

Removal of BTX Compounds from Wastewaters Using Template Free MFI Zeolitic Membrane

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ABSTRACT: MFI zeolite membranes were prepared on porous α -alumina substrates, using secondary growth of nano-seeded layers. The resulting membranes were characterized by means of Scanning Electron Microscopy (SEM), X-Ray Diffractometry (XRD), and pervaporation performance tests for separation of Benzene, Toluene and Xylene (BTX) mixture from contaminated water. The morphology, thickness, homogeneity, crystal preferential orientation and permeation properties of these membranes have been studied in relation to the seed layers. Successful separation of BTX mixture from water was performed by using the manufactured MFI zeolite membrane. The influence of temperature, feed concentration on the membrane separation efficiency systematically investigated. The total permeation fluxes were found to increase with increase in temperature and feed concentration. The separation factors increased with increasing feed concentration and decreased with increasing in temperature.

KEY WORDS: MFI nano-zeolite membrane, Pervaporation, BTX compounds, Wastewaters.

INTRODUCTION

One of the major contaminants of industrial wastewater (petroleum refineries and chemical plants) and ground water are Volatile Organic Compounds (VOCs), particularly chlorinated and aromatic hydrocarbons. The water solubility's of these compounds are low; therefore, the amount of VOCs dissolved in water is too small

to be economically removed from water by conventional chemical process separation technologies such as distillation. Currently, air stripping and activated carbon treatments were deployed for this purpose, however, the former is susceptible to fouling and merely turns a water pollution problem into an air pollution issue while the latter needs

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costly regeneration steps and may not be suitable for VOCs that are easily displaced by other organic compounds. Over the last decade, a growing effort has been devoted to applications of pervaporation (PV) to VOC removal from water in order to determine if this technology is techno-economically feasible and viable for this application [1-4].

Polymeric membranes have used to separate numerous organic mixtures by pervaporation [5-7]. Swelling and low chemical resistance of polymeric membranes, however, often limit the feed mixtures that can consider for separation. The uniform, molecular-size pores and the adsorption properties of zeolites, plus their high thermal, chemical, and mechanical stability make zeolite membranes as promising candidates for separations based on pervaporation processes.

Zeolite membranes may use as alternatives to polymeric membranes for treating of complex wastewaters which contain organic solvents and radioactive elements or when high temperature operation is desired [8-10].

Several strategies have been developed to prepare such zeolitic layers. However, *Taspatis et al.*, reported an alternative approach, referred to as the secondary growth, for synthesis of zeolite membranes [11]. In this method, under a hydrothermal condition, a layer of nanosized zeolite seed crystals is coated on a suitable support followed by secondary growth of these zeolite crystals to achieve a continuous and dense layer. Because of the existence of seed crystals on the support surface, the nucleation step is eliminated. This improves the flexibility of crystal growth, which provides much control on the membrane microstructure. This enhances reproducibility and scalability of the zeolite membrane synthesis [11].

To synthesize the MFI⁽¹⁾ zeolite membranes by means of this method, organic agents (e.g. Tetra Propyl Ammonium (TPA)) employ as template or Structural Directing Agent (SDA). Template is required for formation of zeolite crystal structure. However, follow the membrane synthesis process; a calcination step is also necessary to open the pore structure by removing the organic molecule. During the calcination process, micro cracks tend to form in the zeolite membranes due to thermal stress caused by the difference in thermal expansion of zeolite film and its support as well as by changing of lattice parameters of the zeolite crystals as a

result of the removal of template [12-13]. Nevertheless, many adverse problems such as high production cost, contamination by waste water and air pollution arising from thermal decomposition of the organic templates are of main concern. Therefore, recently, attempts to prepare MFI zeolite membranes without template are growing rapidly [14-17].

In Follow up to our previous works on the environmental applications of various zeolitic materials particularly on the adsorption and degradation of volatile organic molecules [18-23], in this work, template free MFI type zeolite membranes were prepared by seeded growth method in order to minimize defects and inter-crystalline gaps that form during the calcinations step required for template removal. The effect of seed size on the morphology and quality of MFI membranes also investigated. We used the as-synthesized membrane to investigate the pervaporation behavior of ethanol, methanol, BTX mixture and in each case excellent separation efficiency and very good membrane permeation behavior and performance have been achieved.

