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Synthesis and performance of B-ZSM-5 zeolite membranes for the separation of volatile organic from water in pervaporation process

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ABSTRACT

ZSM-5 zeolite membrane on porous α-alumina support was prepared by hydrothermal method with B isomorphously substituted into their structure for separating acetone from water by pervaporation. The effects of feed temperature, concentration, flow rate, and permeate pressure on the membrane performance were investigated. The permeate flux increased with the increasing feed concentration, temperature, and flow rate and decreasing permeate pressure. In addition, the results of permeate pressure show that the separation factor is improved with the increasing permeate pressure dramatically. Moreover, this results show an unlike behavior compared to results reported for organics with low volatility. So, it can be concluded that the behavior of pervaporation process is deeply dependent on the volatility of organics when the permeate pressure change.

Keywords: Pervaporation; Zeolite membrane; Separation factor; Volatility; Acetone

1. Introduction

Pervaporation (PV) is a membrane process that is used for the separation of liquid mixtures by the means of partial vaporization through a permselective membrane. The permeate is obtained as a liquid following condensation [1]. Pervaporation provides an important option for the recovery and recycling of many volatile organics from aqueous media. The use of hydrophobic/organophilic membranes for such purposes has increased in recent years [2]. Generally, distillation can be used to remove organic compounds from water. However, for low organic concentrations or thermally sensitive organic compounds, distillation is neither economical nor suitable. Furthermore, PV has several advantages over traditional distillation: (1) less energy demand, (2) simpler equipment, and (3) lower capital costs. Thus, relatively mild operation conditions and high effectiveness make PV an appropriate technique for such separations [3–5].

Polymeric membranes have widely been investigated for PV membrane-based solvent separations. However, their practical use has been limited due to insufficiency of their thermal, mechanical, and chemical stability. In order to overcome these shortcomings and to improve the membrane multipurpose character, extensive research has been directed in the past decades toward the development of inorganic membranes with suitable PV performance. In this way, zeolite membranes (usually consisting of a

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polycrystalline zeolitic layer grown on porous flat or tubular supports) have attracted widespread attention, as they have the unique properties of zeolites such as highly crystalline ordered structure, molecular-sized pores, thermal stability, and resistance to harsh environments. These attributes make zeolite membranes attractive alternatives for separating mixtures whose components display adsorption or size differences, and using either polymeric membranes or other conventional separation techniques is difficult [6–8]. In a pervaporation process, transport through the membrane is generally described by a so-called "sorption–diffusion mechanism" which consists of three succeeding steps: (1) selective sorption of the species in the liquid mixture at the feed/membrane interface, (2) diffusion through the membrane due to concentration gradient, and (3) desorption at the membrane/permeate interface into the vapor phase permeate side [9].

One of the most common zeolitic membranes for organics separation is MFI membrane which exhibits tendency toward organic substances because of its hydrophobic nature. Organics volatility has significant effect on the separation performance of these type membranes. In high volatile organic/water mixture, as a result of high fugacity (high saturated vapor pressure), adsorption selectivity is more dominant in comparison with low volatile component/water mixture. So, it is expected in aqueous mixtures of high volatile organics such as acetone, the adsorption selectivity is more sensible than molecular sieve [7,10].

In most of the previous studies, MFI zeolite membranes were used for organics separation with low volatility. But, a few works were presented on high volatile organics separation from aqueous mixtures using MFI zeolite membranes; Tuan et al. [11] studied acetone (as organic with high volatility) separation from water by pervaporation using B-ZSM-5 zeolite membrane, Shen et al. [12] studied the separation of acetone/water mixture by pervaporation using silicalite-1 membrane synthesized via vacuum seeding, Bowen et al. [13] prepared B-ZSM-5 membranes on monolith supports and obtained a separation factor of 220 at 333 K for acetone/water in 5 wt% acetone feed as increased with decrease in temperature. Therefore, parametric studies on the hydrophobic inorganic MFI membranes performance in the separation of organics with high volatility such as acetone from water are necessary.

