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High pressure injection technique for hypochlorite treatment of polysulfone hollow fibre membranes

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High pressure injection technique for hypochlorite treatment of polysulfone hollow fibre membranes has been developed. This technique allows injection of the hypochlorite solution into the channel of the fibres at a high pressure. The effect of this treatment on water flux of the membranes is studied. The results are compared with the water flux of identical membranes subjected to traditional hypochlorite treatment. Concentrated polymer solution containing polysulfone (PSf) /poly-vinyl pyrrolidone (PVP-K90)/*N*-Methyl-2-pyrrolidone (NMP) in weight ratio of 15/5/80 together with two types of bore fluids have been used for the production of two types of hollow fibre membranes via dry-wet-spinning process. Distilled water and mixture of NMP/ distilled water are used as bore fluids. Atomic force microscopic analysis and image processing technique (SEM microphotographs) have been employed to investigate performance of PSf hollow fibres treated with the traditional and high pressure injection techniques in relation to the composition of bore fluid. It is observed that in general both treatment methods result in the increase in water flux of the hollow fibres due to elimination of PVP (poly-vinyl pyrrolidone) swelling and alteration in pore size and pore distribution. The rate of increase in water flux in the membranes treated by high pressure injection technique is found to be higher in comparison to traditionally treated membranes. It is also found that the membranes produced using a mixture of NMP/ distilled water as bore fluid exhibit a higher rate of flux increase than those produced using distilled water. High pressure injection technique yields to production of highly permeable membranes. In addition, it is found that the composition of bore fluid controls the performance of the membranes subjected to hypochlorite treatment.

Keywords: Hollow fibre, Hypochlorite treatment, Hydraulic permeability, Pore size, Polysulfone, Water flux

1 Introduction

Hydrophilic membranes are preferential for hemodialysis therapy. Hydrophobic polymers are often blended with hydrophilic additives such as PVP (poly-vinyl pyrrolidone) to increase hydrophilicity of the compound. The preference is due to their good wettability by aqueous solutions, low proteins and macromolecules absorption which lead to lower pores fouling probability, subsequently results in both long term higher filtration rate and ease of membrane cleaning.[1,2]

Diffusive and convective mass transfer occurs across a permeable membrane during hemodialysis therapy, thus changing the composition of body fluids. Diffusive transport in addition to membrane characteristics depend also on solute molecular weight and charge, trans-membrane concentration gradients, blood and dialysis fluid flow rates. Small molecules such as urea are cleared via diffusive transport. Convection results in bulk movement of solvent and dissolved solute across the membrane, caused by the trans-membrane hydrostatic pressure gradient. Convection improves the clearance of poorly diffusible middle sized molecules such as β2-microglobulin[3]. Water flux and convection behavior of membranes are in direct relation. Hence, water flux of the membrane is of paramount importance in hemodialysis therapy.

The influence of bore fluid on water flux of hollow fibre membranes has been the subject of many researchers. It has been found that the addition of solvent into the internal coagulant significantly reduces precipitation rate and increases water permeability of the membrane[4, 5]. Yan and Lau [4] investigated the effect of bore fluid on morphology of PSf hollow fibre membranes, where the mixture of water and 1-methyl-2-pyrrolidone in various

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proportions as bore fluid was used. It was found that the precipitation rate of the inner side of the spun membrane was retarded when 1-methyl-2-pyrrolidone content was increased. Additionally the produced fibre not only had a more open wall structure but also exhibited higher flux and lower trans-membrane resistance. Guang *et al.* [5] investigated the effect of bore fluid temperature on mechanical properties of hollow fibres. It was stated that the reduction in bore fluid temperature enhances fibre tensile strength and retention power but reduces hydraulic permeability.

The influence of post-production operations such as hypochlorite treatment on properties of hollow fibre membrane has also been investigated by many workers [6-10]. Compounded polymers containing hydrophobic polymers such as PVP have been treated by hypochlorite. These treatments have effectively enhanced water flux of the membranes, because hypochlorite leaches out the hydrophobic polymers from the polymer chain, thus increasing pore size[6-10]. Jun Qin *et al.* [6] produced hollow fibre membranes from dope containing PSf/PVP-K90/DMF/1, 2-propanediol via dry-jet wet spinning process. Flux and rejection of membranes treated with hypochlorite solution of 4000 ppm over various treatment times have also been determined. Results showed that while flux of treated membranes has increased to 4.7-5.3 times, the rejection of the treated, in comparison to untreated membranes, was considerably less. Changes in pore size as well as elimination of PVP swelling due to hypochlorite treatment were also observed[6].

Despite vast and extensive studies on the effect of bore fluid and post production treatment on membrane properties, hardly any published scientific work is available that encompasses the simultaneous effects of bore fluid type and hypochlorite treatment methods on performance of hollow fibre membranes.

