ISSN(PRINT) : 2320 -1967
ISSN(ONLINE) : 2320 -1975

GLOBAL SCIENTIFIC INC.

ChemXpress

ORIGINAL ARTICLE

CHEMXPRESS 9(1), 011-019, (2016)

Fabrication of polyvinylchloride based nanofiltration membrane filled with SiO_2 nanoparticles: Performance and physico-chemical characterization

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Received : 18th November, 2014 ; Revised : 07th March, 2015 ; Accepted : 15th March, 2015

Abstract : Polyvinylchloride-co-SiO_2 nanoparticles nanofiltration membranes were prepared by phase inversion method through immersion precipitation technique. For the purpose, PVP and N, N dimethylacetamide were utilized as pore former and solvent in membranes fabrication. The effect of SiO2 nanoparticle concentration in the casting solution on membrane performance and physico-chemical properties was studied. The fabricated membranes were investigated in terms of pure water flux, permeability flux, $MgSO_4$ rejection, water content percent, porosity and tensile strength. Obtained results showed that membrane PWF, permeability, water content, porosity and tensile strength were improved by utilizing SiO2 nanoparticle in membrane matrix. The improving of PWF and permeability continued by addition 0.1 % wt. sio2 nanoparticles and again decreased by addition more concentration of nanoparticles (0.5 and 1 wt. %). The membrane rejection also exhibited nearly constant trend by using additive nanoparticles. The prepared nanocomposite membrane containing 0.1 % wt SiO2 nanoparticles showed more appropriate performance compared to others. In addition the effect of membrane thickness, feed concentration and operating pressure on membranes performance was studied.

Keywords : Filtration; Nanocomposite; PVC-co-SiO_2 nanoparticles; Permeability/rejection; Physico-chemical property; Operating condition.

INTRODUCTION

Nano filtration (NF) is a pressure-driven separation process employing a semi permeable membrane with the separation characteristics in the intermediate range between reverse osmosis (RO) membrane and ultrafiltration (UF) membrane[1-3]. Compared with UF membrane, NF membrane has a smaller pore size, so organic molecules with molecular weight larger than 200 g/mole can be retained. Compared with RO membrane, NF membrane exhibits lower retention rates and higher permeability to monovalent ions and solvent, respectively, so a relatively higher solvent flux can be obtained at lower operating pressure. Therefore, NF process is now extremely attractive for water softening, drinking water purification, waste water reclamation, as well as industrial process fluids treatment[4–9]. Most of NF membrane was made of polymer. The organic polymer has many advantages, such as extensive sources, convenient manufacture, low cost, and easy to achieve the industrialization, but it also has the disadvantage to overcome, such as bad thermo stability,weak anti-fouling and poor anti-swelling etc. In recent years, many new kinds of organic/inorganic blend materials were explored to combine the desired properties of inorganic and organic, enhancing the thermal and mechanical properties, electrochemical and physical properties, hydrophilicity, flexibility and ductility of organic polymers[10–13].

PVC is one of the most flexible and evergreen polymers containing good chemical and environmental properties. There are some modifications enhancing of fabricated PVC membranes (NF, UF, ion exchange membrane and …) performance and properties such as modification it by SBR, PVP, PEG and CA as polymeric additives and nano-silver and iron oxide nanoparticles[14-16].

For inorganic nanoparticles, which have a higher specific area and lots of negatively charged hydroxyl groups existing on the surface, it can bring new good properties for the composite materials. Several types of inorganic materials have been used as additives in organic polymers in UF and NF membrane preparation process, which involves titanium dioxide (TiO2), zirconium dioxide (ZrO2), Al2O3[17-21]and so on. Like other materials, Silicon dioxide (SiO2) has also been widely used in filtration membrane preparation, such as PES–SiO2[22], PVA/SiO2 membrane[11]. Nano-SiO2 has a wide resource and lower price than Al2O3 and TiO2 nanoparticles.

