Preparation Of Zeolite Membrane And Modeling Dehydration Of Organic Compounds On The Pilot-Scale With The Help Of Artificial Neural Network

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Abstract: Nano pore NaA zeolite membranes composed of a continuous intergrowth of NaA zeolite crystals had been synthesized hydrothermally on the surface of a porous tubular support (14 mm outer diameter, 25 cm length). Morphology of the supports subjected to crystallization was characterized by Scanning electron microscopy (SEM). Separation performance of NaA zeolite membranes was studied for water-Ethanol mixtures using pervaporation (PV) in cross flow method. The membranes showed good selectivity towards water in the water- Ethanol mixtures. Water permeates faster because of its preferential adsorption into the nano-pores of the hydrophilic zeolite membrane. The membrane exhibits a hydrophilic behavior, with a high selectivity towards water and a good flux. Thus, the pilot- scale PV plant which produces 5 l/h of solvent (EtOH) at less than 0.2 wt.% of water from 90 wt.% solvent at 75°C has been put into pilot operation. The present study considered the amount of water-alcohol separation within the process of pervaporation with the help of Artificial Neural Network modeling.

Keywords: Nano pore zeolites, Pervaporation, pilot plant; NaA; Membrane; Artificial Neural Network

1. Introduction

The azeotropic mixtures are hard to be separated by using normal distillation process and but can only be done through azeotropic distillation. However, azeotropic distillation is more energy consuming than conventional distillation. Apart from high-energy consumption for azeotropic distillation, benzene, a highly carcinogenic and toxic substance, which is used as an azeotropic dehydrating agent in many plants, is a major health concern. Pervaporation is an economical separation technique compared to conventional separation methods such as distillation especially in processes involving azeotropes, isomers and removal or recovery of trace substances. Due to its high separation efficiency and flux rates, PV results in energy cost saving and safe operation. In this regard, pervaporation eliminates the use of toxic materials and is a promising alternative for energy consuming distillation processes in separating azeotropic mixtures. Table 1 shows energy consumptions required by different separation methods in ethanol dehydration. In terms of energy requirement, pervaporation is an obvious choice in ethanol–water separation [1-3]. Furthermore, PV has several advantages over traditional distillation: (1) reduced energy demand because only a fraction of the liquid that needs to be separated is vaporized, (2) simple equipment since only a vacuum pump is used to create a driving force and (3) lower capital cost. Thus, relatively mild operation conditions and high effectiveness make PV an appropriate technique for such separations. As a result, most PV studies have been focused on dehydration of organic mixtures [4].

Table 1: *Energy requirements for ethanol dehydration*

Purification (Wt. %)	Energy required (kJ/kg EtOH)	Process
8.0–99.5	10376	Distillation
95.0–99.5	3305	Azeotropic distillation
95.0–99.5	423	Pervaporation

Polymeric membranes are not generally suitable for applications involving harsh chemicals due to membrane chemical instability. However, a recent development of chemical-and-temperature resistant hydrophilic ceramic membranes has made it possible to overcome the limitations of hydrophilic polymeric membranes [5]. However, a recent development of chemical-and-temperature resistant hydrophilic ceramic membranes has made it possible to overcome the limitations of hydrophilic polymeric membranes. Zeolite membranes are another kind of pervaporation materials for separating water from highly concentrated ethanol aqueous solution since zeolites are most hydrophilic and have well-defined open crystal structures with a pore size of several angstroms. These unique structural characteristics and hydrophilic nature have rendered zeolite materials possessing pronounced molecular sieving effect and selective adsorption capability (i.e., appreciated separation performance). Therefore, zeolites can be extensively applied in removal of volatile organic chemicals from air streams, separation of isomers and mixtures of gases, shape-selective catalysis and ion exchange. The zeolitic membranes offer several advantages over polymeric ones: (i) they do not swell significantly compared to polymeric membranes, (ii) they have uniform molecular-sized pores that provide differential transport rates and molecular sieve effects, (iii) the zeolitic structures are more chemically stable, tolerant to harsh separation conditions such as strong solvents or low pH, (iv) zeolites are thermally stable up to high temperatures of 1000 ˚C. Nano and uniform pore size of these zeolites makes separation of small molecules possible via molecular sieving. Zeolite membranes were found to be extremely effective for dehydration of ethanol by PV, with separation factors of 10^4 or more being achieved. This has many potential advantages in terms of reproducibility and easy control [6]. A membrane separation system that takes advantage of the adsorption and molecular sieve properties of zeolites requires a continuous zeolite membrane layer. Zeolite membranes have been studied and developed for over 15 years to apply them to separating processes in industry, because they have higher thermal and chemical properties compared with those of polymer membranes [7]. In this study, Nano pore NaA zeolite membranes were fabricated and then used to separate