Therefore, a novel hypochlorite treatment method (high pressure injection technique) has been designed and its effect on water flux of polysolfune (PSf) membranes is compared with those of membranes subjected to the traditional hypochlorite treatment. The PSf hallow membranes were prepared using distilled water and mixture of distilled water/PVP as bore fluids. The simultaneous effect of bore fluid type and hypochlorite treatment on performance of treated hollow fibre membranes is also investigated for the first time. The membranes were treated by high pressure injection technique and the traditional hypochlorite treatments. Hydraulic permeability of the treated samples was measured. AFM and image processing technique (SEM microphotographs) were employed to study sample morphology.

2 Materials and Methods

2.1 Materials

Polysulfone (PSf) (MW = 30,000) , poly vinyl-pyrrolidone (PVP) (K90, MW=1,000,000) and sodium hypochlorite 4% (w/v) were supplied by Aldrich Chemical Co., Rahavard Tamin Pharmaceutical Co. and Chlor Pars Chemical Co. respectively. *N*-Methyl-2-pyrrolidone (NMP) (Merck) was used as solvent.

2.2 Production of Hollow Fibre Membranes

PVP and PSf were dried in a vacuum oven at 100°C for 24 h. PSf/PVP-K90 in weight ratio of 75/25 were gently stirred and dissolved in NMP at room temperature till a 20% wt concentrated polymer solution suitable for dry-wet spinning of hollow fibres was obtained. Two types of hollow fibre membranes (A and B) using distilled water and mixture of NMP/ distilled water as bore fluids were prepared via dry-wet-spinning process. Table 1 shows fibre spinning parameters.

2.3 Treatment of Hollow Fibre Membranes

Table 2 describes the treatment methods used in this work. In traditional hypochlorite treatment, membranes are placed in a given hypochlorite solution bath for defined time periods. In high pressure injection technique, selected hollow fibre membranes were cut to a suitable pre-defined length (150 mm). The cut fibres were embedded at both ends in an epoxy adhesive. The hypochlorite solution was injected into the channel of the fibres at defined

Table 1—Hollow fibre membranes spinning parameters

Parameter	Value
Dope composition	PSf/PVP-K90/NMP(15/5/80)
Dope flow rate	3 mL/min
Bore fluid flow rate	0.2 mL/min
Air gap	30 cm
Take-up speed	10 m/min
Coagulant temperature	27 ± 0.5°C
External coagulants	Distilled water
Bore fluid	Type (A)- Distilled water Type (B)- NMP/ distilled water (50/50)
Spinneret dimension	i/d=0.3 and o/d=0.6 mm
Spinneret temperature	20° ± 0.5°C
Bore fluid temperature	20° ± 0.5°C

pressure(30 psig) over a range of time using apparatus as shown in Fig.1.

In this study, 150 mm long hollow fibres were prepared and then embedded in an epoxy adhesive at both ends. NaOCl 4% (w/v) was injected into the fibre channels at a pressure of 30 psig for 10-60 min.

2.4 Morphological Study of Hollow Fibres

In order to obtain clear-cut fibre cross-section, samples were immersed in liquid nitrogen prior to being fractured. Structural and morphological investigations of the samples were carried out using SEM microphotographs of the fibre cross-section by Philips×I30 equipment at an accelerating voltage of 15 kV. Series of 600 by 200 pixels micrographs was prepared. The prepared micrographs were composed of 256 grey levels. Binary transformation of the micrographs was carried out at threshold level *T*. The binary transformation of fibre cross-section micrographs must be done delicately so that details of SEM such as pores and solid parts are not omitted. For this reason, SEM micrographs were divided into blocks of 10 by10 pixels. The blocks were transformed to binary format using the following Eq.(1). The binary transformed blocks were joined together, and a basic image was created. The equation used for binary transformation is given below:

$$B_i = \text{mean} - \frac{\text{SD}}{2} \quad \ldots (1)$$

where B_i is the binary threshold; mean, the average numerical value of image pixels; and *SD*, the standard deviation of image pixels' value. The ideal 10 by 10 block size and threshold value were obtained by repeating the binary transformation operation so that the transformed blocks with least deleted pores or solid parts were obtained.

Image processing was followed by labeling of the pores in the basic image using the Matlab 2011A watershed algorithm. Mean area and size distribution were calculated by counting each pore pixel and the porosity was calculated using the following equation:

$$\varepsilon = \frac{n}{N} \quad \ldots (2)$$

where ε is the porosity; *n*, the total pores pixels number; and N, the total binary image pixels number.