It attempted to prepare composite PVC/PVP/SiO2 NF membranes by casting solution techniqueand phase inversion method in coagulation bath. Polyvinyl chloride (PVC) and polyvinylpyrrolidone (PVP) dissolved in N, N dimethylacetamide (DMAC) as primary polymer, pore former and solvent, respectively. The effects of addition nano-SiO2 on nanofiltration membrane performances including PWF, permeation flux,and rejection were discussed. In addition % water content, porosityand tensile strength for understanding the effect of addition of nano-SiO2 on hydrophilicity and mechanical properties of PVC/PVP membrane was measured.

EXPERIMENTAL

Materials

Polyvinylchloride grade S-7054 supplied by BIPC, was used as membrane base binder. Polyvinylpyrrolidone (PVP) from Merck was applied as pore former. DMAC from Merck was utilized as solvent. Nano-SiO2 supplied from Degussa GmbH, Germany, was used as inorganic filler additive. The distillated water was used as non-solvent (coagulation bath) for all experiments.

Feed solution

All experiments were done by solution of 2000 mg MgSO4 per one liter of distillated water as feed solution.

Fabrication of PVC/PVP/SiO2 nanocomposite NF membranes

The membranes were prepared by casting solution technique and phase inversion method in deionized water. At first stage, homogenous solutions of PVC/PVP/SiO2 with different concentration of nano-SiO2 dissolved in DMACby stirring at 7000rpm (Multi magnetic stirrer, Velp scientific model, S/N 172203, made in Europe) for 5h. The resultant homogeneous mixtures were transferred to ultrasonic cleaner for 45 min at 20$^{\text{æ\%}}$C (Parsonic11Smodel, S/N PN-88159, made in Iran)to remove entrapped air bubbles from solution and better nano-SiO2 dispersion[23]. After that,they casted onsmooth glass plates by a manual film applicator with constant thickness of 200μm. then they dipped in to the non-solvent (deionized water) as coagulation bath for immersion precipitation step at room temperature (25±2 æ%C). For extracting reminded solvent in membranes structure, they were kept in fresh deionized water 24 h before testing. The composition of the casting solutions are shown in TABLE 1.

TABLE 1 : Composition of casting solutions used in preparation of membranes

Membrane sample no	PVC (%wt)	PVP (%wt)	SiO2 (%wt)	DMAC (%wt)
1	16.5	0.5	0	83
2	16.5	0.5	0.05	82.95
3	16.5	0.5	0.1	82.9
4	16.5	0.5	0.5	82.5
5	16.5	0.5	1	82

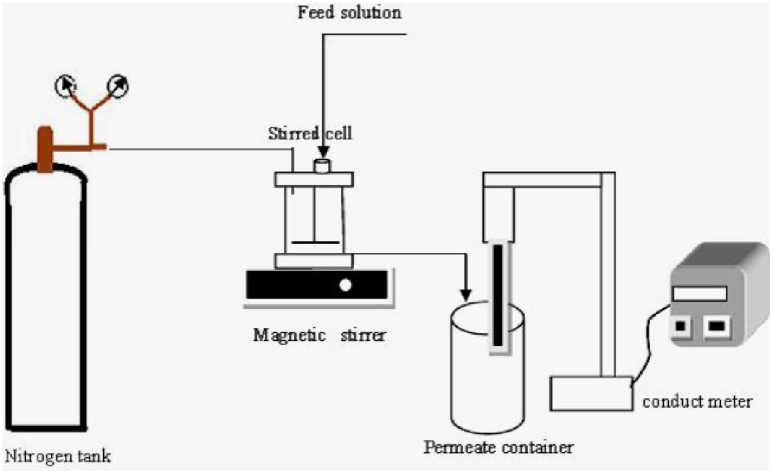

Figure 1 : The nanofiltration experimental setup

Membranes characterization

Filtration experiments

The PWF, permeation flux and rejection of the fabricated nanocomposite membranes were analyzed on the filtration stirred dead end cell withinner diameter 4.5and effective filtration area about 11.94 cm2. The schematic diagram of the experimental setup was shown in Figure 1. Circular membranes with top layer in contact feed were placed into the cell. The prepared membranes were initially pressurizedby gas nitrogen at 7bar for 20 min. PWF and permeability flux were measured by collection permeated water through membranes in a tank reservoir at 6bars as driving force and calculated by below expression[24]:

