matter content present in the municipal effluent. The zeta potential study and impedance analysis of the membranes reveals that the incorporation of f-MWCNT develops negative charge on the membrane surface. However pristine PES membrane is having lesser negative charge. The explanation behind the phosphorous removal can be explained as, P forms complexes with high molecular weight, or as polyphosphates or phosphates, which are repelled by negatively charged membranes [250]. The N removal percentage is less in all cases probably due the low retention of nitrogen containing organic compounds. Only nitrogen present as nitrite and nitrate anions are partially repelled by membranes having negative charge. The main membrane properties affecting the retention are pore size, surface charge, hydrophilicity/hydrophobicity [251]. In general size exclusion would be the foremost mechanism for retention of organic matter i.e. the permeation of small molecules are easier than for larger molecules through the membrane. And retention increases with increase in molecular size. Water quality parameters subsequent to the membrane filtration are summarized in Table 4.8.

Table 4.8 Quality parameters of selected quality effluent after treatment

	M1	M31	M41
COD (mg/L)	20.97	12.22	8.04
UV_{254}(cm^{-1})	0.13	0.06	0.04
TOC (mg/L)	7.05	4.18	1.68
Turbidity (NTU)	0.76	0.7	0.52
Total nitrogen (mg L^{-1})	48.81	26.57	21.07
Total phosphorus (mg L^{-1})	0.23	0.19	0.16

Thus these mixed matrix membranes could be an option for the treatment of secondary effluent from municipal wastewater.

4.1.1.4. Fouling studies of PES/f-MWCNT membrane

Bovine serum albumin (BSA) having approximate molecular weight 68 kDa and isoelectric point at pH 4.7-4.9 was purchased from sigma aldrich. The 500 ppm of BSA solution was used for the protein rejection and fouling studies. The experiment was performed on membrane filtration unit with 50 cm^2 cross section of membranes. All the experiment was performed at 25°C and 71 psi pressure. The concentration of feed and permeate solution was measured UV-Visible spectrophotometer. Thus the rejection was calculated from following equation

$$\boldsymbol{R}(\%) = \frac{\boldsymbol{C_{f1} - C_{p1}}}{\boldsymbol{C_{f1}}} \times \mathbf{100} \qquad \textbf{(3)}$$

Where C_{f1} and C_{p1} are the concentration of feed and permeate solution of BSA respectively measured with UV-visible spectrophotometer at 280 nm. Further DI water was circulated through the membranes for 30 minutes and then pure water flux of all the membranes were measured after BSA filtration test. Antifouling properties of the membranes was evaluated using flux recovery ratio of the membranes by the expression

$$\boldsymbol{FRR}(\%) = \frac{\boldsymbol{J_2}}{\boldsymbol{J_1}} \times \mathbf{100} \qquad \textbf{(4)}$$

J_1 and J_2 are pure water flux of the membranes before and after protein filtration respectively. All the experiments were repeated twice in order to get repeatability of the results. The reversible fouling ratio (R_{ir}) and irreversible fouling ratio (R_r) was calculated in order to study fouling behaviour of membranes in more details

$$\boldsymbol{R_r} = \frac{\boldsymbol{J_2 - J_3}}{\boldsymbol{J_1}} \times \mathbf{100} \qquad \textbf{(5)}$$

$$R_{ir} = \frac{J_1 - J_2}{J_1} \times 100 \qquad (6)$$

Where, J_3 is the protein filtration flux. The BSA rejections from the membranes are shown in Table 4.9. As the size of the BSA molecule is quite large compared to the pore dimensions of the membranes, the rejection are more than 90% for all the mixed matrix membranes. The rejection is increase slightly from pristine PES membrane to the membranes having f-MWCNT as fillers due to the reduced pore dimensions and increased hydrophilicity.

Table 4.9 BSA rejection and fouling ratio of the PES/f-MWCNT mixed matrix membranes

Membrane	Bovine serum albumin			
	Rejection (%)	Flux recovery ratio (%)	Reversible fouling ratio (%)	Irreversible fouling ratio (%)
M1	84.0±2.1	54.3±6.1	12.7±3.1	45.6±1.7
M2003	89.3±1.3	76.4±2.9	28.1±1.8	16.2±2.3
M2005	90.1±2.4	79.7±3.1	28.9±1.5	15.9±2.4
M2007	90.3±1.6	80.1±3.2	29.6±1.7	15.1±1.6
M201	90.8±3.1	81.2±1.0	30.4±1.1	14.3±1.9
M21	91.0±4.6	82.4±3.8	32.1±2.7	13.5±2.9
M3003	92.5±2.6	72.1±2.9	25.3±3.2	23.3±1.2
M3005	92.9±1.7	72.5±2.2	26.2±3.6	21.8±1.3
M3007	93.1±4.2	71.8±3.7	25.9±3.1	22.5±1.8
M301	94.5±1.5	75.3±4.1	27.7±2.5	20.1±1.0
M31	95.0±1.7	80.9±3.8	30.4±4.1	19.1±4.1
M4003	95.9±2.7	81.4±1.2	29.3±2.8	16.7±2.3
M4005	96.2±1.4	81.8±1.6	31.4±2.7	15.8±1.7
M4007	96.9±3.3	83.5±2.3	32.7±3.5	14.9±2.0
M401	97.0±3.2	83.7±3.7	34.5±1.4	14.5±2.2