water/Ethanol mixtures. Zeolite NaA layers were coated on external surface of porous tubular mullite supports using hydrothermal method. Also, we describe a pilot-scale pervaporation plant include of Nano pore NaA zeolite membranes fabricating and the unique properties of tubular-type module and membranes. Also, the results of this study by use of ANN reflected a suitable accuracy.

2. Artificial Neural Network (ANN)

Recently, there have been a number of researches conducted on data processing for problems for which there is no solution, or problems that are not easily solvable. The ANN pattern is inspired by the neural system of living organisms that includes some constituent units called 'Neuron'. Most of the neurons are composed of the three main parts including cell body (that includes necluous and other protective parts), dendrites, and axon. The last two parts are the communicative parts of the neuron. Figure 1 displays the structure of a neuron.

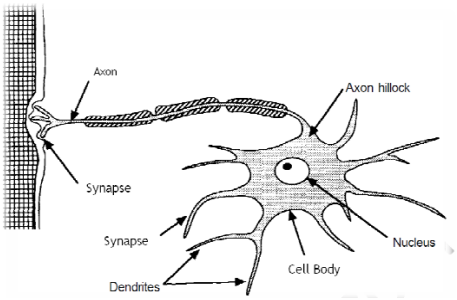

Figure 1. *Major parts of a biological cell*

Dendrites, as electric signal receiving areas, are composed of cell fybers with unsmooth surface and many splitted extensions. That is why they are called tree-like receiving networks. The dendrites transfer the electrical signals into cell nucleous. The cell body provides the required energy for neuron activity that can be easily modeled through an addition and comparison with threshold level. Unlike Dendrites, axon has a smoother surface and fewer extensions. Axon is longer and transfers the received electro-chemical signal from the cell nucluous to other neurons. The cinfluence of a cell's axon and dendrites is called synapse. Synapses are small functional structural units that enable the communication among neurons. Synapses have different types, from which one of the most important ones is the chemical synanpse. Artificial neural cell is a mathematical equation in which p represents an input signal. After strengthening or weakening as much as a parameter w (in mathematical terms, it is called weight parameter), an electric signal with a value of pw will enter the neuron. In order to simplify the mathematical equation, it is assumed that the input signal is added to another signal with b value in the nucluous. Before getting out of the cell, the final signal with a value of pw + b will undergo another process that is called "Transfer function" in technical terms. This operation is displayed as a box in Figure 2 on which f is written. The input of this box is the pw + b signal and the output is displayed by a. mathematically, we will have:

$$a = f(pw + b)$$

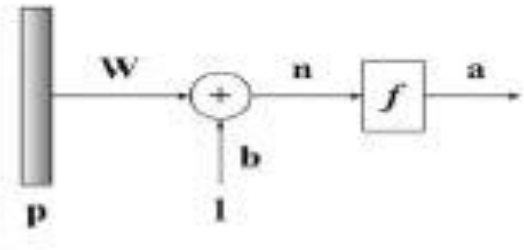

Figure 2. *Mathematical model of a neuron*

Putting together a great number of the above-mentioned cells brings about a big nueral network. As a result, the network developer must assign values for a huge number of w and b prameters; this process is called learning process. Within the structure of neural networks, some times it is needed to stack up a number of neurons in a layer. Moreover, it is possible to take advantage of nueron crowds in different layers to increase the system efficiency. In this situation, the network will be designed with a certain number of inputs and outputs too; while the difference is that there would be more than one layer (instead of having only one layer). In this manner (multi-layer network), the input layer is the layer through which the inputs are given to the system, the output layer is the layer in which the desired the results are delivered, and the other layers are called hidden layer. Figure 3 displays a neural network with three layers. Input layer, output layer, and hidden layer (that is only one layer in this figure). Through changing the number of hidden layers, and changing the number of present neurons in each layer, it is possible to enhance the network capabilities [8].

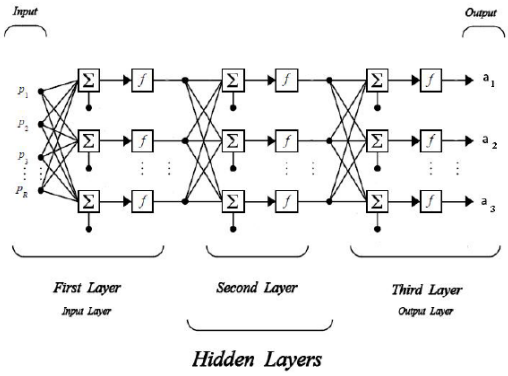

Figure 3. *A schematic view of Neural Network and its constituent layers*

2.1. Modeling dehydration of organic compounds by use of Neural Network

In this research, the influence of ANN input parameters (volumetric flow, pressure and temperature) as well as the flux characteristics (the fluxes are the network output) on the efficiency of dehydration process. One ANN was designed for analysis of the flux parameter. Feed-forward multilayer perceptron ANN and Levenberg-Marquardt function with two inputs and two outputs were used. The Tansig transfer function was used for the hidden layer, and Purelin was utilized for the output layer. Five neurons were determined for the hidden layer. After data processing, 70 percent was dedicated for learning, 30 percent was dedicated for testing. Such organic compounds as ethanol was selected in this research; and, Matlab version R2014b was used. Figure 4

displays a schematic view of a two-layer ANN with only one hidden and output layer. The inputs are multiplied by a w value, and there is a bias factor (b) that is added to the input (bias is a fixed value that is added to the input in order to increase the accuracy). Afterward, the result will undergo a function and the resulted value will be multiplied by a weight and added with a bias. The final result will pass another function (with different form and functionality) and output is made. There are five neurons and two inputs on the first layer; however, the number of neurons in the output layer is the same as the number of outputs.

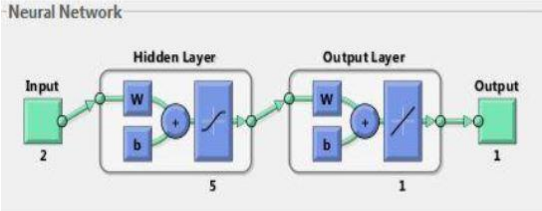

Figure 4. *A schematic view of the ANN*

The following points about the algorithms must be considered: The Data Division compartment totally scrambles the defined data for the system. This compartment randomly defines the Train, Validation, and Test data, so that there will be samples from everywhere of the environment. Levenberg-Marquardt function was used in Training phase. The Mean Squared Error (MSE) functions for performance measurement. The default settings were used for derivative issue. Epoch is accepted from iteration 0 to 1000. It means the weights consecutively changed for 1000 times based on the Levenberg-Marquardt function, and the training procedure was done. If the iteration number reaches 1000, the procedure stops (here it stopped at 24). There was no limit for time (but it could be set for training to stop after 30 seconds for example). Validation check is the maximum number of times that network failure can be tolerated (figs 5 and 6).