$$J_v = Q/A\ (\Delta t) \qquad (1)$$

Where J_v is water flux (L/m^{2}h), Q is quantity of permeate (L), A is membrane area (m^2) and Δt is sampling time (h). Rejection was calculated by the following equation[25]:

$$Rejection\ \% = 1 - \left(\frac{C_p}{C_f}\right) \qquad (2)$$

Where Cp and Cf are the $MgSO_4$ concentration in permeate and feed, respectively that they have measured by conductivity meter (Ohaus Corporation, S/N B143385306,U.S.A).

% water content measurements

For water content percent calculation, the weight of wet and dry of membranes were measured by a digital scale (OHAUS, Pioneer TM, Readability: 10"4 g, OHAUS Corp). Then it calculated by following equation:

$$\%Water\ content = \frac{w_w - w_d}{w_w} \times 100 \qquad (3)$$

Where w_w and w_d are wet and dry samples weight (g), respectively. For preventing of errors in water content measurements, the experiments were done three times.

Membranes porosity

For determining of average membranes porosity, following equation was used:

$$Porosity = \frac{w_w - w_d}{\rho_f V_m} \times 100 \qquad (4)$$

Where ρ_f and V_m are water density(g/cm^3) and membrane pieces volume (cm^3), respectively[26].

Mechanical properties

The tensile strength of prepared membranes was measured to investigate the effect of nano-SiO2addition on membranes mechanical properties. Measuring tensile strength has done in term of ASTM1922-03 standard that reported elsewhere[16].

RESULTS AND DISCUSSION

Characterization of the fabricated nano-composite membranes

Water content and porosity

For investigation the effect of nano- SiO2 addition to casting solution on fabricated membranes hydrophilicity, water content was measured[27]. The results of measured water content have come in TABLE 2. The comparison of values reported in this table shows increasing in water content sharply from 50.25 to 63.31 by addition of different nano-SiO2 concentration. Thus it can be resulted that hydrophilicity of nanocomposite membranes prepared blend of PVC/PVP/SiO2 is more than prepared membrane PVC/PVP without nano- SiO2. In addition, the effect of nano- SiO2 on fabricated membranes porosity (membranes structure) has described in TABLE 2, too. The results reported for membranes porosity in TABLE 2 indicates growing of macro voids in membrane sub layer by addition of nano-SiO2. Presence of materials with the same properties of non-solvent (deionized water) leads to exchanging of solvent and no-solvent faster. In this situation macro voids in membranes structure grow. In another point of view, formation of polymer-nano particles bonds, reduces polymer interaction together and makes casting film unstable. Thus phase inversion in coagulation bath happens with more rates. This type of trend has reported by others[28].

Flux

By means of equation (2), permeability flux and PWF for fabricated NF membranes were calculated. These values have shown in Figure 2. According of this fig, two types of behavior was seen by addition of nano-SiO2 to casting solution. Flux of fabricated NF membranes (both permeability flux and PWF) increases by addition of nano-SiO2 to casting solution just in samples of 2 and 3 containing of 0.05 and 0.1 % wt of nano- SiO2. After it, flux reduces in

TABLE 2 : Water content and porosity of prepared membranes

Membrane	Water content (%)	Membranes porosity (%)
1	50.25	58
2	52.03	59.5
3	57.51	64.08
4	59.42	65.9
5	63.31	68.43

