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Functional analysis of cellulose acetate flat membranes prepared via casting technique

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ABSTRACT

Cellulosic membranes reflect better utilization of renewable resources with minimum impacts on the environment. Significant market for medium pressure application is encountered in water filtration and reclamation. Thus, endeavors are needed to balance advancement of cellulose membrane and manufacturing technology modification. Cellulose membranes have been prepared via phase inversion process from different blends of polymers/solvents/additives. The casting solutions comprising polymer concentration range from 15 to 25 wt%, and acetone, tetrachloroethane and N,N dimethyl formamide as solvents. Different samples of membranes have been prepared and tested using polymer with different acetyl contents. The prepared membranes have been characterized using scanning electron microscope (SEM). Further, performance indicators comprising: flux, operating time, permeability and selectivity has been investigated according to casting solution constituents and membrane matrix morphology. Operating pressures up to 50 bars has been applied. The results indicate that the appropriate polymeric content has been found to be between 20% and 22%. Enhanced performance is also observed in the presence of both polymethylhydrosiloxan (PMHS) and dibutyl phthalate (DBP) denoting better salt rejection. Almost all prepared membranes, could tolerate operating pressures up to 50 bars.

Keywords: Cellulose acetate; Flat membranes; Membrane preparation

1. Introduction

RO membranes are classified as cellulosic and noncellulosic. The formers are made of either cellulose nitrate, cellulose acetate (CA), cellulose triacetate (CTA) or blend of both. Non-cellulosic membranes are formed from a variety of polymers that includes polyamide [2,3], polysulfones [14,15] and others. The most common is the aromatic polyamide membrane, which have the advantages of high rejection capability for salts and organics and are resistant to biodegradation [1,11,20 16].

Several investigators have focused on the development of CA membrane for RO application, which has the advantage of chlorine stability and good salt removal capabilities; however, it is not highly stable against microbial attacks [5,13]. The conventional process for membrane fabrication depends on polymeric mix casting, solvent evaporation, and phase inversion (e. g. immersion in solvent bath). The techniques adopted for preparation of such membranes have been described by [2,4,9,10,17,22].

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Various mechanisms explaining the skin formation of CA membrane have been summarized by [6,7,18,4]. They have addressed the importance of investigating optimum casting solution compositions. Other investigators emphasized the influence of physical conditioning (e.g. mixing, casting, immersions and annealing) on membrane performance [12,19,21]. The influence of polymers type and concentration on membrane performance, flux and rejection, have been studied by Suryo [23], Ani [25] and [26,27]. They have revealed that optimum polymer concentrations have been in the range of 25% and 27.5%, (for both polysulfone and cellulose acetate) where higher concentration gives higher rejection rates of up to 97%. This has been in agreement with Idris [24]. Moreover, studies have been performed to investigate rehological analysis of casting solutions as reported by Idris [27]. It has been concluded that, increase in shear rate has resulted in increase in the salt rejection and flux for flat sheet RO membranes.

The aim of this work is to develop flat CA membrane for RO purposes via wet casting technique depending on using CA derivatives with varying acetyl content using single or mixed solvents. Controlling parameters of the casting process, characterization and performance of the developed membrane have been investigated.

2. Material and equipment

2.1. Material

Cellulose acetate (CA) with 39.7% wt acetyl content, average M_n ca 30,000, lab. grade Aldrich Inc. Cellulose Tri-Acetate (CTA) has also been used with M_n 72,000-74,000 Fluka chemika. .Dibutylphathalat (DBP) with density (1.045-1.047 at 20°C), Merck, Acetone, 1,1,2,2-Tetrachloroethane (TCE), N,N Di-Methyl Formamide (DMF), Methanol and Polymethylhydrosiloxan (PMHS) have been purchased from Sigma Chemicals, ADWC, Merck, Fluka – Chemika, Fisher scientific and Aldrich, USA solution, FP 204 respectively. Moreover, the minimum assay for all chemicals used is more than (99%).