Table 2—Post-treatments methods

Method	Treatment symbol	Description
A_x (HPI)	A_{10}, A_{20}, $A_{30,}$ $A_{40,}$ $A_{50,}$ A_{60}	Treatment times = 10,20, 30, 40,50,60 min Pressure = 30 psig Number of fibres = 6 Cut length of fibres = 150 mm Effective length of hollow fibres = 100 mm
B_x (Traditional)	B_2, B_4, B_6 B_8, B_{10}, B_{12}	Treatment times= 2, 4, 6,8,10, 12 h
C	C	Treatment A_{60} + Treatment B_{12}

Subscript denotes treatment time.

2.5 AFM Study

Atomic force microscopy (AFM) is the universally accepted technique used for the morphological investigation of membrane surface. Membrane surface morphology is expressed in terms of mean surface roughness (R_a). AFM can provide an approximate evaluation of R_a. In this work, interior and exterior surfaces of samples were studied using Bruker-Nanos digital instruments AFM.

2.6 Hydraulic Permeability Measurements

Hydraulic permeability of hollow fibre membranes was investigated. For this purpose, a simplified experimental system employing dialyzer mini-modules as represented in Fig. 2 was use[11]. When

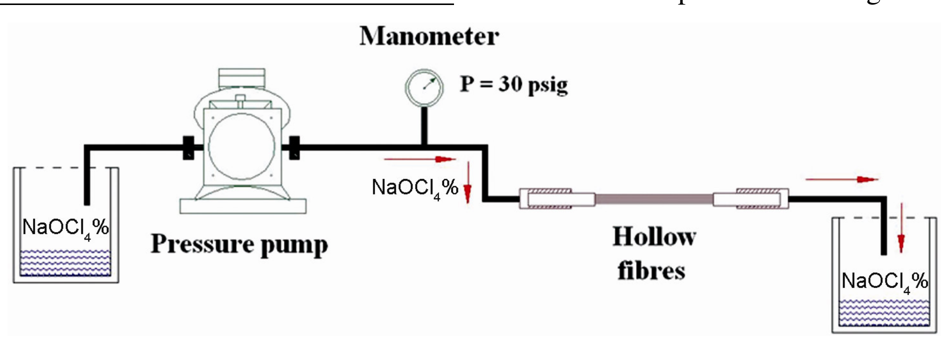

Fig. 1—High pressure injection technique of hypochlorite treatment and apparatus

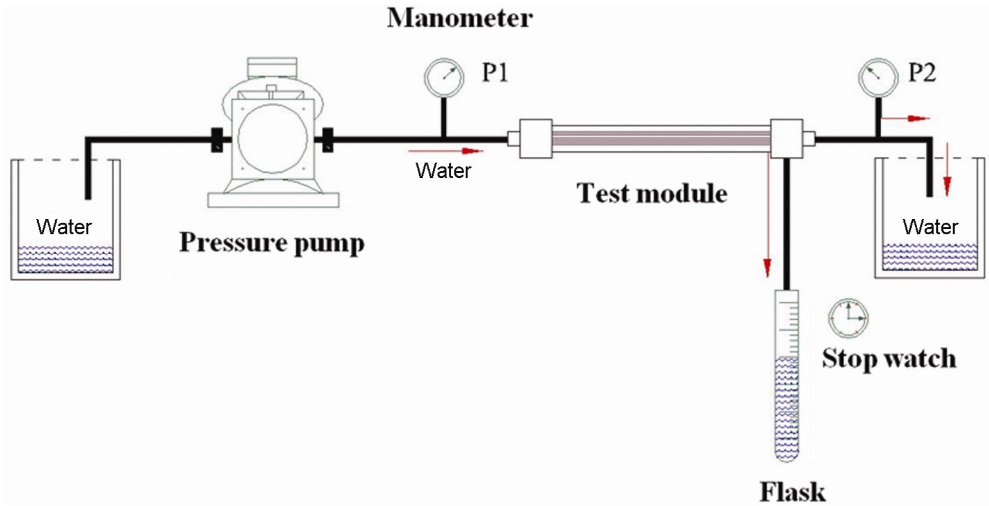

Fig. 2—Schematic diagram of hydraulic permeability (L_p) testing apparatus

pure water is following equation yields to hydraulic permeability (L_p):

$$L_p = \frac{\Delta V / \Delta t}{P\, A} \qquad \dots (3)$$

where V is the ultra-filtrate volume during time interval t; P, the average trans-membrane pressure; and A, the total membrane surface area determined using following equation.

$$A = n.\pi.(id) \qquad \dots (4)$$

where L is the effective hollow fibre length; π, the Pi constant; n, the number of fibres in the test module; and (id), the inner diameter of each hollow fibre.

In order to measure hydraulic permeability of the fibres, six selected hollow fibres were cut to a length of 150 mm. Fibres were embedded in epoxy adhesive at both ends so that an effective length of 100 mm is existed between the two ends of the test mini-module. Water permeation flux in the permeate side was measured at 20 °C.