M41	97.5±2.8	85.6±1.9	37.9±1.2	14.0±3.6

The flux recovery ratio is 54.3±6.1 % for pristine PES which is improved to 82.4±3.8% for the mixed matrix membrane containing 1wt% Ox-MWCNT, 80.9±3.8% for 1wt% Am-MWCNT and 85.6±1.9% for 1wt% Az-MWCNT. The enhancement in FRR value is due to improved hydrophilicity and lower surface roughness [252]. The contact angle of the oxidized nanotubes containing mixed matrix membranes is lower (65.3±2.0^{o} for 1wt% Ox-MWCNT) than the amide functionalized nanotubes containing mixed matrix membrane (66.5±1.4^{o} for 1wt% Am-MWCNT) thus the Ox-MWCNT/PES membranes are showing higher FRR value than the Am-MWCNT/PES membranes. In case of amide functionalized nanotubes the membrane containing 0.07wt% nanotubes shows lower flux recovery ratio than 0.03 and 0.05wt % amide functionalized nanotubes this may be due to the aggregation of the filler. The addition of f-MWCNT into the polymer matrix increased the reversible fouling ratio considerably which led to a reduction in the irreversible protein fouling ratio for BSA protein (Table 4.9).

The reduced irreversible fouling ratio of mixed matrix membranes is possibly because of increased hydrophilicity and excellent dispersion of functionalized nanotubes which avoid the direct contact between the BSA protein molecules and membrane leading to the easy removal of protein molecules by water flushing. In conclusion the reduced irreversible fouling ratio of mixed matrix membranes (14.0±3.6% for 1 wt % Az-MWCNT/PES, 13.5±2.9% for 1 wt % Ox-MWCNT/PES and 19.1±4.1% for 1 wt % Am-MWCNT/PES) signify that simple water washing can be used to remove protein fouling thus membranes can be used several times for protein filtration.

4.1.2. Sulfonated polyethersulfone/ f-MWCNT mixed matrix membranes

4.1.2.1. Permeation studies of f-MWCNT/SPES membranes:

The effect on pure water permeation by using sulfonated poly ether sulfone as polymer matrix and f-MWCNT as filler was also studied. The pure water flux was measured at different pressure and varying pH. When the polymer matrix was replaced by SPES the pure water flux values are summarized in Table 4.10. As can be seen from Table 4.10 the pure water flux of SPES membrane was enhanced compared to the PES membrane, this could be due to the enhanced hydrophilicity of the membranes since the addition of SO_3H group to the PES.

Table 4.10 Pure water flux values of the membranes at different pressure

Membrane	**Pure water flux(L/m²h)**	
	71 psi	**98 psi**
M1	113.36	124.62
S1	150.30	165.30
S201	171.31	190.11
S205	222.1	252.59
S21	450.9	480.00
S301	269.30	293.12
S305	304.52	334.59
S31	394.15	407.92
S401	301.23	320.21
S405	330.71	371.15
S41	383.71	399.91

The pure water flux of SPES membrane was increased in comparison to the PES membrane (Figure 4.8). As revealed by SANS study the pore size of the SPES membrane was increased, and hydrophilicity of the SPES membrane was also enhanced as measured by contact angle meter. This two combined effects are probably the reason behind the enhancement in pure water flux [253]. In case of the mixed matrix membranes having f-MWCNT in the polymer matrix, the pure water flux keep on increasing compared to pristine SPES membrane, due to the enhanced hydrophilicity and bigger pore size of membranes. In addition to this the pure water flux was also improved due to the presence of functionalized nanotubes which provides frictionless transport of water through the nanotube channels [254].

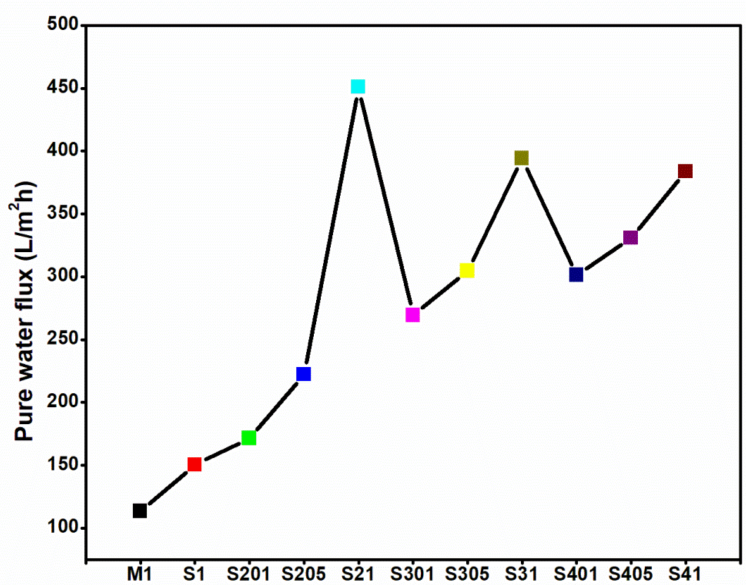

Figure 4.8. Pure water flux values of f-MWCNT/SPES membranes

4.1.2.2. Heavy metal removal studies of SPES/f-MWCNT membranes

The feed solutions for Heavy metal removal studies are prepared with the same procedure as described in section 4.1.1.2. The experiment was carried out in the membrane filtration setup fabricated in-house. The filtration experiment was carried out at 25 ^{o}C temperature. The Az-MWCNT/SPES membranes were tested at two pressure 71 psi and 98 psi to observe the effect on rejection by enhancing pressure. Cr(VI), Pb(II), Cu(II) are the metals which were selected for analyzing the pressure effect. The rejection (%) of Cr(VI), Pb(II), Cu(II) at 71 psi were 19.4, 18.9, 22.1 for pristine SPES membrane, which were reduced to 16.9, 15.6 and 20.4 respectively at 98 psi pressure. The same phenomenon occured for the rest of the mixed matrix membranes having Az-MWCNT as fillers, the values are summarized in Table 4.11. On augment of pressure the rejection percentage of metals decreased, this was probably due to the enhanced flow rate of permeate [255].