2.2. Equipment

The equipment used for experimental set-up and membrane testing and evaluation comprises: Mixing tank equipped with mechanical stirrer (Heidolph instrument model RZR1, Germany) with average velocity between 100 and 2200 rpm, Doctor Blade, glass plate, glass flit applicator, Scanning Electron Microscopy (SEM) ISM-840. Membrane Testing Apparatus (which comprises 3-compartments membrane cell housing supplied with high pressure pump that creates pressure up to 120 bars) and a Digital/ Calibrator (Measurement of membrane thickness), Mitutoyo, Japan.

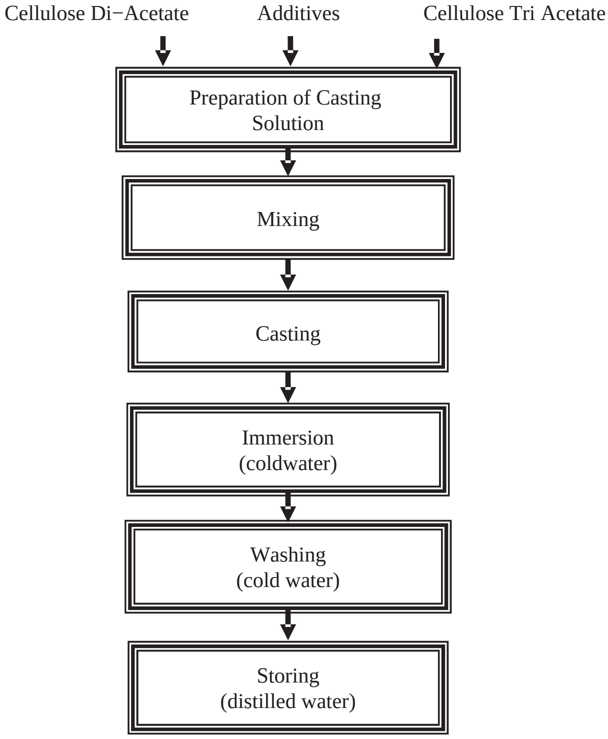


Fig. 1. Process block flow diagram for preparation of cellulose acetate membrane by casting.

3. Experimental setup

Block flow diagram of membrane preparation process is depicted in Fig. 1. The steps adopted are summarized as follows.

3.1. Preparation of casting solution

Different casting solutions have been prepared containing different blends of cellulose acetates with varying acetyl contents. Different solvents have been tried ranging from single to mixed solvents with different blending ratios. The casting solution has been thoroughly mixed at temp between 10 and 15°C to obtain the desired homogeneous solution. Table 1 depicts casting solutions matrix that includes cellulose polymers as the basic materials.

3.1.1. Casting

The casting solution is casted into glass plate using doctor blade withdraw down thickness between 10 and

Table 1
Casting Solution Composition

Membrane	CTA	CA	Acetone	TCE	DMF	Water	PMHS	DBP
Sample	%	%	%	%	%	%	%	%
M1		20	76			4		
M2	5	15	60	20				
M3	5	15	40	20	20			
M4	15	5	20	60				
M5	4.5	15	40	20	20		0.5	
M6	10	10	40		40			
M7	10	10	30	40	10			
M8	10	10	40	40				
M9	8	12	48	32				
M10	8	12	32	32	16			
M11	8	12	30.5	30.5	15		2	2
M12	8	12	32	31	15		2	

50 μm to form flat membranes at time range between 5 and 10 min.

3.1.2. Immersion

The glass plates are immersed into a coagulation bath containing pure water and methanol at a temperature ranging from 10 to 15°C for 30 and 180 min.

3.1.3. Washing

The glass plates are immersed into washing bath containing distilled water at a temperature between 10 and 15°C.

3.1.4. Storage

Cellulose sheets are stored in distilled water bath after addition of formalin at slightly acidic pH (5.5).

3.2. Membrane characterization

Prepared membranes have been characterized for surface morphology, sheet thickness and pore radii.

3.3. Performance evaluation

Performance evaluation including operating pressure and relevant flux indicators have been investigated using apparatus shown in Fig. 2. It consists of three compartments flat membrane testing cells, supplied with stainless steel membrane supports, feed tank with level indicator, high pressure pump, measurements and control instruments.