This paper focuses on the separation of acetone–water mixtures using hydrophobic MFI zeolite membrane, and the effects of operating parameters such as feed temperature, feed composition, feed flow rate, and permeate pressure on the selectivity and membrane flux were also examined. The B-ZSM-5 as an effective hydrophobic zeolite membrane with strong ability in organics separation from water was synthesized and used in this research, and acetone was used as an organic component with $\alpha >> 1$ (α, organic's relative volatility based on the water). To the best of our knowledge, the effects of feed flow rate and permeate pressure have been investigated for the first time in this work.

2. Experimental

2.1. Membrane synthesis and characterization

The homemade tubular alumina supports (OD = 12 mm, ID = 6 mm, length = 65 mm) were applied [14]. Zeolite layers were hydrothermally crystallized on the outside surface of the supports. The synthesis gel used 1 M tetrapropyl ammonium hydroxide (TPAOH, Merck, 40%) as the structure-directing template, tetraethyl orthosilicate (TEOS, Merck, 98%) as the silicon source and boric acid ($B(OH)_3$, Merck, ≥99.5%) as a source of B. To prepare the membranes, both ends of the support tube were wrapped with Teflon tape and left overnight at room temperature. They were placed into a Teflon-lined, stainless steel autoclave, which was placed in an oven at 458 K. The first zeolite layer was synthesized for 24 h and all other layers were synthesized for 48 h. The molar composition was 1.6 TPAOH:19.5 SiO_2:0.2 $B(OH)_3$:438 H_2O. Before deposition of each subsequent layer, the membrane was rinsed with deionized water and dried in an oven at 373 K. The number of layers in the synthesized membrane increases till the membrane to be impermeable to N_2 at 298 K. The organic template was then removed by calcination the membrane at 753 K for 8 h using a furnace.

The membrane sample was broken and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Single gas permeance of N_2 was measured to determine the membrane quality. The permeation of N_2 after calcination can be due to not only opening of zeolite pores but also creating non-zeolite pores in membrane layer structure during the calcination.

2.2. Acetone/water mixture separation

The alumina-supported B-ZSM-5 membrane was used to separate acetone (C_3H_6O, Merck, ≥99.9%, 0.47-nm kinetic diameter) from water by pervaporation. The membrane was sealed in a stainless steel module with O-rings, and the liquid feed flowed through the outside of the membrane. The retentate was recirculated to the feed side of the membrane by a centrifugal pump and a mechanical pump evacuated the permeate side of the membrane. The membrane had permeable area of approximately 18.4 cm^2. Permeate samples were usually collected and measured every 2 h, to determine the membrane flux. The permeate concentration was measured offline by a Teif Gostar Co. gas chromatograph (GC) equipped with a PORAPAK-Q packed column and a thermal conductivity detector. The injection temperature for the GC was 473 K.

The separation factor was calculated as:

$$\alpha_{\text{Acetone/Water}} = \frac{Y_{\text{Acetone/Water}}}{X_{\text{Acetone/Water}}} \tag{1}$$

where X and Y are the weight fractions in the feed and permeate, respectively.

3. Results and discussion

3.1. Membrane characterization

The XRD pattern of the synthesized B-ZSM-5 membrane is shown in Fig. 1(a). All peaks have the same positions as those reported by [15] for ZSM-5 (Fig. 1(b)), and additional peaks were referred to alumina support.

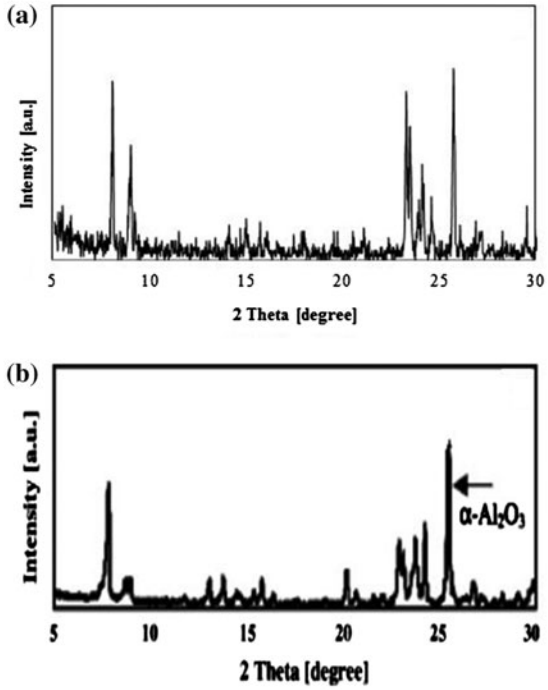

Fig. 1. XRD patterns for (a) the synthesized membrane and (b) Ref. [15].