Table 4.11 Rejection studies of metal ions at pH 2.5 for azide functionalized MWCNT/PES membranes at pressure 71 psi and 98 psi

Membrane	**Removal capacity (%)**					
	Cr(VI)		**Pb(II)**		**Cu(II)**	
	71 psi	**98 psi**	**71 psi**	**98 psi**	**71 psi**	**98 psi**
M1	20.0	17.1	19.0	16.3	22.9	21.3
S1	19.4	16.9	18.9	15.6	22.1	20.4
S401	64.5	56.1	54.8	43.5	79.3	70.2
S405	71.1	62.4	64.7	50.9	90.3	81.3
S41	76.1	65.2	70.7	61.6	91.8	79.6

The filtration experiment was also carried out at acidic as well as neutral pH for Cr(VI) metal. The pH was maintained at 2.5 by the addition of HCl solution to the Cr(VI) feed solution. The effect of pH on rejection of Cr (VI) metal is shown in Figure 4.9.

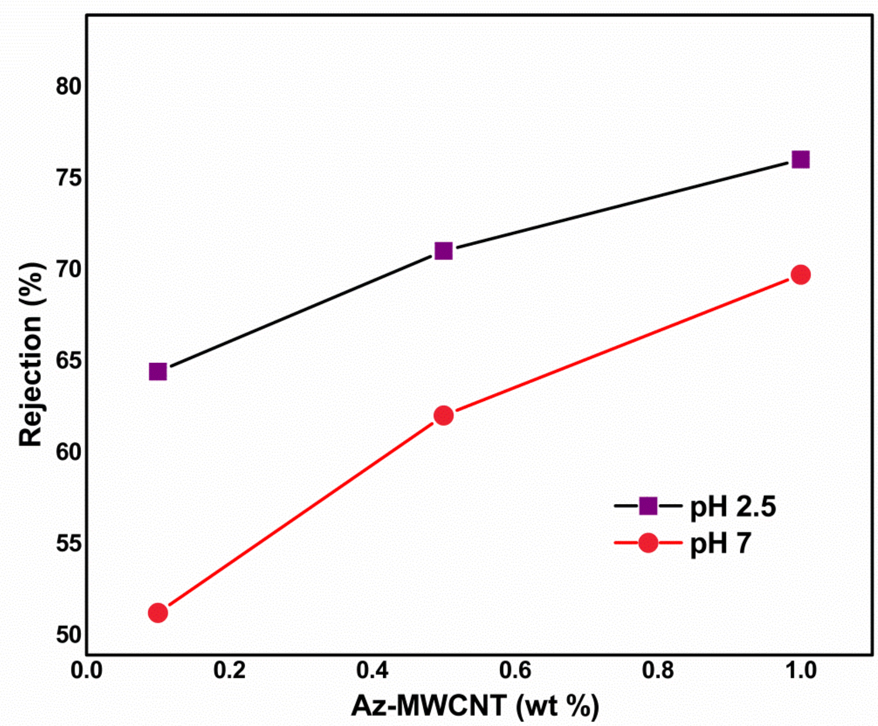

Figure 4.9 Percentage removal of Cr(VI) metal ion at acidic and neutral pH for different mixed matrix azide functionalized MWCNT/SPES membranes at 71psi pressure

For mixed matrix membrane having 0.1, 0.5 and 1 wt% Az-MWCNT, Cr (VI) rejection was 64.5, 71.1, 76.1 respectively at 2.5 pH which was reduced to 51.3, 62.1, 69.8 respectively in neutral environment. The removal of chromium was higher at acidic pH as compared to neutral pH, this result was in agreement with the result reported by Anah et al [256]. Thus the optimum condition could be obtained as 2.5 pH and 71 psi pressure for metal removal studies.

The filtration experiment has been performed for different weight percentage of Ox, Am and Az-MWCNT incorporated SPES mixed matrix membranes. The rejection of nanotube incorporated mixed matrix SPES membrane was higher than the pristine SPES membrane due to the active sites present at membranes because of functionalized nanotubes. On increasing the functionalized nanotubes concentration in to the membrane matrix the rejection percentage keep on increasing, this may be accredited to the reduced pore size, enhanced number of active sites on MWCNTs due to functionalization. The metal removal was found to be more prominent in case of azide (Table 4.14) and amide (Table 4.13) group containing membranes. The azide and amide groups were probably having better metal binding capacity in comparison to the carboxylic group and hence 78.7% As and 91.8% Cu was rejected from azide MWCNT/SPES MMM, while only 74.5% As and 77.3% Cu rejection was obtained from oxidized MWCNT/SPES MMM (Table 4.12).

In case of azide MWCNT/SPES MMM 0.1% azide gave 87.3% Cu(II) rejection while 1 % azide has given 91.8% rejection. With the increased concentration of nanotubes the pore dimension is decreased resulting higher flux as compared to pristine SPES membrane, thus giving better removal of heavy metal ions and could be considered as most suitable for metal removal out of other mixed matrix membranes. On the other hand virgin SPES membrane gave very less rejection.