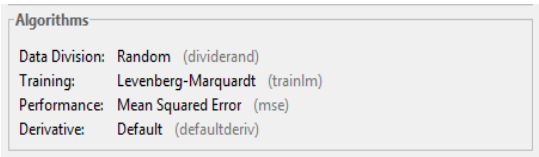

Figure 5. *Algorithms compartment in ANN*

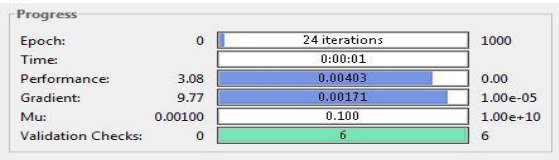

Figure 6. *Graph of Water and ethanol dehydration progress by Polydimethylsiloxane polymer membrane and Polyvinylidene fluoride*

3. Experimental

3.1. Membrane preparation

In ceramic membranes, thin dense layers are usually deposited over porous supports. The porous supports provide mechanical strength for the thin selective layers. Porous supports can be made from alumina, cordierite, mullite, silica, spinel, zirconium, other refractory oxides and various oxide mixtures, carbon, sintered metals and silicon carbide. NaA membrane was grown hydrothermally on the surface of a porous tubular support [9-15] (14 mm outer diameter, 25 cm length). The hydrothermal synthesis of NaA zeolite membrane was performed as follows. An aluminate solution was prepared by dissolving sodium hydroxide and aluminium hydroxide in distilled water. A silicate solution was prepared by dissolving sodium silicate in distilled water. The aluminate solution was added to the silicate solution and the resulting mixture was stirred vigorously, producing a homogeneous gel. The molar composition of the resulting gel was SiO2/ Al2O3=1.926, Na2O/ Al2O3=3.165 and H2O/ Al2O3= 128. The porous support coated with the seed crystals of NaA zeolite was dipped in the gel. After hydrothermal treatment at 100°C for 3 h, the support was taken out, washed by water and dried in reduced pressure. The treated tube was checked by X-ray diffraction (XRD) for the formation of zeolite membrane on its surface. The surface morphology of the membrane was observed by a scanning electron microscopy (SEM) [16-20].

3.2. Pervaporation tests

We used a PV experimental set up (Figure 7 and 8) to be sure of successfully fabrication Nano pore NaA zeolite membranes before installed in to the Tubular-type module. The tubular-type module with NaA zeolite membrane is consisting of many pieces of the membrane with 25 cm long. Membranes sealed at their one ends are inserted alternatively at the designated pitch from both tube sheets and fixed at the tube sheet. The feed flows to the outer side of the zeolite membrane and rushed across the bundle of zeolite membrane. The permeated vapor mixture through the inside of the membrane is collected by a condenser. PV tests were carried out using a standard PV apparatus. Feed solution, preheated to a constant temperature, was introduced to the outer side of the zeolite membrane in the PV cell. For most tests, the downstream pressure was maintained at 133 Pa throughout the test operation. The zeolite membranes were used for dehydration of aqueous Ethanol. ethanol mixtures were used and experiments were carried out at operation temperatures within a period of 30-60 min. Permeate concentrations were measured using GC (TCD detector, Varian 3400, carrier gas: hydrogen, column is polyethylene glycol, sample size: 5 micron, column and detector temperatures: 120 °C- 150 °C, detector flow rate: 15 ml/min, carrier flow: 5 ml/min, column pressure: 1.6 kPa, GC input pressure: 20 kPa). Performance of PV was evaluated using values of total flux (kg/m2.h) and separation factor (dimensionless) [21]. Typical and actual experimental setups were employed as presented in Figures 7-8.

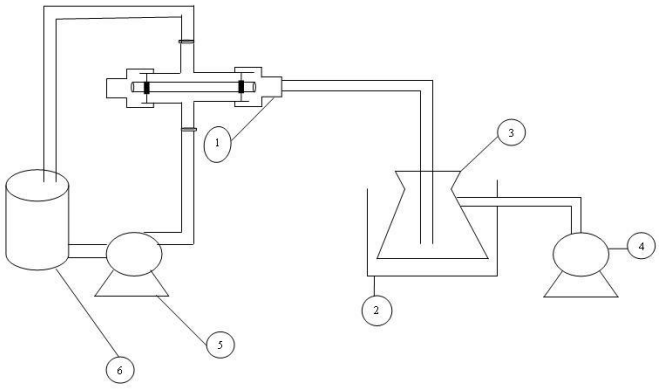

Figure 7: *PV setup; 1- feed container and PV cell 2- liquid nitrogen trap 3- permeate container 4- three stage vacuum pump 5- centrifuge pump 6- tank feed*