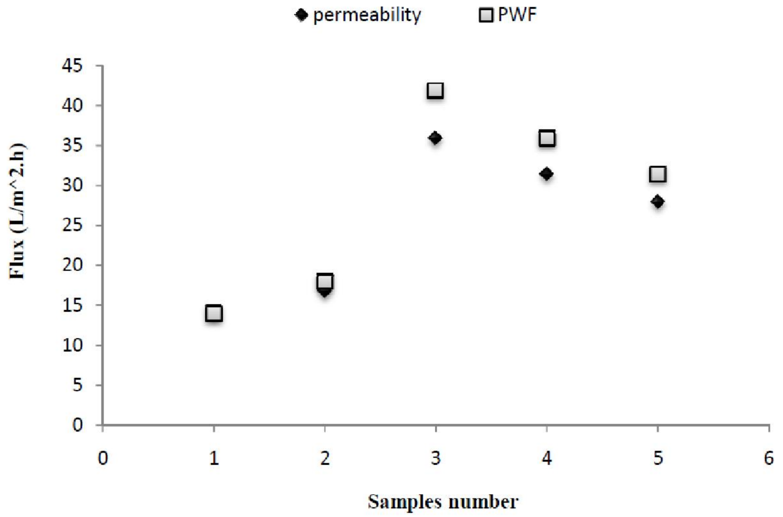

Figure 2 : PWF and permeability flux versus different nano-SiO2 concentration

samples of 4 and 5 containing of 0.5 and 1 % wt nano- SiO2. By comparison of these results, it can be resulted; addition of nano-SiO2 with 0.1 % wt in casting solution has the most effect on flux due to its good dispersion. One of the reasons for decreasing of flux in samples 4 and 5 may be related to aggregation of nano particles in these concentrations. In this situation the active surface area of nano-SiO2 decreases. Then the effects of nano-SiO2 on membrane matrix become less. Thus flux reduces. In addition, another reason of decreasing flux for membranes containing of nano-SiO2 with concentration more than 0.1 % wt, may relate to reducing of pore diameters and making pore blockage by nano-SiO2 that lead to decline in passing water from fabricated membrane and decreasing of flux[26]. In this section it should mention, the flux of sample 3 (contain of nano- SiO2 with concentration of 0.1 %wt) was about 1.5 times more than sample 1 (without nano-SiO2).

Rejection

Figure 3 shows the effect of nano- SiO2 concentration on MgSO4 rejection. As it can be seen in this fig, the percentage of rejection has increased from 34.27 in sample 1 to 43.66 in sample 3 (containing of 0.1 % nano- SiO2). It can be concluded from this Figure that presence of nano-SiO2 just with 0.1 % wt to casting solution improves rejection. It is because that nano- SiO2with adequate concentration (0.1 % wt.) in membrane matrix and surface (with completely dispersion and no pore blocking) leads to more adsorption of water during filtration process(The results of water content measurements