3 Results and Discussion

3.1 Morphological Study of Hollow Fibres

3.1.1 Effect of Bore Fluid Type on Untreated Membrane Structure

Using the SEM microphotographs, the internal and external diameters of the membranes are found to be 200 and 380μm respectively. SEM cross-section micrographs of untreated hollow fibres produced using distilled water and mixture of NMP/ distilled water as bore fluids are shown in Fig.3. It can be seen that both membranes simultaneously encompass sponge-like and the finger-like micro-structures. However, sponge-like structure in membrane produced using mixture of NMP/ distilled water as bore fluid is more pronounce than the membrane formed by distilled water as bore fluid. This is due to possible retardation of the precipitation rate in the inner side of the nascent membrane which suppresses the formation of macro voids and finger-like pores. When distilled water is used as internal bore fluid, the solvent and non-solvent exchange rate on the inner and outer surfaces is nearly equal. This results in formation of porous structures known as sandwich structure. Figure 3 also indicates

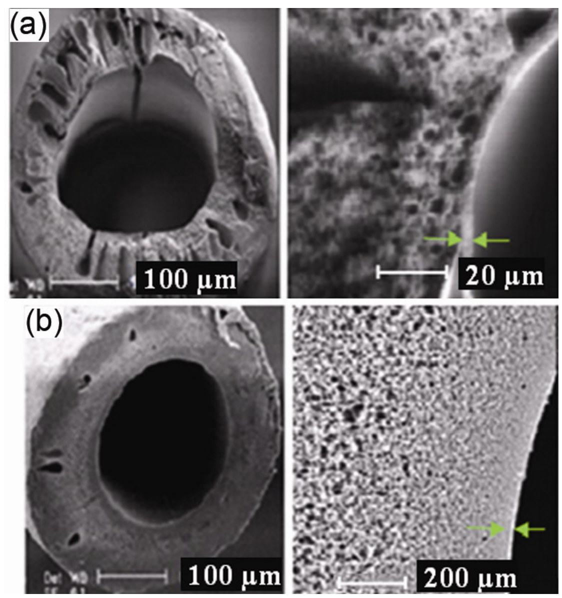

Fig. 3—SEM microphotographs of untreated hollow fibres [(a) Bore fluid - distilled water and (b) Bore fluid -NMP/ distilled water]

that asymmetric structure forms when mixture of NMP/ distilled water is used as bore fluid. Cross-section of the hollow fibres consists of two dense layers and one porous layer. Results show that the relative position of the macro voids depends upon the composition of bore fluid. While in case of distilled water, macro voids are encapsulated by the two dense layers, in case of NMP/ distilled water, macro voids are positioned near the outer dense layer. In the case of NMP/ distilled water, dense layer on the lumen side tends to disappear. The thickness of the dense layer on the lumen side of the hollow fibre produced using a mixture of NMP/ distilled water as bore fluid has been measured and is found to be approximately 1 μm. This value is half of that of the hollow fibre membrane produced using distilled water.

3.1.2 Effect of Treatments on Membranes Structure

Figure 4 shows the SEM microphotographs of cross-section of the untreated, high pressure injection technique (A_{60}) and traditional (B_{12}) hypochlorite treated membranes produced using distilled water (Type A) and NMP/ distilled water (Type B) as bore fluids. Initial microphotographs and binary images of cross-section of untreated, high pressure injection technique (A_{60}) and traditional (B_{12}) hypochlorite treated membranes produced using distilled water and NMP/ distilled water as bore fluids are shown in Fig. 5. The hollow fibres cross-section morphological parameters evaluated from image processing analysis such as mean and standard deviation of pore size and porosity are listed in Table 3. It is clear that both hypochlorite treatments tend to increase pore size and porosity of both membranes. However, enlargement rate in type (B) membrane is higher than in type (A). Pore size distribution of both types of membranes is improved after both hypochlorite treatments. This is in line with findings of previous researches confirming the removal of PVP from the matrix by the hypochlorite treatment and the noticeable enlargement of the pores.[6-10]