SEM micrographs of surface and cross section of the zeolite membrane show structure of the outer layer on the support (Fig. 2(a)) and thickness of the membrane layer (Fig. 2(b)) after the calcination. SEM micrographs confirm that the membrane have continuous defect-free zeolite layer on the porous α-Al_2O_3 support with about 10 μm thickness.

Single gas (N_2) permeance through the zeolite membrane as a function of transmembrane pressure (TMP) is presented in Fig. 3. As can be seen, with the increasing number of layers, N_2 permeance decreases dramatically, revealing a considerable decrease of non-zeolite pores. After the final layer, single gas permeance through zeolite membrane cannot be measured, confirming the formation of a defect-free zeolite membrane layer on the support.

Measured permeance of the membrane after calcination at TMP 1.5 bar and 298 K was 4.24×10^{-8} mol/(Pa s m^2).

3.2. Organic/water pervaporation

The α-alumina supported B-ZSM-5 membrane was used for pervaporation of acetone/water solution as a model mixture for any other high volatile organic aqueous mixtures and the influence of process parameters on zeolite membrane performance was examined.

3.2.1. Effect of feed temperature

The feed temperature has a remarkable effect on permeate fluxes because of the direct and strong influence of temperature on the vapor pressures in the feed side. Fig. 4 shows that the total flux increases with temperature. It is due to the fact that with the increasing temperature, vapor pressure of feed and then driving force for pervaporation increases, resulting in high permeate flux.

The influence of temperature on the membrane performance shows when temperature increases, the saturated vapor pressure of acetone and then its fugacity enhances, resulting in a high adsorption selectivity of acetone/water and therefore acetone permeates more than water through zeolite pores. This trend has been shown in Fig. 5.

3.2.2. Effect of feed concentration

As shown in Fig. 6, total flux through the B-ZSM-5 membrane increases with the increasing acetone concentration in feed. As reported in the literature [7], the feed fugacity for acetone is determined as:

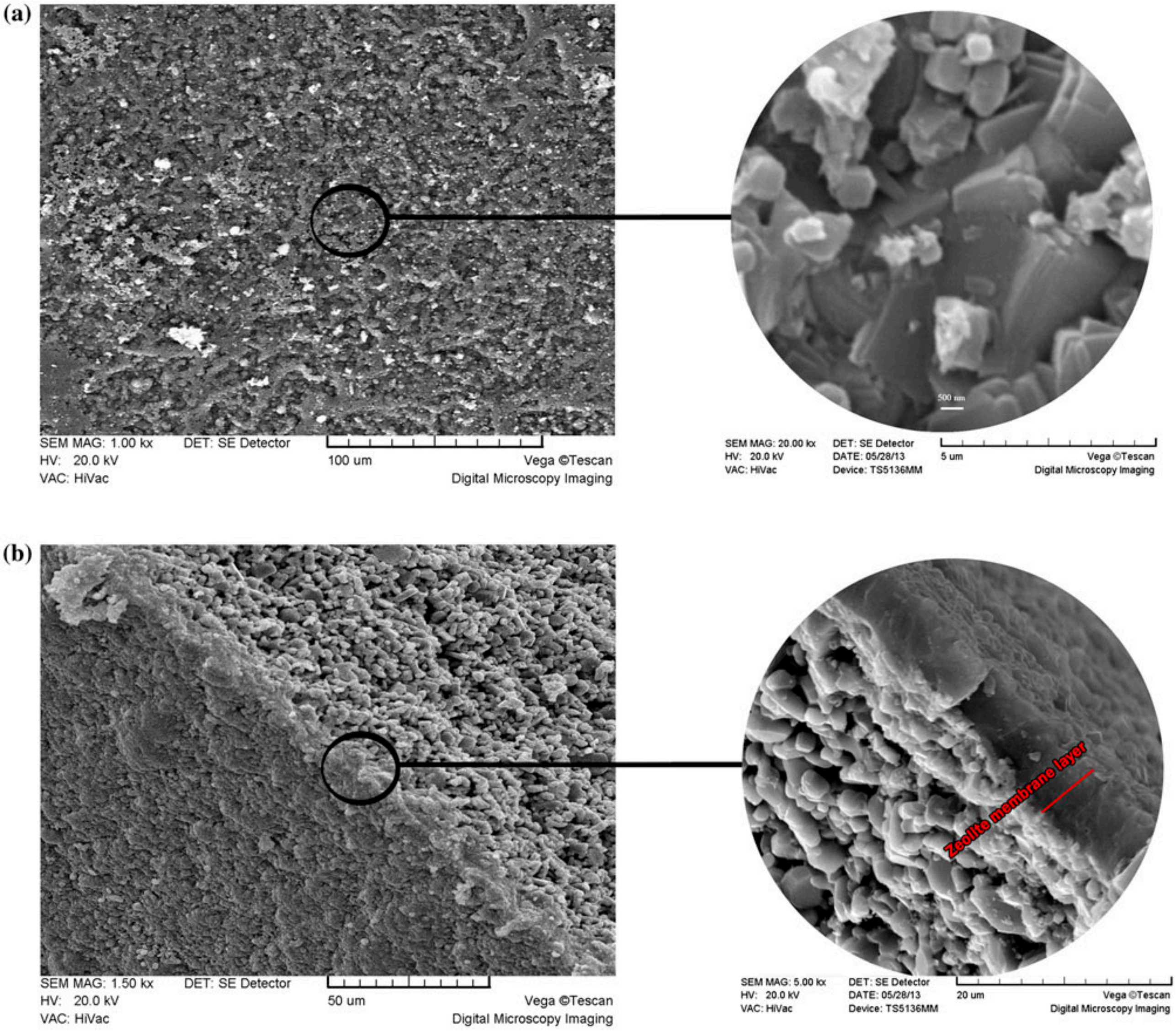

Fig. 2. Top-view (a) and cross section (b) SEM micrographs of the B-ZSM-5 membrane.

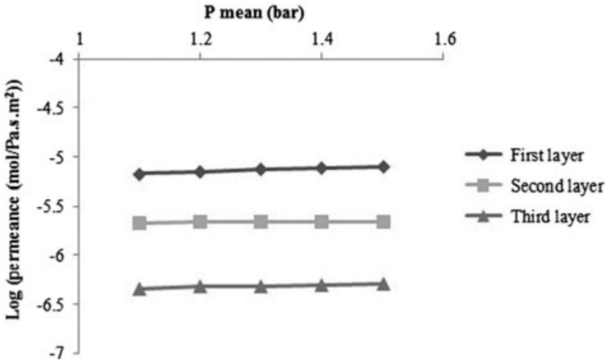

Fig. 3. Single gas permeance through the B-ZSM-5 zeolite membrane before calcination at $T = 298$ K.

$$f_{\mathrm{A}}^{\mathrm{F}} = x_{\mathrm{A}} \gamma_{\mathrm{A}} P_{\mathrm{A}}^{\mathrm{sat}} \tag{2}$$

where x_{A} is the feed mole fraction, γ_{A} the activity coefficient, and $P_{\mathrm{A}}^{\mathrm{sat}}$ the saturated vapor pressure of acetone. At constant temperature, feed fugacity for acetone increases by feed concentration, and then acetone sorption into zeolite membrane increases, resulting in high flux at high acetone contents.

On the other hand, sorption selectivity of acetone/water appears to increase as the ratio of feed fugacities increases at high feed concentrations. Therefore, acetone concentration in permeate and separation factor of acetone/water increase by increasing acetone concentration of feed. This trend is clearly shown in Fig. 7.