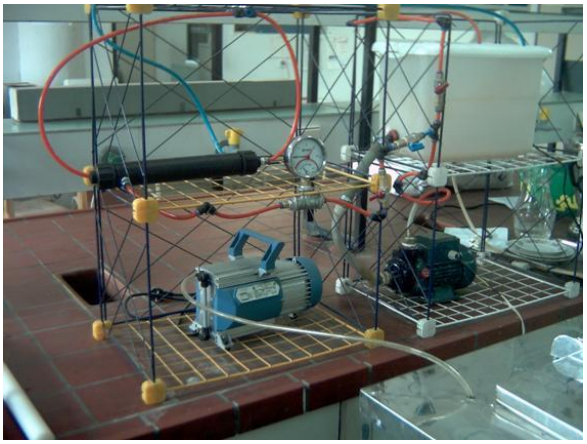

Figure 8: *Experimental PV setup*

Performance of PV is usually evaluated by total flux (kg/m^{2}h) and separation factor (dimensionless). Separation factor of any organic aqueous solution can be calculated from the following equation:

$$Separation\,factor\,(\alpha) = \frac{\left[X_{H_2O} / X_{Organic}\right]_{permeate}}{\left[X_{H_2O} / X_{Organic}\right]_{feed}}$$

Where X_{H_2O} and $X_{organic}$ are weight fractions of water and organic compound, respectively.

4. Results and discussion

4.1. NaA zeolite membrane

The NaA membrane is highly selective for permeating water preferentially with the high permeation flux be-cause of the micropore filling of water in the zeolite pores and/or the intercrystalline pores between zeolite crystals to afford water-selective permeation through the membrane. Porosity of the supports has been measured by water absorption method. The phases Mullite, Cristobalite and SiO2 identification was performed by XRD (Philips PW1710, Philips Co., Netherlands) with CuKα radiation. Morphology of the support and the membrane was examined by SEM (JEM-1200 or JEM-5600LV equipped with an Oxford ISIS-300 X-ray disperse spectroscopy (EDS)). Phase identification has been performed by X-ray diffractometry with CuK_α radiation. The XRD pattern of NaA zeolite membranes confirm that crystal of zeolite NaA has been formed. Figure 9 shows XRD of the mullite support and membranes synthesized using the above-mentioned methods. In this figure, the only phases, which can be observed, are zeolite NaA and mullite.

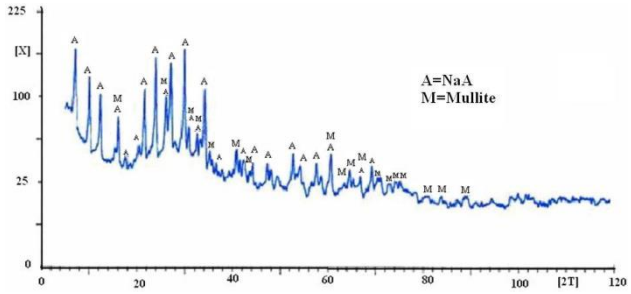

Figure 9: *XRD patterns of support and membrane*

It has been shown morphology of support and membrane by SEM micrograph. Figure 10 shows SEM photographs of the mullite support and NaA zeolite membrane (surface and cross section). Porous structure of the support and thin layer of the membrane can be easily observed.