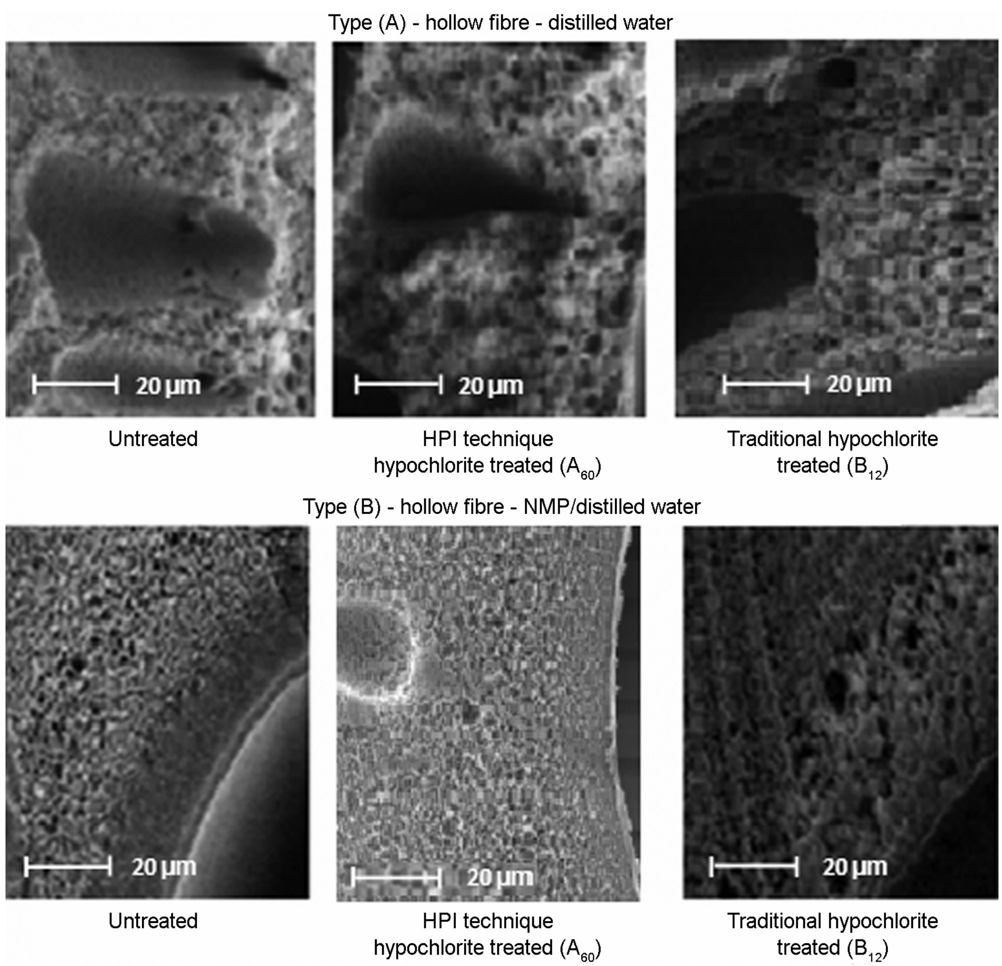

Fig. 4—SEM microphotographs of treated membranes using two different bore fluids Bore fluid_Distilled water