EXPERIMENTAL SECTION

Materials

LUDOXAS-30 (Aldrich, 30 wt% colloidal suspension of SiO₂ particles in water) used as the silica source. Sodium aluminate (Riedel-de-Haen 45% Na₂O, 54% Al₂O₃) used to prepare the aluminate solution. The alkali sources were NaOH pellets (99% Merck) and tetrapropylammonium hydroxide (TPAOH 40% in water, Merck) as template. α -Alumina cylindrical discs with dimensions of \varnothing 20 · 1.2 mm, and an inner top layer of pore size around 500 nm (made by Material and Energy Research Center, Iran) with 30% void fraction, were used as support for membrane preparation. All of the chemicals were used without further purification.

Synthesis of MFI zeolite seeds

The seeds were synthesized from clear solution according to the general procedure of *Li et al.* [24]. Seeds were synthesized using a batch composition of 1.4 TPAOH: 5SiO₂: 100 H₂O: 0.04 Na₂O: 20 EtOH at 100 °C under a reflux condition (atmospheric pressure) without stirring in a silicon oil bath for 48h and 96h. The synthesis mixture was aged by stirring vigorously at room temperature for 24 h before synthesis. MFI nanocrystals

(1) Mobile Five

were recovered after three cycles of centrifuging and dispersion in deionized water and dried overnight at 100 °C.

Preparation of Membrane

A 1 wt% aqueous seed suspension of MFI crystals was prepared for dip-coating. The supports were placed vertically in the solution by using PTFE holders. The vertically positioned supports were immersed into and removed out of the seed suspension slowly. After 15 min contact time, the seed coated supports were kept at 100 °C for 4 h, to adhere the seeds to the support surface. The dried supports were calcined at 450 °C for 8 h with a heating and cooling rate of 20 °C/h. The calcination was done to enhance to bonding between the zeolite seeds and the support. A synthesis solution with molar composition $1\text{Na}_2\text{O}: 3.5 \text{SiO}_2:0.05\text{Al}_2\text{O}_3: 140 \text{H}_2\text{O}$ were prepared for secondary growth membrane.

The seeded supports were placed vertically in a Teflon autoclave by using PTFE holders. The solution was carefully poured into the autoclave and then the autoclave was sealed. Crystallization was carried out in an oven at 170 °C for 24 h. Then, the samples were taken and the synthesized membranes were washed several times with distilled water. The samples were then dried in the oven at 100 °C for 24 h.

Characterization

The powder X-Ray Diffraction (XRD) data of the samples were collected by Philips X'PERT MPD diffractometer using $\text{CuK}\alpha$ radiation. A Philips XL30 Scanning Electron Microscope (SEM) equipped with a LaB6 emission source was used to study film thickness and morphology of the membranes.

BTX Pervaporation test

Pervaporation experiments were carried out at different temperature using a BTX aqueous solution, ethanol-water or methanol-water as feed. The membrane was sealed in a PTFE module using Teflon o-rings. A centrifugal pump re-circulated liquid feed through the inside of the membrane from a feed reservoir at approximately 0.5 L/min to minimize concentration polarization. The feed and membrane were insulated and heated with heating tape. A thermocouple measured feed temperature, and a temperature controller was used to stabilize the feed temperature. During the permeate

collection the system was connected to a vacuum pump and the permeate vapor was frozen in a cold trap using liquid nitrogen. The composition of the feed and permeate streams was analyzed by a liquid chromatograph Nora-Pak@C18 60Ao column. The amount of permeation was measured by weighing the cold trap before and after the pervaporation experiment. The pervaporation performance was evaluated by considering the flux and the separation factor calculated according to the following expression:

$$\alpha_{i/j} = \frac{y_i/y_j}{x_i/x_j} \quad (1)$$

Where x_i and x_j are mole fractions of components i and j in the feed stream; y_i and y_j are mole fractions of i and j in the permeate stream.

$$\text{flux}(\text{kgm}^{-2}\text{h}^{-1}) = \frac{Q}{At} \quad (2)$$

Where $Q(\text{kg})$ = weight of permeate liquid; $A (\text{m}^2)$ = effective membrane surface area; $t (\text{h})$ = measuring time.

RESULTS AND DISCUSSION

Seeded Supports

XRD patterns of the seeds after 48h and 96 h are illustrated in Fig. 1. The results show that the characterized peaks of MFI zeolite phase exists, which confirm the formation of pure MFI zeolite. Fig. 2 illustrates the IR spectra of seeds and the bands at 462, 555, 797 cm^{-1} reveal that MFI phase is formed.