Virgin SPES membrane gave 22.1% Cu rejection, which is very less as compared to mixed matrix membranes.

Table 4.12 Rejection studies of heavy metal ions at pH 2.5 for oxidized MWCNT/PES membranes at pressure of 71 psi

Membrane	Removal capacity (%)				
	Cr(VI)	Pb(II)	Cd(II)	Cu(II)	As(III)
M1	20.0	19.0	20.5	22.9	18.3
S1	19.4	18.9	19.8	22.1	18.5
S201	30.9	23.1	48.9	44.3	50.9
S205	48.8	28.6	53.9	47.9	54.7
S21	59.4	37.2	65.4	77.3	74.5

Table 4.13 Rejection studies of heavy metal ions at pH 2.5 for amide functionalized MWCNT/PES membranes at pressure of 71 psi

Membrane	Removal capacity (%)				
	Cr(VI)	Pb(II)	Cd(II)	Cu(II)	As(III)
M1	20.0	19.0	20.5	22.9	18.3
S1	19.4	18.9	19.8	22.1	18.5
S301	63.9	53.6	74.7	87.3	73.9
S305	68.8	64.1	77.6	91.7	79.4
S31	74.3	67.5	78.9	93.6	81.5

Table 4.14 Rejection studies of heavy metal ions at pH 2.5 for azide functionalized MWCNT/PES membranes at pressure of 71 psi

Membrane	**Removal capacity (%)**				
	Cr(VI)	**Pb(II)**	**Cd(II)**	**Cu(II)**	**As(III)**
M1	20.0	19.0	20.5	22.9	18.3
S1	19.4	18.9	19.8	22.1	18.5
S401	64.5	54.8	72.2	89.3	73.7
S405	71.1	64.7	75.2	90.3	76.1
S41	76.1	70.7	76.8	91.8	78.7

4.1.2.3. Tertiary wastewater treatment

The secondary effluents used in this study were received from municipal wastewater treatment plant located in Tarsali (Vadodara, India). The water samples were stored at 25^{o}C until use. The major effluent quality parameters are tabulated in section 4.1.1.3 in Table 4.6. The filtration setup and experiment conditions are same as given in the section 4.1.1.3.

4.1.2.3.1. Membranes

The membranes used for this study are 0.5 wt% amide MWCNT/SPES (S305), 1 wt% amide MWCNT/SPES (S31), 0.5 wt% azide MWCNT/SPES (S405) and 1 wt% azide MWCNT/SPES (S41). The composition of the membranes is given in Table 3.1 in Chapter 3.

4.1.2.3.2. Rejection for several water quality parameters

The parameters selected to analyze water quality test of effluent water are chemical oxygen demand (COD), Ultraviolet absorbance at 254 nm (UVA), Total organic content (TOC), Turbidity (TURB), Nitrogen present (N), Potassium present (P). All the parameters were measured as standard procedure. The rejection percentages are summarized in Table 4.15.

Table 4.15 Rejection percentage of water quality parameters

Membrane	R_{COD} (%)	R_{UVA} (%)	R_{TOC} (%)	R_{turb} (%)	R_{N} (%)	R_{P} (%)
S1	50.4	55.3	51.7	73.6	19.1	52.6
S305	56.6	58.9	53.0	77.9	21.9	54.0
S31	73.3	78.5	71.7	74.8	54.5	57.9
S405	80.4	81.3	84.5	80.8	60.6	65.3

S41	81.1	83.9	85.3	81.9	63.5	65.9

The charge on the membranes can accounts for the removal of the pollutants as reported by Manttari et al [257]. The membranes are having negative charge as analyzed by zeta potential analysis. The phosphorous exist as polyphosphate or phosphate which is repelled by negatively charged membranes. The removal of N is least out of all the pollutants probably since the low retention of nitrogen containing organic compound. N present as nitrate and nitrite are only that are repelled by the negatively charged membrane as explained earlier. The main mechanism for the removal of these organic pollutants is size exclusion. The pore size of SPES membranes is found to be larger as compared to the PES membranes [258], thus in case of sulfonated polyether sulfone membrane slight reduction in the rejection percentage is observed. In case of the mixed matrix membranes containing azide and amide nanotubes, the addition of f-nanotubes has decreased the pore size of the membranes, which resulted in enhancement of effluent treatment. The best rejection is obtained from 1wt% azide MWCNT/SPES membranes which is ~80% for COD, UVA, TOC, TURB and ~60% for N, P removal. Table 4.16 shows the parameters of effluent quality after membrane treatment.

Table 4.16 Quality parameters of selected quality effluent after treatment

	S1	**S305**	**S31**	**S405**	**S41**
COD (mg/L)	24.94	21.83	13.43	9.85	9.50
UV_{254}(cm^{-1})	0.14	0.13	0.06	0.05	0.05
TOC (mg/L)	7.67	7.47	4.49	2.46	2.33
Turbidity (NTU)	0.81	0.68	0.78	0.59	0.56
Total nitrogen (mg L^{-1})	49.42	47.71	27.80	24.07	22.30

Total phosphorus (mg L^{-1})	0.24	0.23	0.21	0.18	0.17

These membrane can be promising option for the treatment of secondary effluent from municipal waste water treatment plant, with the intend to get permeate with good physico-chemical properties. The treated water could be reused for various applications such as irrigation, recharge of aquifers etc.