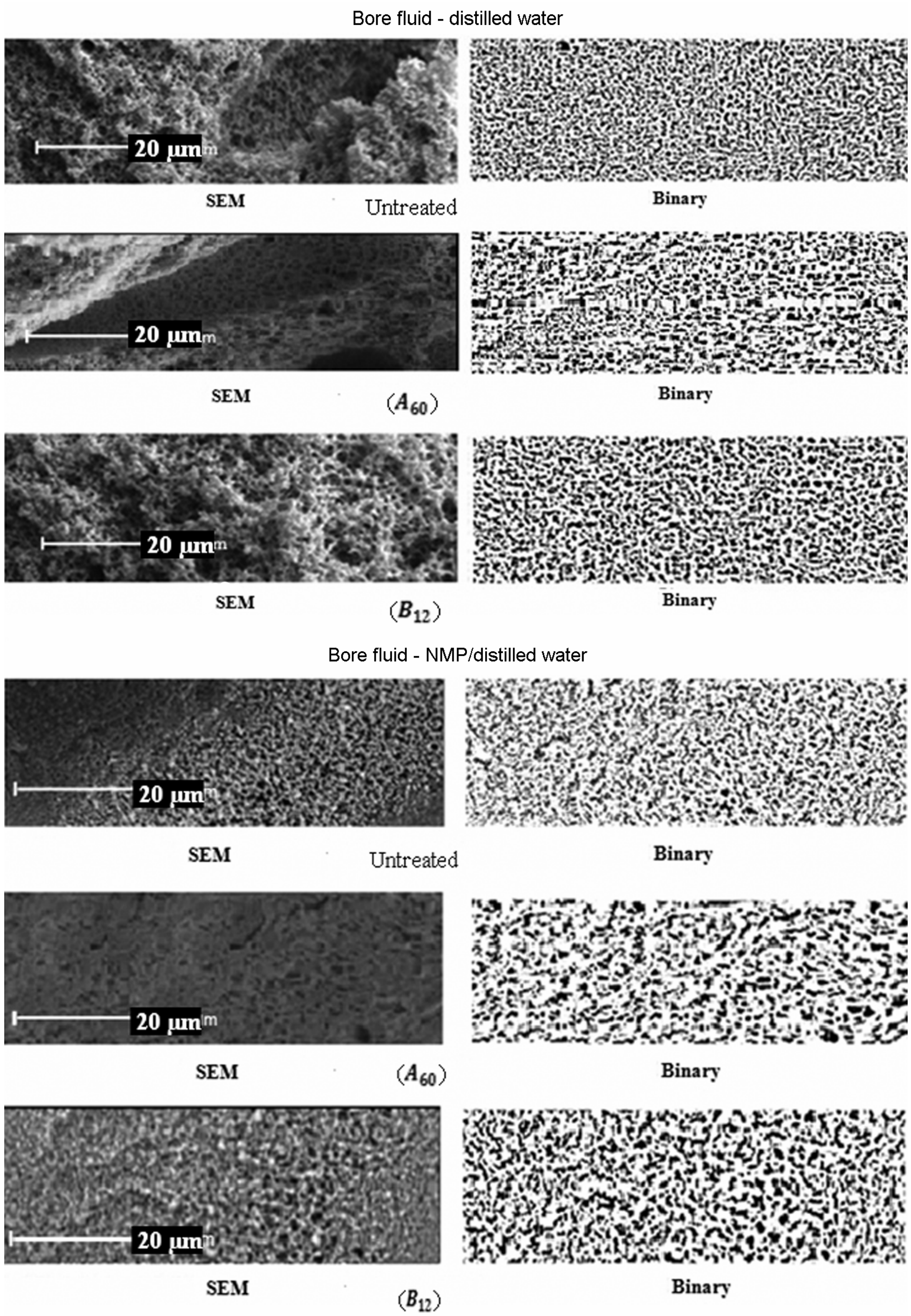

Fig. 5—SEM microphotographs and binary images of hollow fibre cross-section

Table 3—Morphological parameters of hollow fibre membranes

Treatment	Mean pore size, pixel	Mean pore area, µm^2	Pore size STD	Pore size CV%	Porosity, %
(A)-Untreated	21.4789	0.2147	30.4565	25.69	32.18
(A)-A_{60}	26.2401	0.2624	36.3031	22.96	32.31
(A)-B_{12}	28.7371	0.2873	42.512	22.69	32.65
(B)-Untreated	27.6705	0.2767	48.5612	25.18	32.13
(B A)-A_{60}	31.5678	0.3156	51.4436	22.72	32.24
(B)-B_{12}	42.4118	0.4241	79.3001	21.00	32.40

3.2 AFM Observation

Figure 6 shows 3D AFM images of inner and outer surfaces of untreated and treated hollow fibres produced using distilled water and NMP/ distilled water as bore fluids respectively. Roughness characteristics of the membranes surfaces are described in Table 4.

Table 4 shows that rougher inner surface is obtained when mixture of NMP/ distilled water is used in comparison to distilled water. This can be attributed to the formation of larger pores when mixture of NMP/ distilled water is used. Fibre

Table 4—Roughness characteristics of untreated and treated hollow fibres

Treatment	Type (A)		Type (B)	
	Outer surface roughness nm	Inner surface roughness nm	Outer surface roughness nm	Inner surface roughness nm
A_{60}	11.9	14.4	13.5	19.5
B_{12}	21.3	32.21	22.5	38.72
Untreated	9.2	8.94	9.68	10.54