SEM images of the surface of seeded layers on α -alumina substrate by two different seeds were shown in Fig. 3. A homogeneous and relatively compact layer of round shaped seeds is deposited on top of the support by the seeds synthesized after 48h. Longer synthesis time increases the particle size of the seeds from 80 nm to 400 nm. The seed layer is denser and more uniform with the decrease of seed size. However, when the 400 nm seed is used, there are some large voids existed within the seed layers.

Membrane preparation

The SEM image of the cross section and surface of the MFI type zeolite membranes after secondary growth can be seen in Fig. 4. Two different seed layers were used for preparation of membranes (M1: using 80 nm seed and M2: using 400 nm seed). Fig. 4a shows that most of

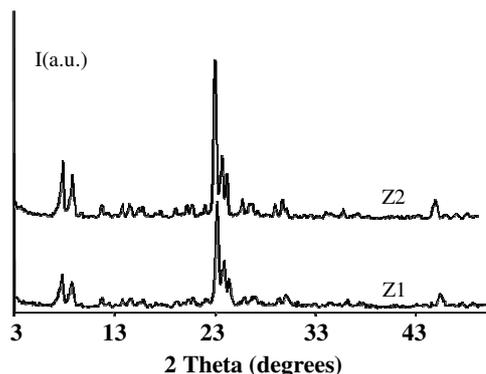


Fig. 1: XRD patterns of the seeds, Z1 (48h) and Z2 (96h).

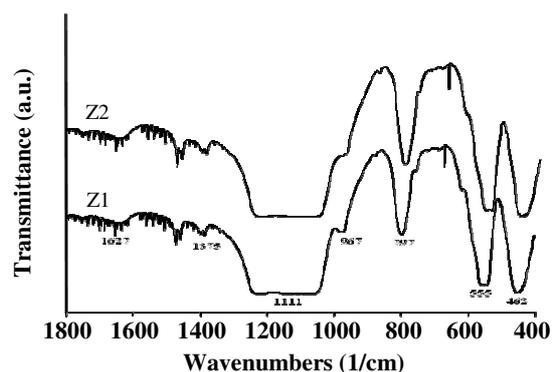


Fig. 2: FT-IR spectra of the seeds, Z1 (48h) and Z2 (96h).

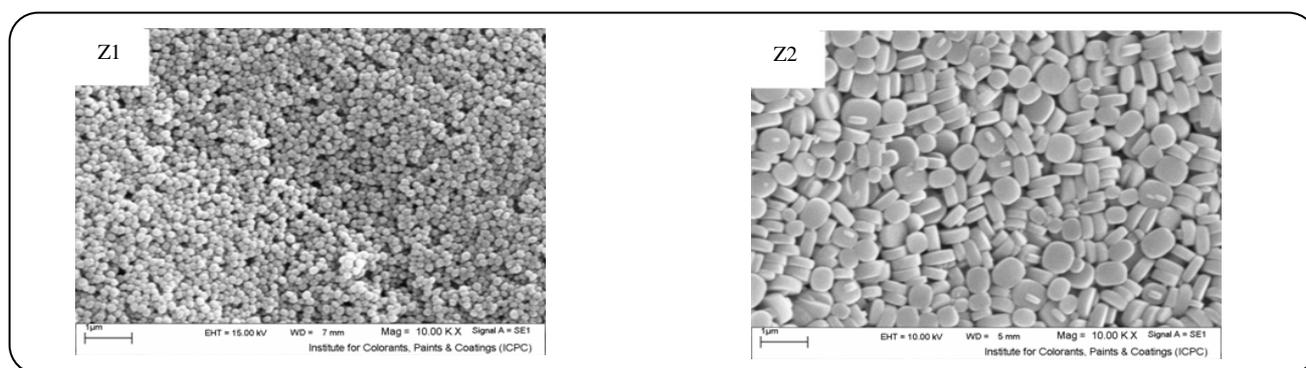


Fig. 3: SEM images of the surface of seeded layers on α -alumina substrate by Z1 (48h) and Z2 (96h).

crystals with average size of 80 nm grew on surface of the alumina support. Furthermore, most of the zeolite nanocrystals oriented in the direction of c-axis perpendicular to the substrate surface and a uniform and dense coverage of high silica MFI crystals observes on the alumina support. The average thickness of the MFI layer is $3.3\mu\text{m}$ that is fairly uniform throughout the membrane.