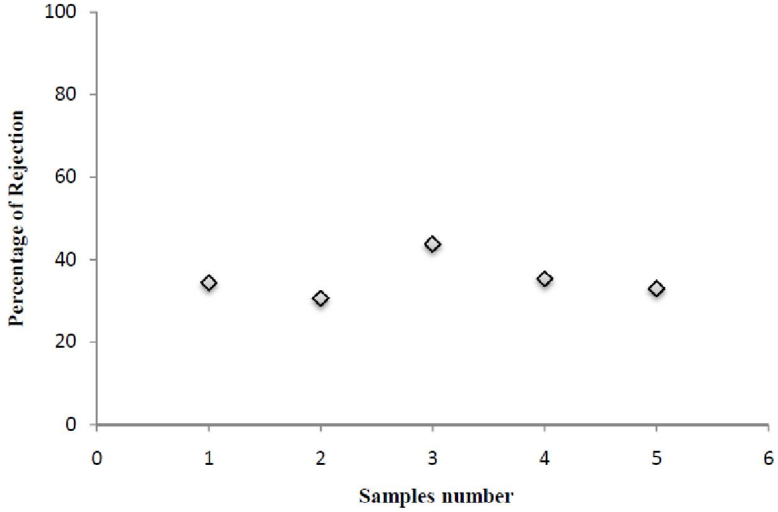

Figure 3 : Percent of salt rejection versus different nano-SiO2 concentration

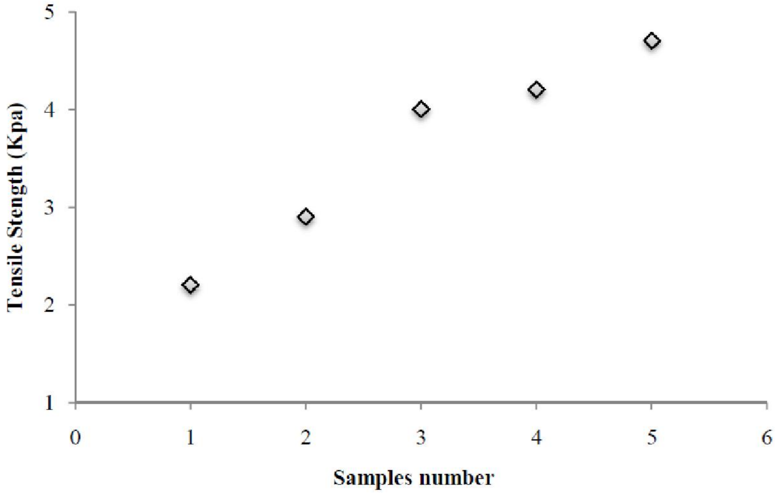

Figure 4 : The effect of different nano-SiO2 concentration on PVC/PVP membrane tensile resistance

in TABLE 3 confirmed increasing of membrane hydrophilicity by addition nano- SiO2with 0.1 % wt). In fact presence of more water in the surface of fabricated membraneleads to less accumulation of ions on membrane surface. Then rejection increases.

Tensile strength measurement

For study on mechanical properties if fabricated nanocomposite membranes, the tensile strength was measured. The results of measured tensile strength of nanocomposite membranes have come in Figure 4. This Figure indicates improving of tensile strength by addition of nano- SiO2with different concentration to the casting solution. Blending of mixed polymers (PVC/PVP) and nano- SiO2have stronger interaction in comparison of pure mixed of polymers. Then the slipping of polymer continuum on together becomes moderate. In another word, formation of PVC/PVP/nano- SiO2bonds prevents the movement of PVC/PVP molecules. Thus tumbling of PVC/PVP composition restricts. Therefore it can be resulted; presence of nano- SiO2can help membranes structure versus of strength forces.

Effect of membrane thickness on PWF

For investigate the effect of membrane thickness on flux permeated from fabricated membranes, the PWF versus different membrane thickness just for samples 1 and 3 (containing of 0 and 0.1 % wt nano-sio2) was experimented. Figure 5 shows the effect of different thickness on PWF of fabricated membranes. In this experiment driving force (operating pressure) was kept constant (6 bar). As it is clearly in this figure, while membrane thickness increases, the PWF reduces in both sample 1 and 3. By increase of membrane thickness, the resistances against of flux among of membranes increase. In fact, it is noticeable that there is a liner relationship (with negative slope) between PWF and membrane thickness. By this experiment can result that thickness has the similar effect on both samples (with and without nano- SiO2)behavior in term of pure water flux.

Effect of feed concentration on Permeability flux

Figure 6 indicates the effect of feed solution concentration on permeability flux of samples 1 and 3. As it can be seen in this figure, increasing of feed solution concentration (1000-2500mg/l) have negative effect on permeability flux. This kind of behavior is may contribute to membranes pore blockage with ions dissolved in water. Because of placing, association and accumulation of ions in membranes surface, theeffective area for passing water throughthe membrane became less. Thus, by means of increasing feed solution concentration, the number of pores in membranes structure and surface filled with ions increase and consequently, permeability flux reduces. The nano- SiO2was embedded in the organic polymer structure (PVC/PVP)makes nanofiltration structure with less dense top layer than pure membrane without nanoparticles[29]. Therefore permeability flux of sample 3 was noticeable more than pristine membrane (sample 1).