4.1.2.4. Fouling studies of SPES/f-MWCNT membranes

The details of Bovine serum albumin filtration study of fouling measurement are given in section 4.1.1.4. In brief, to measure antifouling characteristics of the membranes, the pure water was passed through the membrane for at least half an hour to stabilize the flux. The pure water flux was first measured and then feed tank was refilled with 500 ppm BSA solution and flux was measured as J_3. After BSA filtration the pure water was passed through the membrane for 1 h and then pure water was filled as feed to determine fouling, after which the flux with the cleaned membrane represented as J_2 was measured. The protein rejection measured by equation 3 (section 4.1.1.4). In order to appraise the resistive ability of the modified membranes against fouling, flux recovery ratio (FRR) is calculated by equation 4 (section 4.1.1.4). To study the fouling process in detail, some more expressions reversible fouling ratio (R_r), irreversible fouling ratio (R_{ir}) are defined and calculated according to the equation 5 and 6 (section 4.1.1.4). The results obtained is summarized in Table 4.17.

Table 4.17 BSA rejection and fouling ratio of the SPES/f-MWCNT mixed matrix membranes

Membrane	**Bovine serum albumin**			
	Rejection (%)	**Flux recovery ratio (%)**	**Reversible fouling ratio (%)**	**Irreversible fouling ratio (%)**
S1	82.0±2.1	58.9±5.1	19.5±2.2	30.1±1.7
S205	83.1±2.7	69.1±1.3	32.5±1.3	10.9±1.6
S21	89.0±3.2	76.1±2.6	43.1±1.9	9.1±1.3
S305	90.4±2.6	75.6±1.6	23.6±3.1	15.7±2.5
S31	91.0±2.1	85.5±1.4	40.8±2.3	13.1±1.0
S405	90.9±1.5	78.4±2.5	38.3±2.8	12.4±4.1

S41	94.0±1.9	89.5±3.1	50.3±3.1	10.1±1.5

Accumulation of the foulants on the membrane cause fouling of membranes, thus the interaction between foulant and the membrane surface govern the antifouling performance of the membranes [259]. The recycling properties of the membranes can be shown by flux recovery ratio (Figure 4.10). The enhanced FRR indicates the better antifouling properties of the membranes. The FRR of the virgin SPES membrane is 58.9±5.1 which is higher than the value for PES membrane (54.3±6.1). The enhancement is FRR is probably due to the better hydrophilicity of the SPES membrane than PES membrane which is confirmed by the contact angle measurement. In the same way, addition of f-MWCNT to the SPES polymer matrix further reduce the contact angle and thus increased FRR value. It is observed that on increasing the weight percentage of functionalized nanotubes, the FRR value increases. And out of three functionality azide functionalized membranes shows the best antifouling properties. The highest value of FRR is 89.5±3.1 for the Az-MWCNTs 1 wt% membrane (Table 4.17).

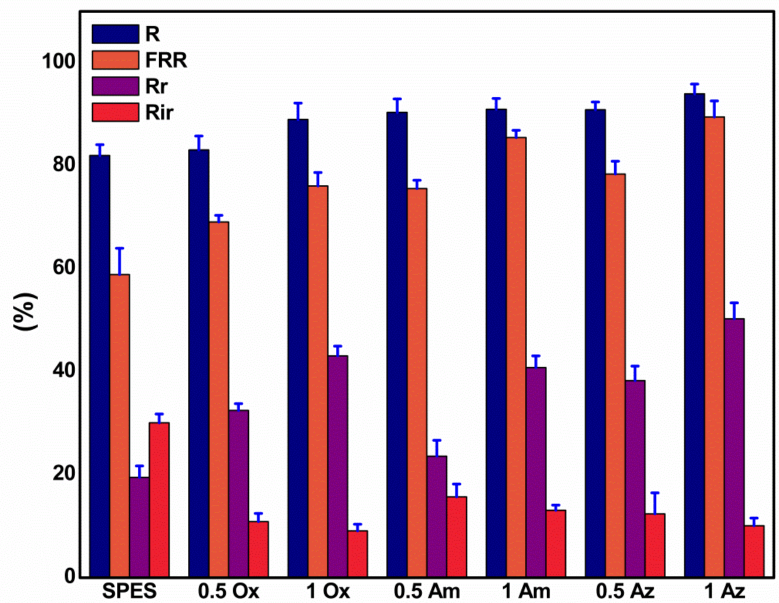

Figure 4.10. Representation of BSA rejection (R), Flux recovery ratio (FRR), Reversible fouling ratio (Rr), Irreversible fouling ratio (Rir) of SPES and f-MWCNT/SPES mixed matrix membranes

Membranes fouling comprise reversible fouling ratio and irreversible fouling ratio. Monolayer of protein adsorption on the membrane surface cause irreversible fouling which cannot be removed by simple water flushing due to the strong adsorption. However deposition of proteins on the adsorbed layer gives rise to of reversible fouling since these proteins are loosely attached, which can be removed by simple hydraulic cleaning [260, 261].

The reversible protein fouling ratio increased with increasing wt% of nanotubes for all the three functionality of MWCNT (oxidized, amide, azide) (Table 4.17). The lowest value of irreversible fouling ratio is for 1wt% oxidized MWCNTs membrane (9.1±1.3) which is possibly because of excellent dispersion of nanotubes and enhanced hydrophilicity thus avoiding the direct contact between protein molecules and the membrane [262]. Hence protein molecule can be removed by simple water washing. However the irreversible fouling ratio is also significant for the 1 wt% azide MWCNTs membrane (10.1±1.5) and as azide membranes are giving better rejection, they are most suitable for several run of protein filtration.