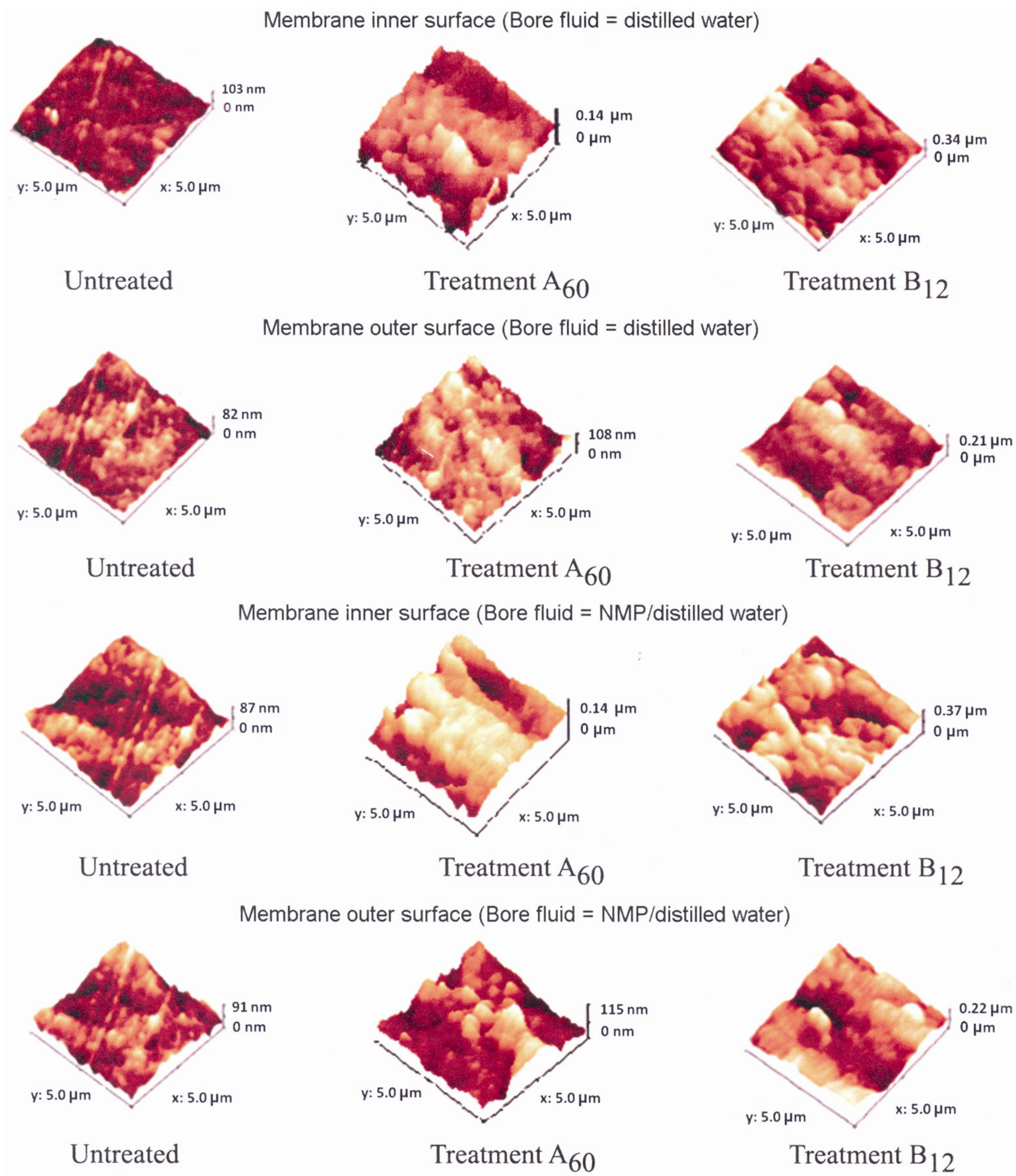

Fig. 6—AFM (3D) images of the inner and outer surface of untreated and treated membranes

formation is based on solvent/non-solvent exchange mechanism. The use of distilled water as bore fluid due to significant concentration gradient results in rapid exchange mechanism. Exchange mechanism is significantly slower when bore fluid contains solvent. Despite differences in roughness of the inner surfaces, the roughness of the outer surfaces of the two types of hollow fibres is almost identical.

Table 4 also shows the intense roughness of inner and outer surfaces of both hollow fibre membranes subjected to HPI technique and the traditional hypochlorite treatment. This is due to the increase in pores dimension as a result of PVP removal. AFM results also show that the increase in inner and outer surface roughness of Type (B) treated hollow fibre is much higher than in Type (A). This can be attributed to the effect of NMP solvent on inner surface morphology of type (B) fibre.

3.3 Hydraulic Permeability

The measured hydraulic permeability of the treated and untreated hollow fibre membranes are listed in Table 5.

3.3.1 Effect of Bore Fluid Type on Untreated Membrane

Table 5 shows membrane prepared by bore fluid containing NMP exhibits better permeation performance than membrane prepared by NMP free bore fluid. Measured hydraulic permeability of the membrane produced by mixture of NMP/ distilled water as bore fluid is found to be 8.01 E -8, which is higher than the hydraulic permeability of 5.60 E -8, obtained by using distilled water as the bore fluid. This implies that the structure of hollow fibre is the key factor affecting hydraulic permeability behavior of the membranes. The existence of macro voids in the fibre structure is not desirable. Higher presence of the macro voids in Type (A) membrane probably tends to deteriorate the permeation performance. Salient permeation performance of the hollow fibre membrane produced by mixture of NMP/ distilled water as bore fluid is also related to the thinner effective thickness of the dense layer on the lumen side.