4. Results and discussion

4.1. Membrane characterization

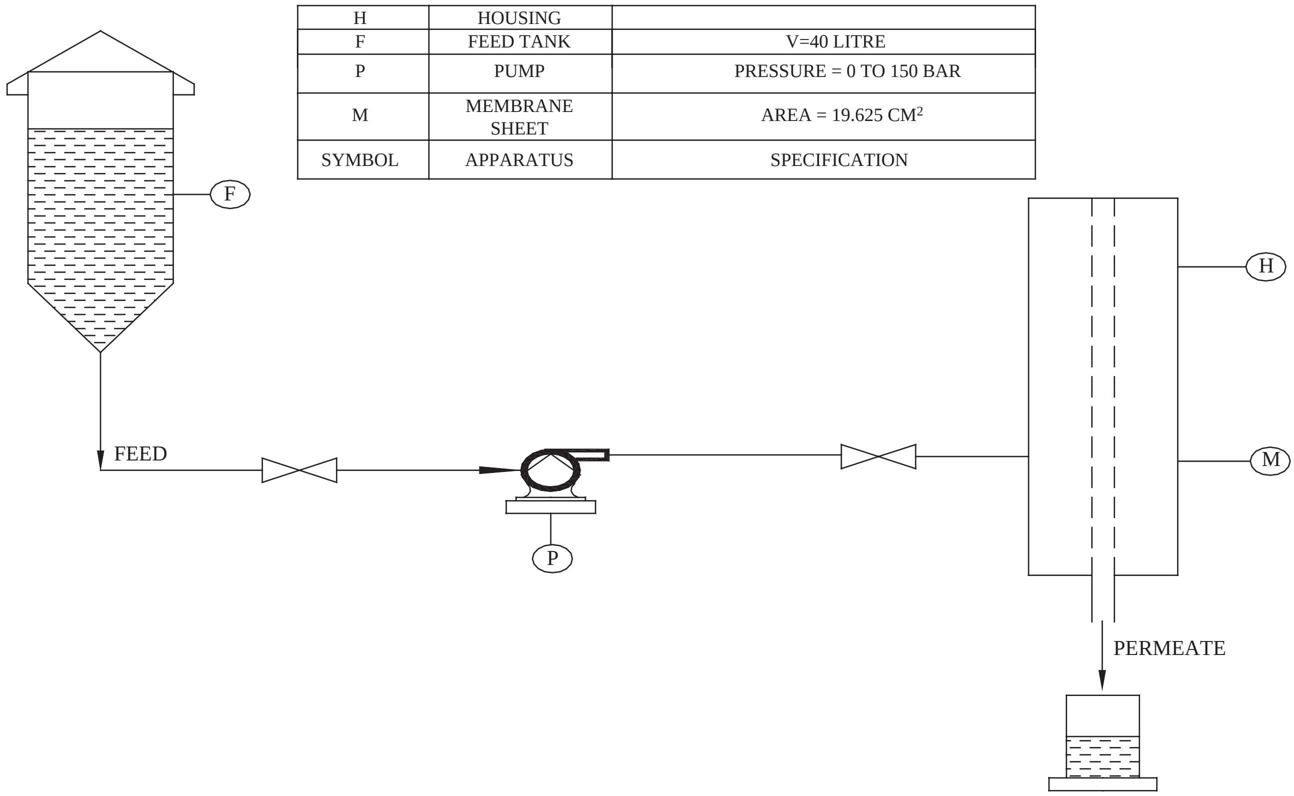
4.1.1. Morphology and thickness

Thickness of the prepared sheets have been draw down and measured to be 20 μm while the surface morphology is shown in Fig. 3. SEM for M1 depicts rather uniform surface with no apparent micro cracks. Due to the presence of DMHS as an additive the SEM of M5 depicts noticeable pores than the surface morphology of M3 that manifests relatively tight openings. M10 shows a typical smooth surface with apparent uniform size. Surface photograph of M11 manifests micro roughness with irregular apparent pores.