4.1.3. Click reaction modified PES/Az-MWCNT mixed matrix membrane

4.1.3.1. Permeation studies of f-MWCNT/SPES membranes

Pure water flux of the modified as well unmodified membrane is determined at different transmembrane pressure and varied pH. It was observed that on decreasing the pH from 7 to 3, the pure water flux value decreased (Figure 4.11). In this study we observed the increase in the pure water permeability when pH is changing from acidic to neutral condition. This result is in agreement with the study reported by Bossau [263] while using NF membrane NFPES10. The explanation for the said phenomenon is given Barghetta et al. [264] as arising due to swelling of membrane matrix at different environment. Even though the pore size of click reaction modified membrane is not small as in case of M41 (Table 4.18), the rejection performance is much better than the Pristine PES membrane which is attributed to the surface modification of the membrane. The enhanced membrane flux at high pH value is because of the charged functional groups of the membrane matrix which force adjacent polymers apart at high pH value. However, at lower pH values the membrane polymers come close to each other since the charge of membrane matrix is shielded hence resulting in lower flux. As we can see from Figure 4.12 at acidic pH the rejection of chromium metal is more in comparison to the neutral pH which can be explained in terms of higher complexation tendency of surface active sites of composite membranes.

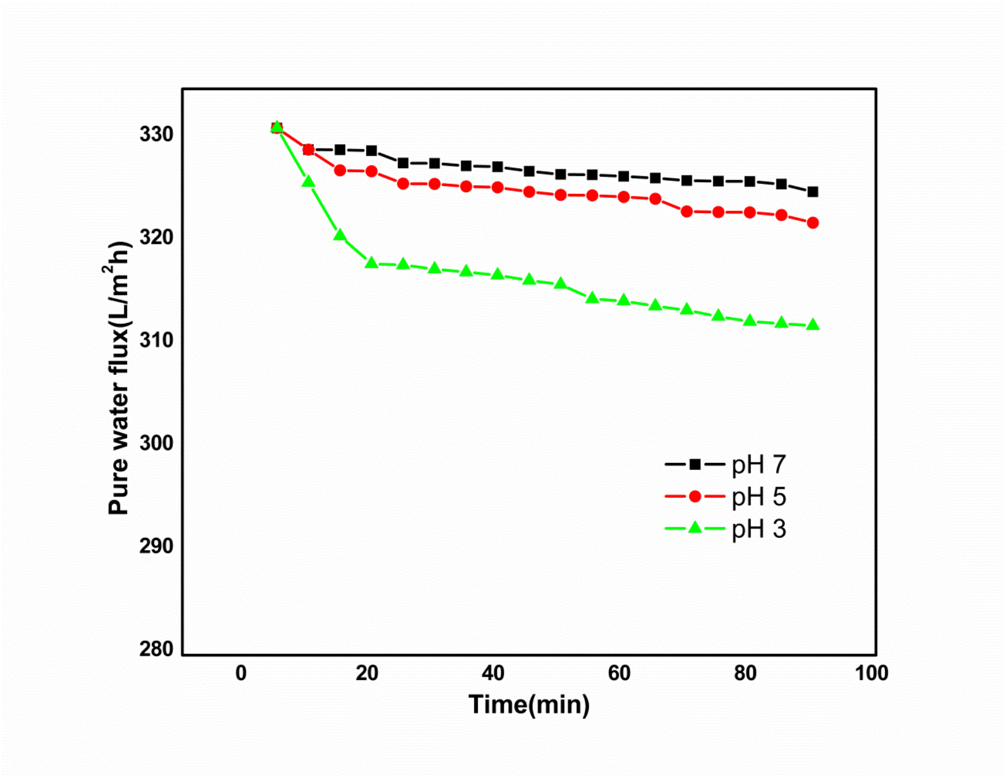

Figure 4.11 Pure water flux versus time of click reaction modified membrane at different pH values

4.1.3.2. Heavy metal ions removal studies of Click reaction modified PES/Az-MWCNT membrane

The heavy metal ions form the most hazardous environmental pollutants [265] in nature as they are non-biodegradable and environmentally retained [266]. Heavy metal ions (Cr(VI), Pb(II), Cd(II), Cu(II), As(III)) rejection experiment was carried out via membrane filtration. Aqueous solutions of heavy metals were prepared according to the process mentioned in section 4.1.1.2. In Table 4.18 the rejection percentage of heavy metals for pristine PES, 1 % azide functionalized MWCNT, click reaction modified membrane is given. The rejection of chromium ion is studied at two different pH (acidic and neutral). We are getting the higher rejection at acidic pH which is consistent with earlier reports [267,268]. Concerning the rejection of other heavy metals at optimized condition, the modified and unmodified membranes do not show much difference in the rejection capacity at acidic pH. Both the membranes show the rejection of heavy metals up to 70 percentages. The click reaction modified membrane gives slightly higher rejection performance. The slight enhancement in the rejection may be attributed to the availability of more surface active sites on the membrane matrix. The maximum removal we obtain for Cu (II) metal due the complexation ability of triazole group with copper metal [269]. The removal of heavy metals is attributed to charge and sieving mechanism. However, the exact mechanism of the rejection is a matter for further study.