Table 5—Hollow Fibre Membranes Hydraulic Permeability

Treatment	L_p , cm/smmHg	
	Fibre type(A)	Fibre type (B)
Untreated	5.60E-08	8.01 E -8
A_{10}	6.27E-08	1.00E-07
A_{20}	6.94E-08	1.13E-07
A_{30}	8.13E-08	1.37E-07
A_{40}	9.05E-08	1.73E-07
A_{50}	1.08E-07	2.17E-07
A_{60}	1.30E-07	2.60E-07
B_2	9.64E-08	1.63E-07
B_4	1.13E-07	2.00E-07
B_6	1.24E-07	2.37E-07
B_8	1.37E-07	2.89E-07
B_{10}	1.49E-07	3.47E-07
B_{12}	1.58E-07	4.00E-07
C	2.60E-07	1.04E-06

3.3.2 Effect of Bore Fluid Type on Treated Membrane

Results show that, in general, the measured hydraulic permeability of the membranes treated by high pressure injection technique hypochlorite treatment over time range of 0 – 1 h significantly increases. Considering the results shown in this Table 5, it can be deduced that the measured hydraulic permeability of the treated hollow fibre Type (A) membrane and treated hollow fibre Type (B) membrane is nearly 2.3 and 3.2 times more than those of untreated membranes respectively. It can be seen that the measured hydraulic permeability of the hollow fibre Type (B) membrane treated for 12 h is nearly 5 times more than those of untreated membrane. The increase in flux rate is found to be approximately 2.8 times higher for type (A) membrane.

In general, hydraulic permeability of the two types of membranes subjected to the HPI technique and traditional hypochlorite treatments has significantly increased. However, increase in the rate of flux of membrane Type (B) is higher than that of Type (A) due to the use of these treatments. This is in line with finding of other researches[6-10] and confirms that water flux of membranes increases by treatment with hypochlorite due to removal of PVP. In this work higher rate of water flux in comparison to the previous researchers is obtained due to use of higher concentration of NaOCl.

Table 5 also shows that the measured hydraulic permeability of the membranes treated by high pressure injection technique hypochlorite treatment after 1 h is nearly equal to measured hydraulic permeability of the membranes treated by the traditional hypochlorite treatment after 6 h. The increase in the rate of flux of high pressure injection technique hypochlorite treated membranes is higher than those of traditional hypochlorite treated membranes. high pressure injection technique hypochlorite method removes PVP and noticeably enlarges the pores located on dense lumen side of fibres. This is due to contact of high pressure flow of hypochlorite with effective layer of the lumen side.

In treatment C, initially the hollow fibre membranes are subjected to high pressure injection technique hypochlorite treatment for 1 h followed by the traditional hypochlorite treatment for 12 h. Table 5 shows that the measured *L*p values for treated hollow fibres Type (A) and Type (B) membrane are 2.60E-07 and 1.04E-06 cm/s mmHg respectively. These are nearly 4.6 and 13 times higher than those of untreated membranes. It is clear that the increase in rate of flux of the hollow fibre membrane subjected to this treatment is much higher than those in hollow fibre subjected to either treatment A_{60} or B_{12}. This is due to combine effect of high pressure injection technique and the traditional hypochlorite treatment, which enhances water flux of the membranes, composed of blend of poly-vinyl pyrrolidone (PVP).

4 Conclusion

It has been found that fibre structure affects membrane hydraulic permeability. PSf hollow fibre membrane produced by mixture of NMP/ distilled water as bore fluid exhibits a higher rate of flux than those produced by distilled water. Asymmetric structure is formed when mixture of NMP/ distilled water is used. This is found to be due to unequal rate of exchange on inner and outer surfaces of hollow fibre and also reduction in formation of macrovoids and finger-like pores as a result of rapid solvent/non-solvent exchange mechanism.

As far as roughness of inner surface of the fibres is concerned, it is stated that the use of NMP/ distilled water as bore fluid results in intense roughness and larger pores of the inner surface in comparison to that obtained using distilled water as bore fluid. The membrane prepared using bore fluid containing NMP exhibited better permeation performance than that prepared using NMP free bore fluid.

High pressure injection technique and traditional hypochlorite treatments are not only found to be responsible for the increase in pore size and porosity, but also increases water flux of the membranes. However, it is found that the increase in rate of flux of high pressure injection technique hypochlorite treated membranes is higher than that of traditional hypochlorite treated membranes. It is established that high pressure injection technique of hypochlorite treatment is a successful tool for the enhancement of water flux of membranes. Removal of PVP resulted in rapid enlargement of the pores on the dense lumen side. It is found that the contact of high pressure hypochlorite flow with lumen side not only causes rapid enlargement of pores but also tends to increase the flux at a higher rate in the membranes treated by high pressure injection technique method in comparison to those treated by the traditional method.

It is concluded that hydraulic permeability of the hollow fibres significantly increases by simultaneous use of high pressure injection technique or the traditional hypochlorite treatments. However, combination of these methods is found to profoundly enhance flux of PSf membranes composed of blend of PVP. It is found that this method is an effective means of improving the convection behavior of hollow fibre membranes, thus the method can yield to production of high flux hollow fibre membranes.

Results also pointed out to the fact that properties of PSf hollow fibre membrane can be greatly influenced by the composition of bore fluid. In this regard, bore fluid composition can be considered as the most influential factor that controls the inner surface topology. Additionally, it is found that the composition of bore fluid improves performance of the membranes subjected to a particular treatment.

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