4.2. Membrane performance

4.2.1. Operating pressure

All membrane sheets have been tested to operate under pressures up to 70 bars. The results indicate that: the max applied pressure, without cracking, has been found to be up to 40, 35 and 35 bars for casting solution M1, M3, and M5 respectively. The maximum tolerated pressure approaches about 70 bars for membrane samples M10, M11 and M12 respectively. It has been found that, the separation of salt increased approaching the max removal at pressure (50 bars). For feed salinity of 14,000 ppm the salt rejections are 25%, 45%, 69%, 73%, 93% and 94% for membrane samples: M1 M3, M5, M12, M11 and M10, respectively. The differences are related to pores structure and pores size distribution which is in agreements with reported trends [8]. Further, superior performance and higher rejection has been noticed for samples blends of cellulose acetate and triacetate with 3: 2 ratios that has been concluded also by Idris [24].



H	HOUSING	
F	FEED TANK	V=40 LITRE
P	PUMP	PRESSURE = 0 TO 150 BAR
M	MEMBRANE SHEET	AREA = 19.625 CM^2
SYMBOL	APPARATUS	SPECIFICATION

Fig. 2. Schematic diagram of the experimental apparatus setup.

4.2.2. Flux

The time dependence of flux of the prepared membranes is shown in Fig. 4. Membranes samples M3, M12 manifest low initial flux, followed by sudden increase after about 50 min (to above 100 $m^3/m^2/h$). Generally, all membrane samples have been characterized by relatively low initial flux that increases with the operating time. The pores structure of the membrane reflects heterogeneous dynamic surface morphology. The pores structure needs about 40 min to manifest almost full widths. The relatively high flux seems to cause partial locking and consequently lowering flux value after about 100 min. It is also noticed that M11 manifests lower flux as compared with M12 which may be due to the presence of DBP. This is may be due to DBP made the membrane structure denser as follows the smallest free volume between the polymer chain (interchain) this reason made the flux of the M11 was lower than the flux of the M12 [23].

The polynomial equation that characterizes membrane flux has been generally expressed as a fourth order polynomial equation that has been formulated as follows:

$$Y = at^4 \pm bt^3 \pm ct^2 \pm dt \pm e \qquad (1)$$

where Y is membrane flux in $m^3/m^2/h$, t is operating time in min and a, b, c, d, e, are constants denoted for every membrane sample as follows:

Sample no.	a	b	c	d	e	R^2
M1	3E−06	−0.0006	0.03	0.69	−2.5	0.98
M3	6E−06	−0.002	0.2	−4.7	13.4	0.95
M5	−3E−06	0.0005	−0.02	0.38	−0.04	0.99
M10	6E−06	−0.0017	0.1	−2.6	6.1	0.8
M11	5E−06	−0.002	0.18	−3.8	9.1	0.97
M12	−1E−06	9E−05	0.009	0.16	−2.1	0.95

Except for M10, equation prediction (denoted as solid lines) and experimental results (denoted as scattered points) indicate good agreement for the initial and tail values while it is rather deviated at medium values. This mathematical equation is valid for operating time up to 140 min at pressure 30 bars.

4.2.3. Rejection

Membrane desalting efficiency has been investigated as a function of operating time for selected