The SEM images of the membrane surfaces indicate that the better zeolite membrane intergrowth can be achieved from smaller seeds and the resultant membrane posses a smoother surface. In the other hand, the membrane grew from larger seeds, display a coarser surface and poorer intergrowth of the crystals. The average grain size of zeolite crystallites increases with increasing of the seeds size. However, some imperfections and defects on the membranes formed from large seeds were created during the synthesis, as shown by the voids trapped within the membrane layer. Even it is shown in Fig. 4b that the membrane grew from the seed of 400 nm, is not continuous and uniform. This should be attributed to the non-continuous seed layer formed with the seed of 400 nm.

Pervaporation results

The MFI membrane preferentially permeated methanol and ethanol from aqueous solutions. Table 1 shows the separation factors and the fluxes for methanol (5%)/water (95%) and ethanol (5%)/water (95%) mixtures at 30 °C. M1 sample (seed 80 nm) showed higher separation factors for the two alcohol-water mixture than M2 sample (seed 400 nm). Tuan *et al.* [25] obtained a separation factor of 7-14 for methanol/water with a feed of 5 wt% methanol, and it decreased with increasing methanol concentration. Their results are comparable to the separation factors of 9-20 are obtained in this work (Table 1). Also, they reported separation factor of 10 for ethanol/water mixtures which can be comparing with the values of 7-15 are obtained in this work. As well as, the permeation flux of $0.07\text{ (kg/(m}^2\text{h))}$ on a silicalite-1 membrane was reported in the article that one order of magnitude is lower than our results in Table 1, which shows remarkable improvement in the membrane performance. Furthermore, the high fluxes are observed with M1 because it was defect free and also thickness of this membrane was smaller than M2.

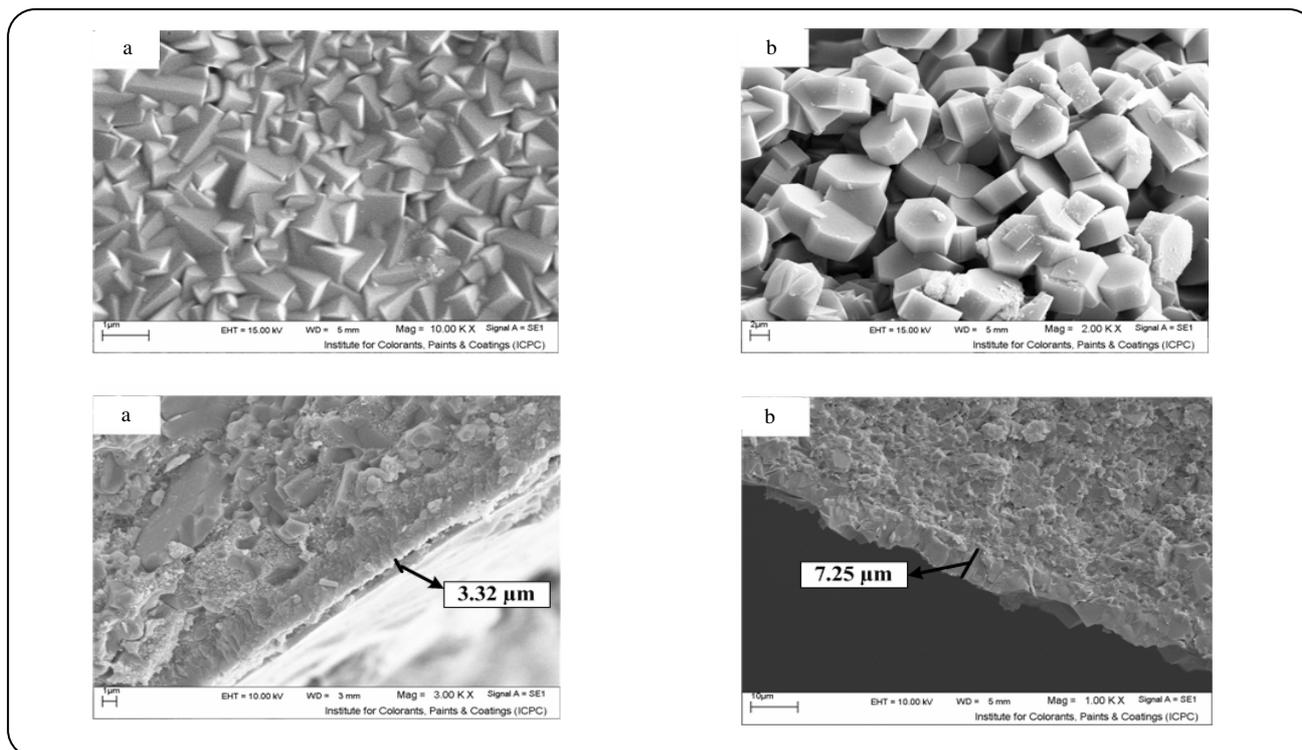


Fig. 4: SEM images of the cross section and surface of the MFI type zeolite membranes, (a) 80 nm seed layer (M1), (b) 400 nm seed layer (M2).