The effect of different operation pressure on PWF

Figure 7 has demonstrated the influence of driving force (operating pressure) on pure water flux.

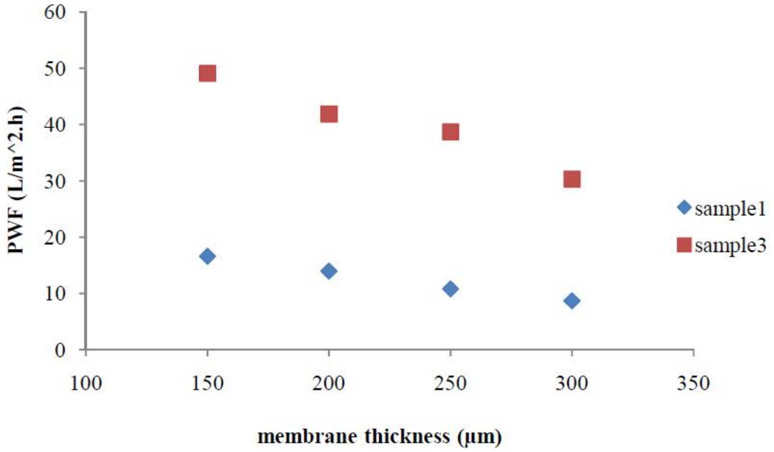

Figure 5 : The effect of membrane thickness on PWF at 6 bar as operating pressure

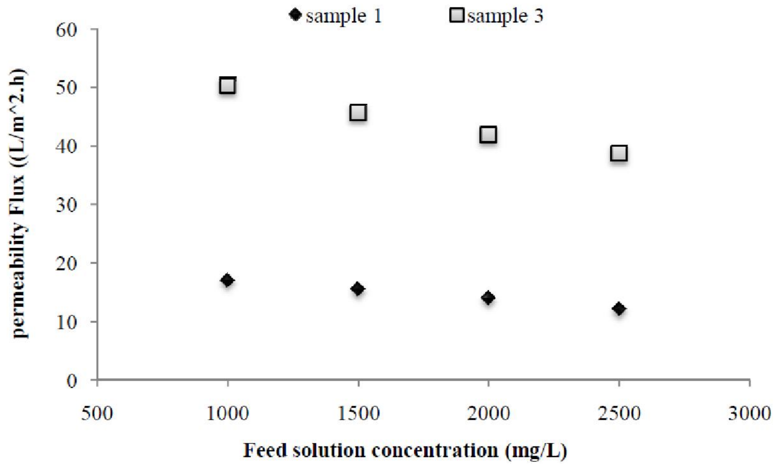

Figure 6 : The effect of feed solution concentration on Permeability flux at 6 bar as operating pressure