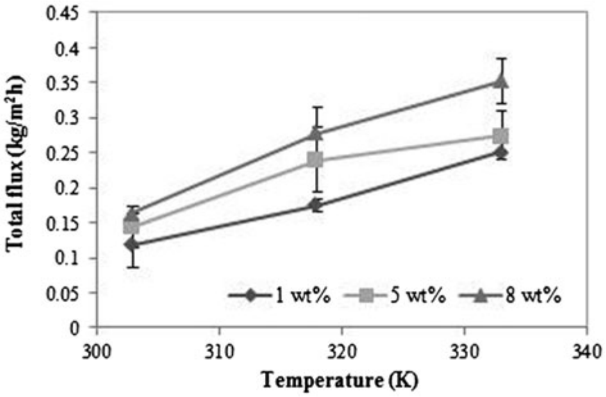

Fig. 4. Total flux through the B-ZSM-5 membrane as a function of temperature at different concentrations (permeate pressure: 160 mmHg).

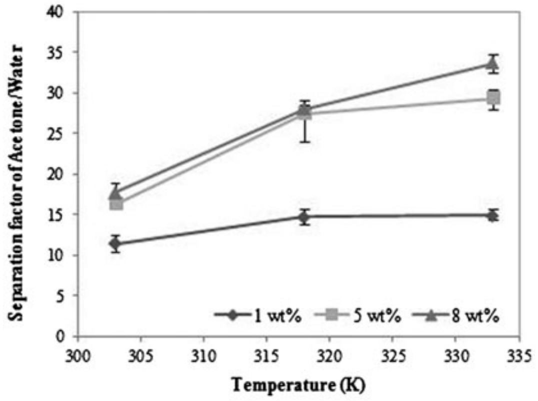

Fig. 5. Effect of temperature on the separation factor of acetone/water in the B-ZSM-5 membrane at different concentrations (permeate pressure = 160 mmHg).

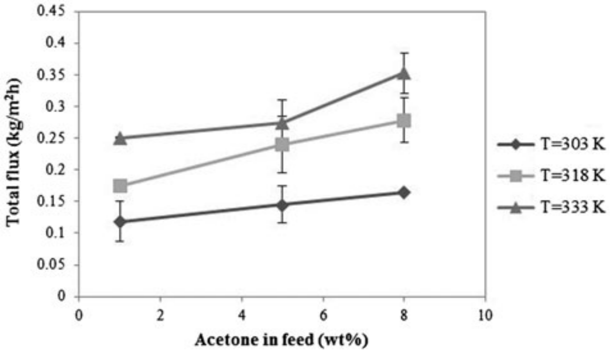

Fig. 6. Total flux through the B-ZSM-5 membrane as a function of feed concentration at different temperatures (permeate pressure = 160 mmHg).

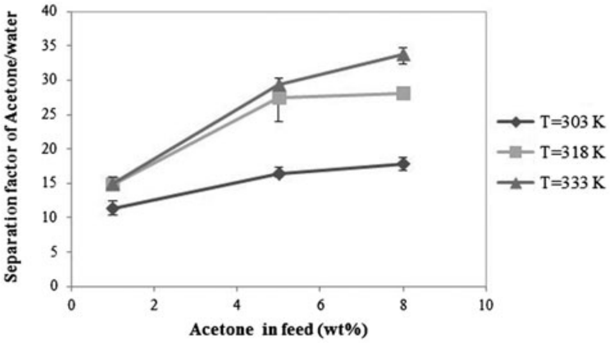

Fig. 7. Effect of acetone concentration on the separation factor of acetone/water in the B-ZSM-5 membrane at different temperatures (permeate pressure = 160 mmHg).