Table 1: Pervaporation of 5% alcohol/95% water feed through silicalite-1 membrane.

Mixture	Membrane No.	Total Flux (kg/(m ² h))	Separation factor
Methanol/water	M1	0.5	20
	M2	1.7	9
Ethanol/water	M1	0.3	15
	M2	1.3	7

Therefore, high separation factors and flux is obtained for free template membrane by small seeded particle. The pervaporation experiment results confirmed the SEM observations. The results was complementary, there was very good agreement between the result of the SEM and pervaporation tests. Based on the characterizations results, the membrane with highest separation performance at the optimum synthesis condition was selected for removal of BTX compounds from water.

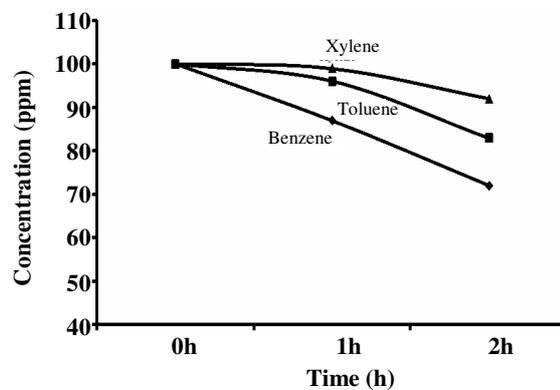


Fig. 5: Decrease in BTX concentration in the feed (300 ppm) as a function of time for MFI membrane.

Results of separation performance of the MFI membrane toward mixture of benzene, toluene and xylene with initial concentration of 100ppm in water, is illustrated in Fig. 5. After 2 hours of pervaporation, the concentrations of benzene, Toluene, and xylene were reduced to 70ppm, 81ppm and 93 ppm respectively. The overall selectivity of MFI membrane is as following; benzene > toluene > xylene. Further purification of the wastewater stream is possible but it needs a much longer

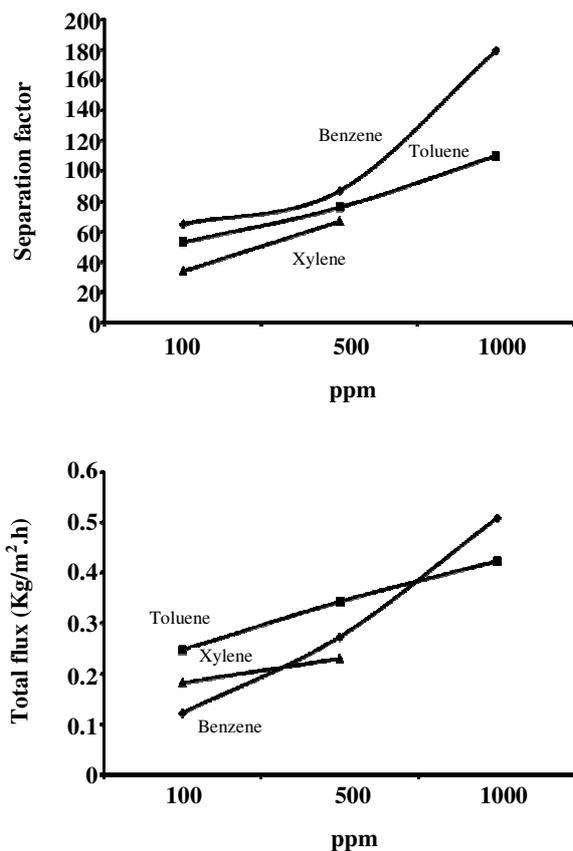


Fig. 6: The effect of feed concentration on the total fluxes and separation factors.

time of the process due to the negligible driving force over this concentration range. The driving force for PV is the difference in chemical potential (or partial vapor pressure) of each component across the membrane. For convenience, it is often approximated as the concentration difference as expressed in the following permeation flux formula [1]:

$$J_{\text{VOC}} = k_{\text{VOC}}^{\text{Overall}} \rho' [(C_{\text{VOC}})^L - (C_{\text{VOC}})^V] \quad (3)$$

Where k_{VOC} (m/s), ρ' (moles/m³), C_L (dimensionless), C_V (dimensionless) are the overall mass transfer rate constant, total molar density of feed, bulk liquid concentration (mole fraction) and bulk vapor phase concentration (mole fraction, reported as an equivalent liquid phase mole fraction), respectively for component i .