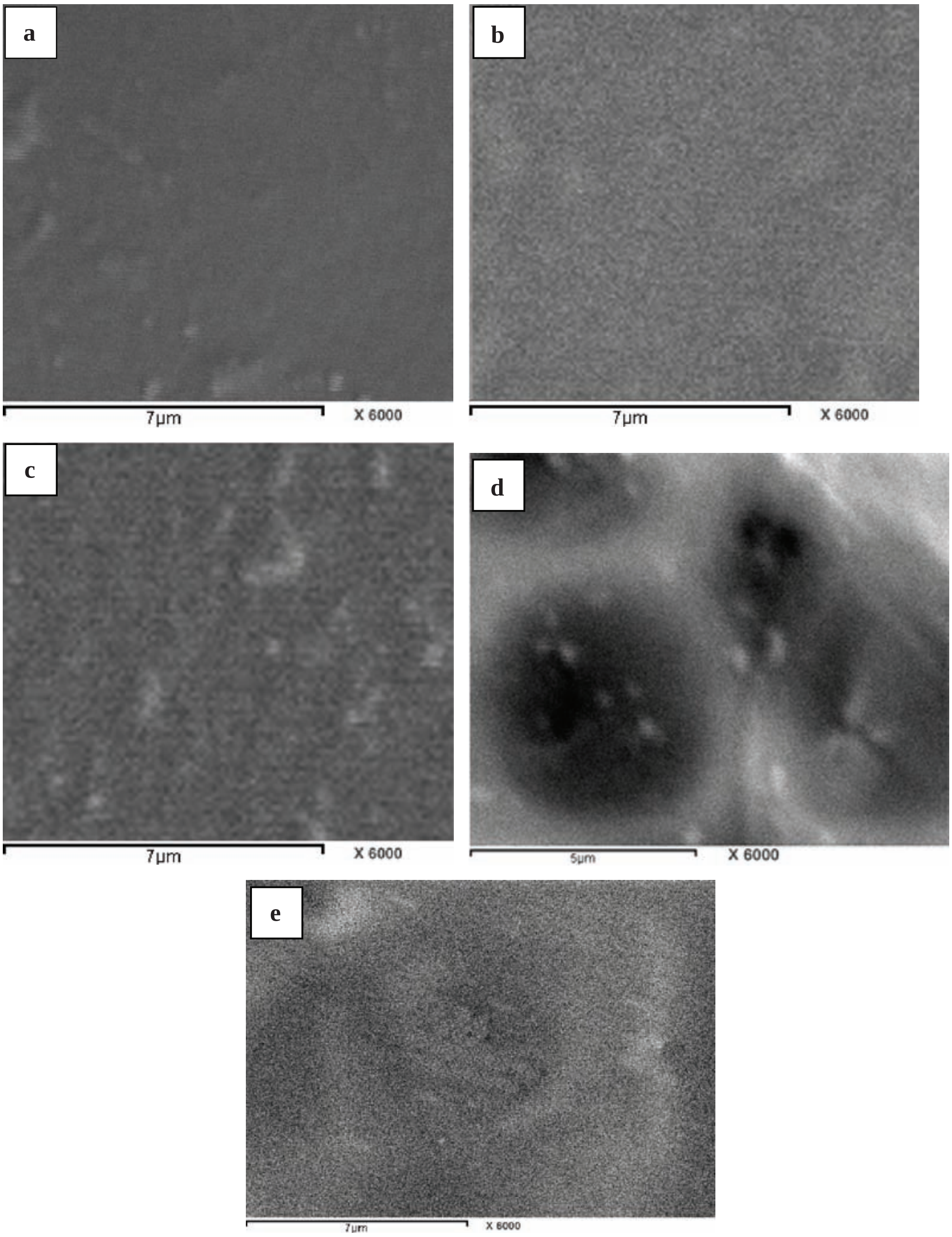


Fig. 3. SEM for a: M1, b: M3, c: M5, d: M10, e:M11.

membrane samples as presented in Fig. 5. It has been noticed that the best desalting efficiency is manifested by M5 which has been blended with PMHS as an additive that enhance surface morphology and pores distribution. Fig. 6 depicts the change of permeate salinity with time at constant pressure (30 bars) for different feed salinities for selected membranes. At operating pressure approaching 30 bars the salt rejections are 0.44%, 89% and 64% for membrane sample M10, M11, M12, respectively. The enhancing effect as contributed to the addition of DBP is also observed in Fig. 6 depicting better salt rejection of M11over M12 regarding this pressure.

Fig. 7 depicts the change of salt removal profile for each individual membrane. In general, salt rejection is improved by increasing applied pressure up to 50 bars. It is also noticed that M5 shows better salt rejection at lower pressure due to the presence of PMHS as

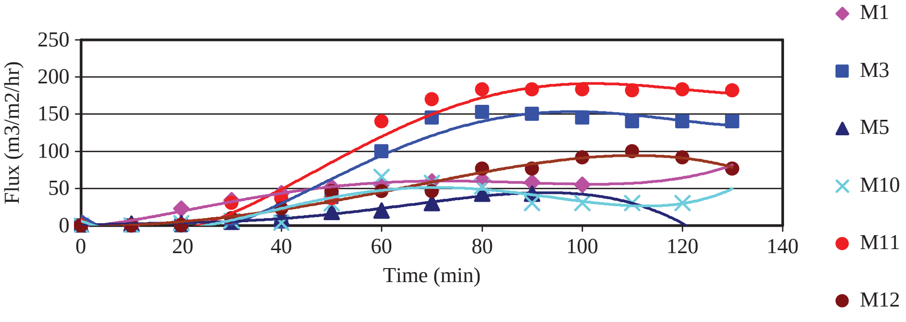


Fig. 4. Change of flux with time for different membranes.