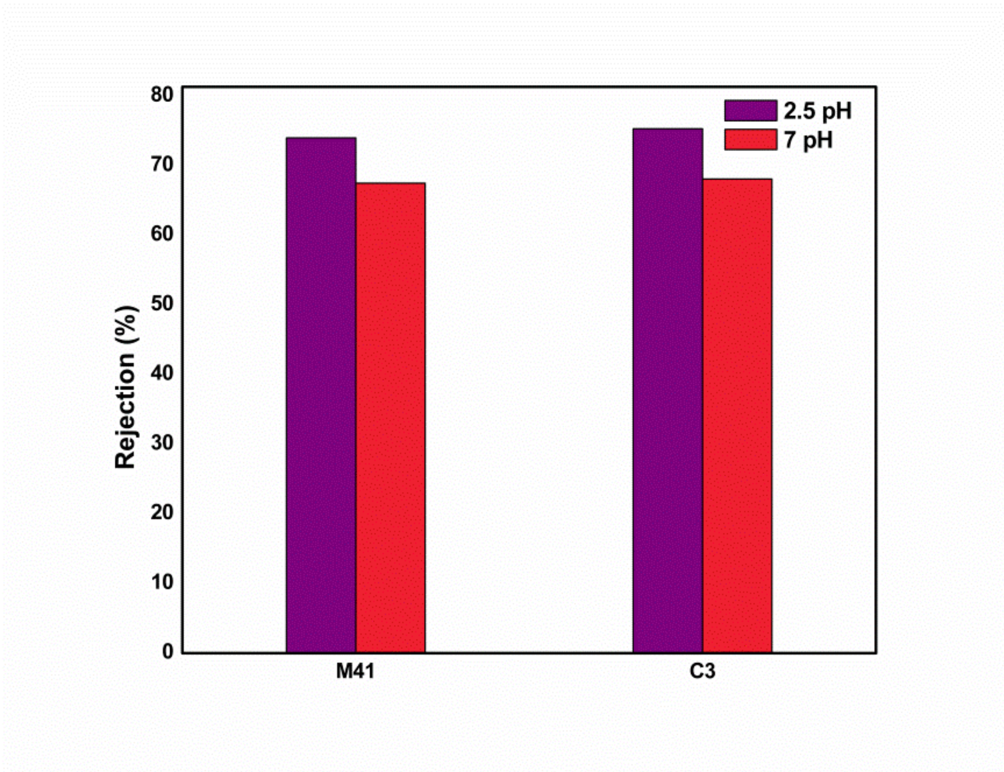

Figure 4.12 Effect of pH on rejection of Cr(VI) metal from unmodified (M41) and modified (C3) membranes

Table 4.18 Rejection capacity of Pristine PES (M1), 1% Az-MWCNT/PES (M41), Click reaction modified 1% Az-MWCNT/PES (C3) membranes

Membrane	Removal capacity (%)				
	Cr(VI)	Pb(II)	Cd(II)	Cu(II)	As(III)
M1	20.0	19.0	20.5	22.9	18.3
M41	74.0	69.2	77.9	92.5	79.9
C3	75.3	69.9	78.5	93.2	80.6

4.1.3.3. Tertiary wastewater treatment by click reaction modified membrane

The secondary effluents used in this study were taken from municipal wastewater treatment plant located in Tarsali (Vadodara, India). The water samples were stored at 25 ^{o}C until use. The major effluent quality parameters are tabulated in section 4.1.1.3 in Table 4.6. The filtration setup and experiment conditions are same as given in the section 4.1.1.3.

4.1.3.3.1. Membranes

Click reaction modified 1wt% Az –MWCNT/PES membrane (C3) and 1wt% Az –MWCNT/PES membrane (M41) were used for experiment.

4.1.3.3.2. Rejection for several water quality parameters

The parameters selected to analyze water quality test of effluent water are chemical oxygen demand (COD), Ultraviolet absorbance at 254 nm (UVA), Total organic carbon (TOC), Turbidity (TURB), Nitrogen present (N), Potassium present (P). All the parameters were measured as standard procedure. Rejection percentage of different parameters are given in Table 4.19.

Table 4.19 Rejection percentage of water quality parameters

Membrane	R_{COD} (%)	R_{UVA} (%)	R_{TOC} (%)	R_{turb} (%)	R_{N} (%)	R_{P} (%)
M1	58.3	59.0	55.6	75.5	20.1	54.3
M41	84.0	85.7	89.4	83.1	65.5	67.9
C3	82.9	84.0	86.9	82.3	62.4	66.6

The click modified Az-MWCNT membrane is giving considerable rejection of COD, UVA, TOC, TURB, N and P content present in the municipal effluent. The negative charge present on the click modified membrane accounts for the rejection [270]. The rejection from modified membrane is nearly same as obtained by the 1wt% Az-MWCNT/PES membrane (M41) which is considerable. The click reaction modified membrane follows the same trend as here in this case nitrogen content removal is least. While highest removal is for total organic carbon. The value of water quality parameter is summarized in Table 4.20.