Effect of feed concentration

The influence of feed concentrations studies were performed to see how varying the concentration affects

fluxes, which was carried out for different feed concentrations, feed-solution velocity of 0.5 L/min and at full vacuum. As shown in Fig. 6, the total flux increases relatively linearly with increasing concentration. This can be explained in driving force in the right hand term of Eq. (3). Usually, the VOC partial pressure at the permeate-side of the membrane is negligible and therefore, the local flux is a linear function of the feed side concentration. Separation factors and total fluxes increase dramatically as the feed concentration increases because the water flux is constant.

Tuan et al. [25] reported a separation factor for methanol/water mixture decreased with increasing methanol concentration. The difference between their results by our results is the effect of defect on zeolite membrane. Their zeolite membrane obtained by template and defect observed in the surface after removal of template by calcination, hence by increasing methanol concentration, the fluxes of water and methanol increased and separation factor decreased. In addition, selectivity of MFI zeolite membrane for separation of benzene, toluene and xylene is higher than for methanol, which is caused to increase separation factor.

Effect of operating temperature

The studies of the influence of operating temperature were performed to see how varying the temperature affects fluxes and selectivity, using the membrane module earlier described, operated at a feed-solution velocity of 0.5 L/min and at full vacuum, BTX feed concentration of 300 ppm and at various temperatures ranging from 30 to 50 °C. The results are shown in Fig. 7 depicted, an increase in temperature increases the permeation fluxes of both BTX and water, but the increase in water flux is more significant than the BTX flux. However, total fluxes increases with increasing temperature and separation factors decreases at high temperature.

CONCLUSIONS

High quality MFI type zeolite membranes were prepared by secondary growth process without organic template and were minimized defects and intercrystalline gaps that form during the calcinations step required for template removal. Our studies showed that the quality of seed layers is very important parameter on the morphology

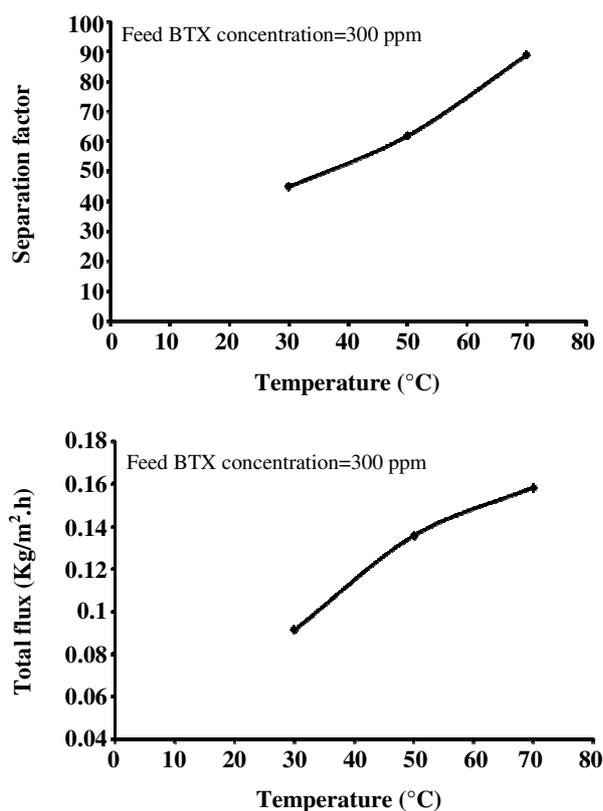


Fig. 7: The effect of operating temperature on the total fluxes and separation factors.

and quality of the manufactured MFI membranes because smaller seeds result a better intergrowth and consequently possess a smoother surface. The separation of mixture of benzene, toluene and xylene (BTX) of a contaminated water was successfully achieved by using MFI zeolite membrane at optimum condition.

The total permeation fluxes were found to increase with increasing of the temperature and feed concentration. The separation factors increased with increasing feed concentration and decreased with increasing of temperature.

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