additive, while M10 shows higher salt rejection at relatively higher pressure due to the presence of higher content of CTA that enhances mechanical properties.

Membranes rejection has been mathematically described according to change in operating pressure. The mathematical equation has been developed as a second order polynomial as follows:

$$Y = \alpha\varepsilon^2 \pm \beta\varepsilon \pm \gamma \tag{2}$$

where Y is the % rejection, ε is applied pressure, and α, β, γ are constant denoted according to the membrane type as follows:

In general, the developed equation expressed good correlation coefficient (R^2) for all type of membranes.

Sample No.	α	β	γ	R^2
M1	−0.0006	0.06	0.93	0.94
M3	−0.02	1.9	−3.6	0.96
M5	−0.04	3.4	−5.45.9	0.97
M10	0.07	−1.6	5.9	0.93
M11	0.06	−1.2	9.5	0.97
M12	0.03	0.44	−3.3	0.97

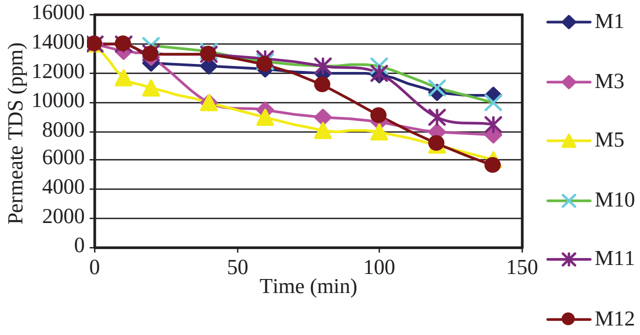


Fig. 5. Effect of operating time on desalting efficiency.

This mathematical equation could be successfully applied up to an operating pressure of 50 bars and feed salinity up to 14,000 ppm at room temperature.

5. Conclusions

Flat cellulose acetate membranes have been prepared via wet casting technique using different blends of polymers, additives and solvents. The prepared membranes have been investigated for both characterization and performance evaluation. The results indicate that mixed solvents are preferable than using single solvents to obtain better performance and uniform structure. Appropriate polymeric content that gives good mechanical properties was found to be in the range of 20–22%. All prepared membranes manifest low initial flux that increases with the operating time except for M3 and M12 which are characterized by sudden increase in flux after 50 min of operation at pressure 30 bars. In all cases membranes with DMHS show better performance and fairly good mechanical properties as manifested by the tolerable applied pressure (50 bars). M5 manifests better rejection at medium pressure as compared with the other membrane samples Moreover, M11, M12 emphasize better rejection at higher pressure. Further, the presence of DBP causes better salt rejection of M11 over M12.

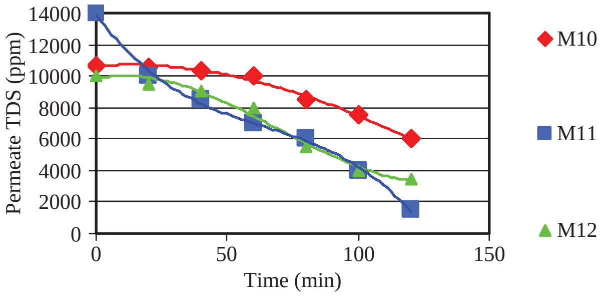


Fig. 6. Change of desalting efficiency with time at constant pressure (30 bar) for selected membrane samples.