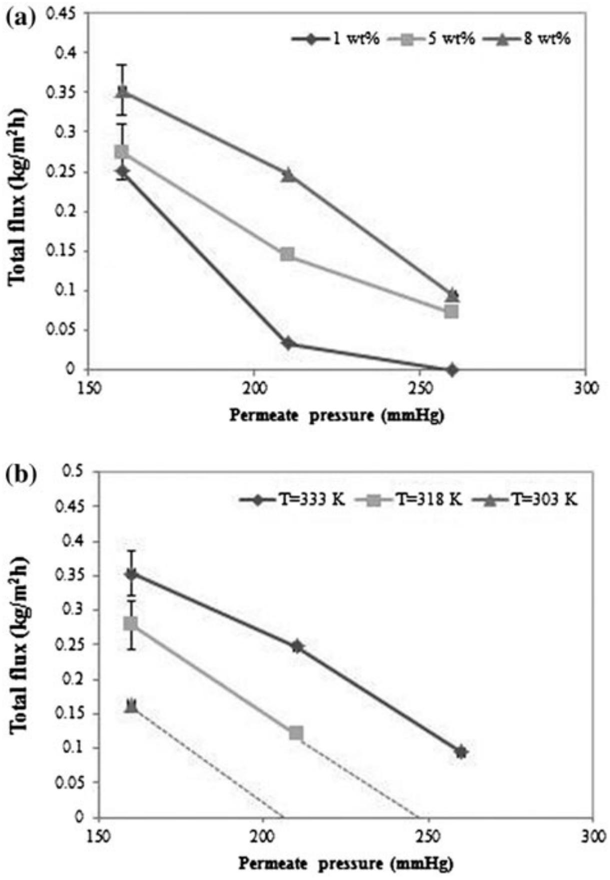

Fig. 8. Total flux through the B-ZSM-5 membrane as a function of permeate pressure (a) at $T = 333$ K and different acetone concentrations and (b) at acetone concentration = 8 wt% and different temperatures.

3.2.3. Effect of permeate pressure

As illustrated in Fig. 8, diminishing permeate pressure at different temperatures and compositions, increases the total flux. A decrease in permeate pressure enhances driving force and thus the total flux increases. At low temperatures and high permeate pressures, total flux through the B-ZSM-5 membrane decreases considerably, so that studying and sampling under these conditions is impossible which has been illustrated in Fig. 8(b) as dashed lines.

On the other hand, with the increasing permeate pressure, an increase in separation factor is observed (see Fig. 9). Permeate pressure is kept lower than the saturated vapor pressure of the volatile (organic) compound in the mixture at the examined temperature. So, the relation between permeate pressure and separation factor depends on the volatility of organic component. As reported in the literature [16], the separation factor of organics such as alcohols decreases by increasing permeate pressure. A contrary behavior of acetone compared to alcohols can be explained by its high vapor pressure (volatility). It means that if rapid permeate component is an organic molecule with high volatility increasing permeate pressure leads to rising in the separation factor.

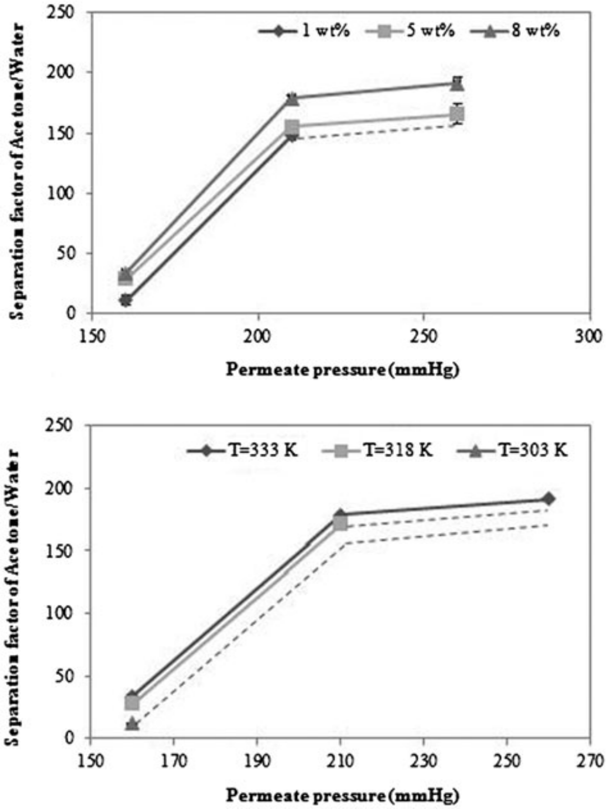

Fig. 9. Effect of permeate pressure on the separation factor of acetone/water in the B-ZSM-5 membrane (a) at $T = 333$ K and different acetone concentrations and (b) at acetone concentration = 8 wt% and different temperatures.