Table 4.20 Quality parameters of selected quality effluent after treatment

	M1	**M41**	**C3**
COD (mg/L)	20.97	8.04	8.60
UV_{254}(cm^{-1})	0.13	0.045	0.05
TOC (mg/L)	7.05	1.68	2.08
Turbidity (NTU)	0.76	0.52	0.54
Total nitrogen (mg L^{-1})	48.81	21.07	22.9
Total phosphorus (mg L^{-1})	0.23	0.16	0.17

4.1.1.4. Fouling studies of click reaction modified PES/Az-MWCNT membranes

Membrane fouling is a key factor which accounts for the efficiency of liquid filtration membranes. Fouling in the membrane arises due to pore blockage, concentration polarization and cake layer formation which cause reduction the water flux [271]. Fouling is caused by the hydrophobic nature of the membrane surface as behaviour of the membrane surface plays crucial role in the fouling mechanism [272]. Increase in membrane hydrophilicity including material modification, polymer blend and surface modification are some approaches which have been used to improve membrane permeability and antifouling property [273].

Bovine serum albumin (BSA) was used as model protein for the antifouling studies of the membrane. The details of BSA filtration study of fouling measurement are given in section 4.1.1.4. In brief, to measure antifouling characteristics of the membranes, the pure water was passed through the membrane for at least half an hour to stabilize the flux. The pure water flux was first measured and then feed tank was refilled with 500 ppm BSA solution and flux was measured as J_3. After BSA filtration the pure water was passed through the membrane for 1 h and then pure water was filled as feed to determine fouling, after which the flux with the cleaned membrane represented as J_2 was measured. The protein rejection measured by equation 3 (section 4.1.1.4). In order to appraise the resistive ability of the modified membranes against fouling, flux recovery ratio (FRR) is calculated by equation 4 (section 4.1.1.4). To study the fouling process in detail, some more expressions reversible fouling ratio (R_r), irreversible fouling ratio (R_{ir}) are defined and calculated according to the equation 5 and 6 (section 4.1.1.4). The results obtained are summarized in Table 4.21.

Table 4.21 Values of flux recovery ratio (FRR), reversible fouling ratio (R_r) and irreversible fouling (R_{ir}) of membranes

Membrane	Bovine serum albumin			
	Rejection (%)	**Flux recovery ratio (%)**	**Reversible fouling ratio (%)**	**Irreversible fouling ratio (%)**
M1	84.0±2.1	54.3±6.1	12.7±3.1	45.7±1.7
M41	98.0±2.8	85.6±1.9	37.9±1.2	14.4±3.6
C3	96.0±1.7	92.5±1.3	69.0±1.5	7.5±3.1

After performing the click reaction on the surface of 1wt% Az-MWCNT/PES membrane the hydrophilicity of the membrane surface is decreased drastically which is measured by contact angle and description is given in Chapter 3. The hydrophilic surfaces impede the adsorption of protein and other fouling materials as due to the absorption of water these surfaces forms water layer [274]. This change in surface of the membrane does affect the flux recovery ratio, reversible fouling ratio and irreversible fouling ratio. Better antifouling properties of the membranes are given by the higher flux recovery ratio value. FRR for click reaction modified membrane was higher (92.5%) than the virgin PES and Az-MWCNT/PES membrane. PES membrane showed about FRR of 54.3% while for 1%Az-MWCNT/PES mixed matrix membrane the value is 85.6. This indicates click modification have improved the antifouling performance of the modified membrane.

As already discussed in section 4.1.2.4 membrane fouling are classified in two category: reversible fouling and irreversible fouling. The reduced membrane productivity and increased operational cost is observed in reversible fouling due to backwashing process. While in irreversible fouling the lifetime of membrane is reduced due to the chemical cleaning of membranes. The reversible fouling ratio and irreversible fouling ratio are depicted in Figure 4.13. The results indicate that the flux recovery ratio of the modified membrane is higher while the resistance factor is lower. The irreversible ratio of the remarkably reduced from 14.3% for 1%Az-MWCNT/PES membrane to 10.0% for click reaction modified membrane. These results illustrate that the modified membrane's antifouling properties has been improved considerably. In conclusion, the surface properties of the membrane were modified as the flux recovery ratio (FRR), reversible ratio (Rr), irreversible fouling ratio (Rir) values increased.

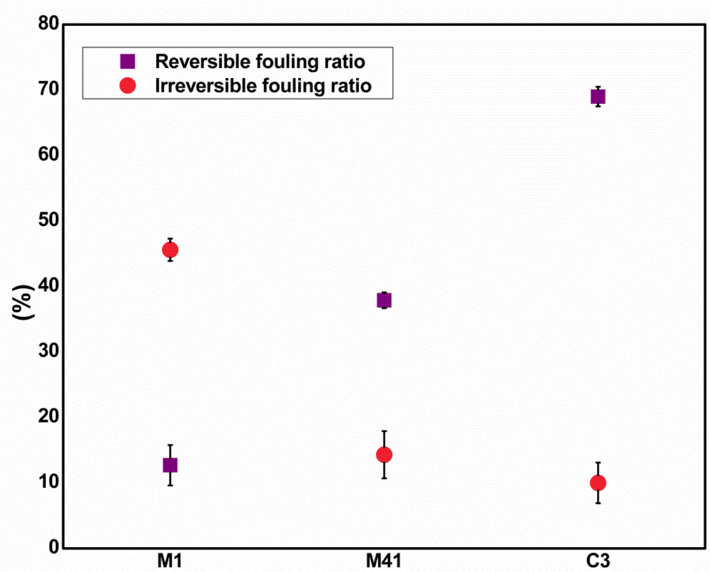

Figure 4.13. Fouling ratios of the pristine PES (M1), 1%Az MWCNT/PES and click reaction modified membranes