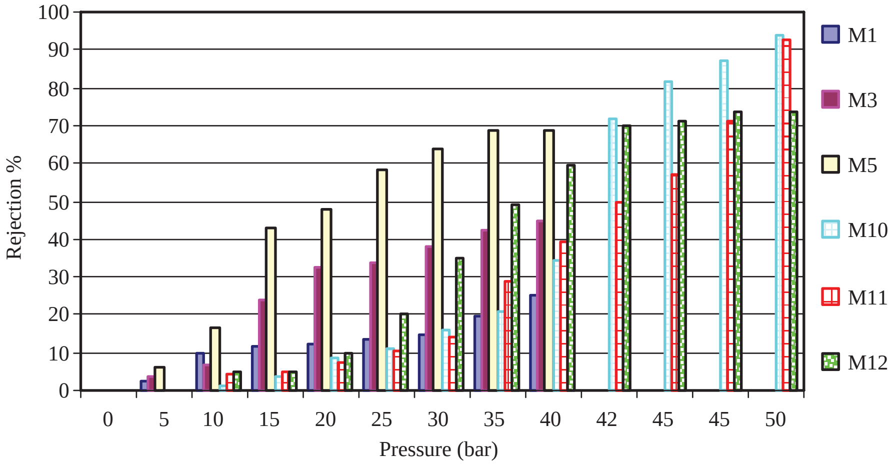


Fig. 7. Effect of applied pressure on water desalting efficiency for different membrane samples.

References

[1] B.Y. Cai et al., Desalination, 146 (2002) 331–336.
[2] A.T. El Gindi, S.A. Ahmed, et al., Egyptian Patent Office, Patent No. 23692, 2006.
[3] A.T. El-Gendi, S.A. Ahmed, and A.T. Talaat, Desalination, 204 (2007) 226–237.
[4] Farnand et al., U.S. Pat. No. 4,814,084 (1989).
[5] E. Ferjani et al., Desalination, 2 (2002) 41–46.
[6] B. Keilin, Office of Saline Water Research and Development, Report No. 84, U.S. Government Printing Office, Washington, D.C, 1964.
[7] H. Lansdale, Desalination by Reverse Osmosis, U Merten, Ed., M.I.T. Press, Cambridge, Mass, 1966.
[8] F. Liu et al., Chin. J. Chem. Eng., 16 (3) (2008) 441–445.
[9] Loeb et al., U.S Pat. Nos. 3,133,132 and 3,133,137, 1964.
[10] MacDonald et al., U.S. Pat. No. 3,842,515, 1972.
[11] M. Mulder, Basic Principles of Membrane Technology, 2nd Ed., Dordracht: Kluwer Academi Publisher, 1996.
[12] T. Murthy et al., Ind. J. Pharm. Sci., 69 (2007) 646 –650.
[13] L. Pageau et al., Desalination, 3 (1972) 342–349.
[14] A. Rahim Pour et al., Desalination, 5 (2007) 231–237.
[15] A. Rahim Pour et al., J. Membr. Sci. 305 (2007) 299–312.
[16] A. Sieman, Progr. Polym. Sci. 130 (2005) 1–14.
[17] M. Ulbricht, Polymer, 47 (2006) 2217–2262.
[18] T. Uremura et al U. S. pat. No. 4, 239,545, 1980.
[19] D. Walmsley et al., U.S. Pat. No. 3,807,571, 1974.
[20] R.A. Ward, Membrane Materials for Therapeutic Application Medicine, in Material Science of Synthetic Membranes, D.R. Loyd Ed, ACS Symposium 269, 99–118, 1985.
[21] Watson et al., U.S. Pat. No. 3,522&335, 1966.
[22] M. Zhao et al., J. Membr. Sci., 336 (1–2) (2009) 149–153.
[23] G. Suryo, JMS, 3 (2) (1998) 105–113.
[24] A. Idris et al. J. Teknol., 43, F (2005) 51–64.
[25] B.H. Ani et al., Proceeding of the World Engineering Congress 1999, 1–5.
[26] S. Manjikian et al., Proceedings of the 1st International Symposium on Water Desalination, US Department of Interior, Washington, DC, pp. 159–173, 1965.
[27] E.G. Hans, Reverse Osmosis and Synthetic Membranes, National Research Council Canada, Ottawa, pp. 111–128, 1977.
[28] A. Idris et al., J. Membr. Sci., 202 (2002) 205–215.