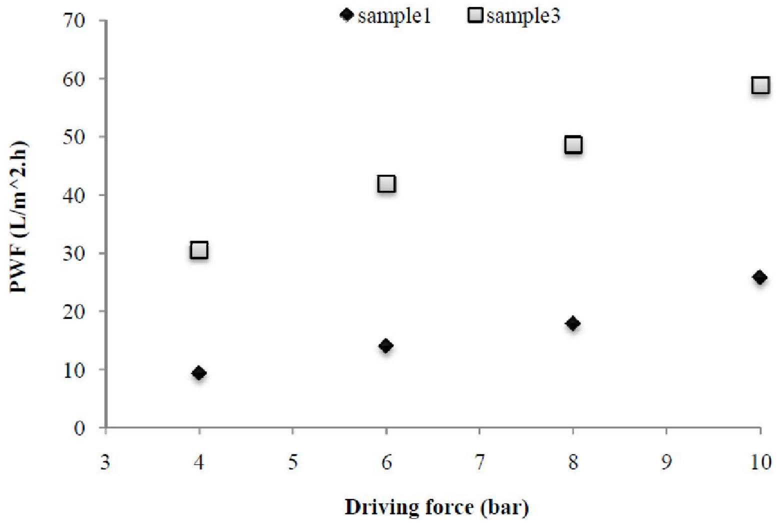

Figure 7 : The effect of different operating pressure as driving force on PWF

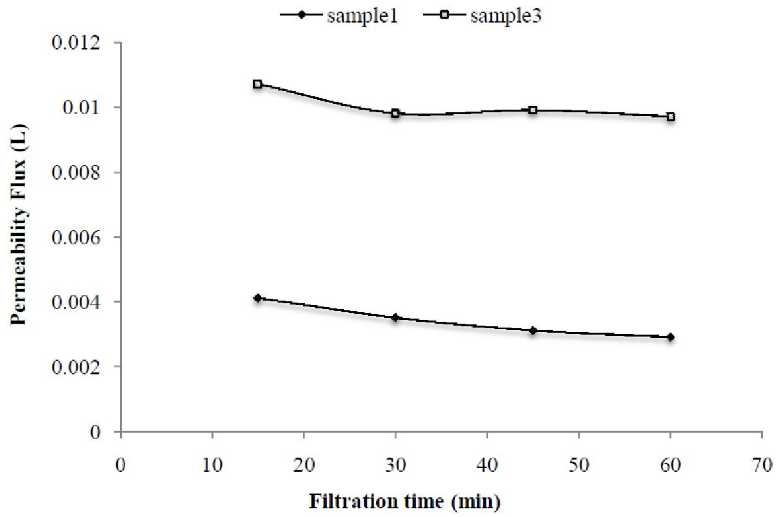

Figure 8 : Flux decline behavior versus filtration time at 6 bar operating pressure

The pure water flux of fabricated NF membrane with and without nano-SiO2 at different operating pressure was shown in Figure 7. It was resulted that the PWF was liner function of operating pressure. As it is clearly seen, the PWF of sample 3 (containing of 0.1 % wt nano- SiO2) is more than sample 1 without nanoparticles. As it mentioned in the section 3.1.1 (about increasing of water content of samples by addition nano- SiO2), its reason should be because of increasing sample 3 hydrophilicity due to existing of nano- SiO2.

Flux decline behavior

Figure 8 has displayed trend of permeability flux for sample 1 without nano-Sio2 and sample 3 with 0.1 % wt nano- SiO2versus of filtration time (min). Both sample 1 and 3 showed decline by increasing of filtration time. But as it can see, the decline of sample 1 is more significant compared to sample 3. The addition of nano-SiO2 to the membrane structureclearly has decreased fouling of sample 3 and this sample has more stability during of filtration time. In fact it can say permeability flux of sample 3 has become stable after 15 min after starting of filtration experiment. There are the same results in literature[30].

CONCLUSION

In the present research, the effect of different concentration of nano-SiO2 on PVC/PVP nanofiltration membrane was studied in terms of PWF, permeability flux, rejection, water content percent, porosity and tensile strength. The most effective nano-SiO2 concentration on flux and rejection was found 0.1 % we. The flux increased from 14 to 43 (L/m^2.h)by increasing of nano-SiO2 (from 0 to 0.1 % wt). Additional more nano-SiO2 due to pore blocking reduced flux. In concentration of 0.1 % wt nano-SiO2 rejection increased 27 percent compared to pristine membrane without nanoparticles. Water content percent, membrane porosity and tensile strength grew sharply by nano-SiO2 concentration. In addition more experiment in term of membrane thickness, feed solution concentration and operating pressure effect on flux were studied and results were reported for sample 1 and 3 (with and without nanoparticles respectively).

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