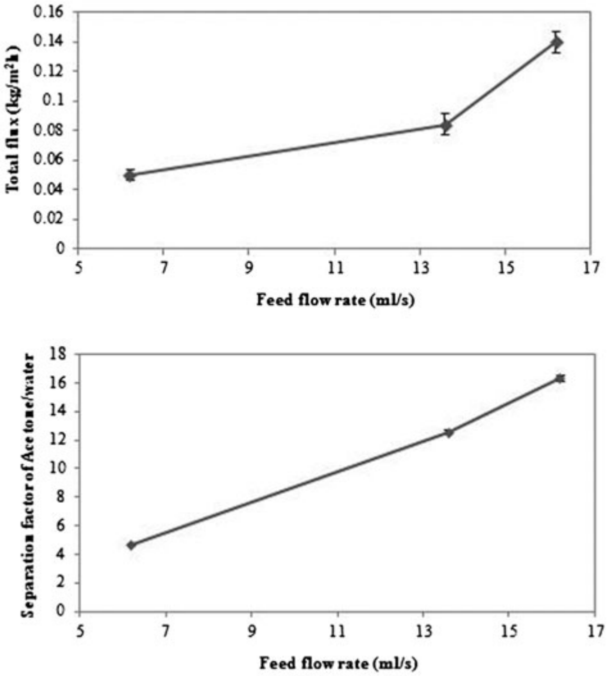

Fig. 10. Effect of feed flow rate on (a) total flux through the B-ZSM-5 membrane and (b) the separation factor of acetone/water at acetone concentration = 5 wt%, $T = 303$ K, and permeate pressure = 160 mmHg.

With the increasing difference between permeate pressure and the saturated vapor pressure of organic component in the examined temperatures, observing enhance in the permeate flux is a natural behavior. But, the separation factor of organic/water as a competition between the permeations of organic and water molecules shows two different behaviors; for high volatile organics (acetone), sorption selectivity is dominant due to the high fugacity of volatile organic component and decrease in permeate pressure not only has no positive effect of separation factor but also results in a substantial water permeation and then a considerable decrease in separation factor, however, for low fugacity molecules (ethanol), decrease in permeate pressure might be expected to have a positive influence on their separation factor because sorption selectivity decreases with reducing the ratio of feed fugacities.

3.2.4. Effect of feed flow rate

Fig. 10 shows variations of total flux and separation factor with feed flow rate for the B-ZSM-5 membrane. In this experiment, the flow was laminar (average Reynolds number was about 500). The results show that both the variables increase with the increasing feed flow rate. Because of the reverse relation between boundary layer thickness and Reynolds number, with increasing Reynolds number (as a result of increasing feed flow rate), a decrease in boundary layer thickness happens and then mass transfer resistance decreases. As presented in the literature [17], the liquid boundary layer mass transfer resistance for organics reduces when the feed flow rate increases, however, water flux is independent of feed flow rate and it is relatively constant. So, the separation factor enhances at higher feed flow rates.

4. Conclusions

Separation of acetone/water was carried out by pervaporation using the B-ZSM-5 zeolite membranes. The zeolite membrane was synthesized and the effects of feed temperature, concentration, flow rate, and permeate pressure on total flux and separation factor were investigated. It was shown that in the synthesized membrane, increase in temperature and feed concentration improves total flux of the membrane. The membrane B-ZSM-5 shows a better selectivity at higher feed concentration and temperature. So, it can be concluded that the membrane has better performance in higher concentration and temperature. Increasing permeate pressure, decreases total flux and improves acetone separation factor unlike other organics and it can be due to higher volatility of acetone. So, enhancing permeate pressure has a good influence on the separation factor for organics with high volatility. Increasing feed flow rate can diminish boundary layer thickness and increases the performance of synthesized membrane. As a result, it can be said that for the separation of organics like acetone from water in the membranes with high quality, high temperature, and pressure is preferential and increasing feed flow rate and feed concentration is desirable, too.

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