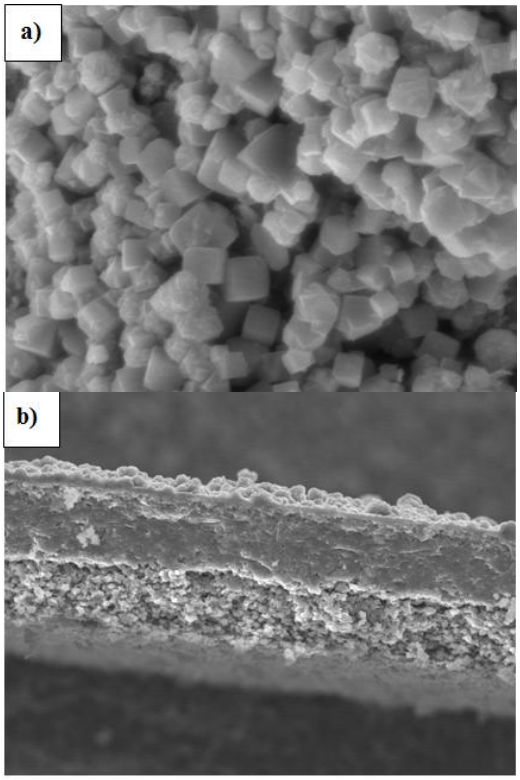

Figure 10: *SEM micrograph of a) the surface of membrane b) the thickness of membrane*

4.2. PV Operating Conditions

Effect of operating conditions at PV process was evaluated by cross flow PV pilot. The Trans membrane pressure is adjusted between 1 and 3 barg. The feed temperature is varied between 20 and 60 °C by means of a small heat exchanger employed into the feed tank. Feed rate is varied

between 0.5 and 3 lit/min by means of centrifuge pumps and recycles line. Permeate collected in a sample bottle is measured. The outlet flow of the cell can be led out of the system or returned to the tank. A shown in table 2, effect of feed rate on permeate flux were measured at constant temperature (20°C) and constant pressure (1 bar). Increasing feed rate increases the permeate flux. As shown in table 2, increasing pressure increases the permeate flux. Increasing rate increases turbulence and hydrodynamic effects cause to increasing permeate flux. Temperature is known as a main parameter. Increasing temperature causes an increase in viscosity reduction. Table 2 shows the experimental data for the flux as a function of temperature. As seen, the flux increases with temperature. According to the results, it can be said the optimum operating conditions were 60°C, 3 bar and 3 lit/min.

Table 2: *cross flow results by zeolite membrane*

Run	Concentration of Ethanol in feed (wt %)	P (bar)	Q (lit/min)	T ($^{\circ}C$)	Flux $kg/m^2.h$
1	80	1	0.5	20	1.082
2	80	1	1.5	20	1.407
3	80	1	3	20	1.673
4	80	1	0.5	20	1.082
5	80	2	0.5	20	1.421
6	80	3	0.5	20	1.764
7	80	1	0.5	20	1.082
8	80	1	0.5	40	2.237
9	80	1	0.5	60	2.772

4.3. Comparison of ANN output and experimental Data

The comparison of the performance of the neural network with the experimental results is shown in the figs 11-13. As can be seen, the neural network model has been able to predict the results of the experimental data well and the resulting error is less than 1%.

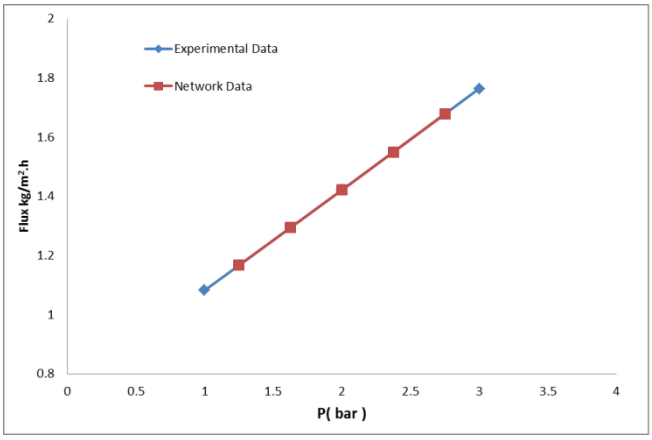

Figure 11: *Comparison of ANN model data and experimental data (pressure parameter)*

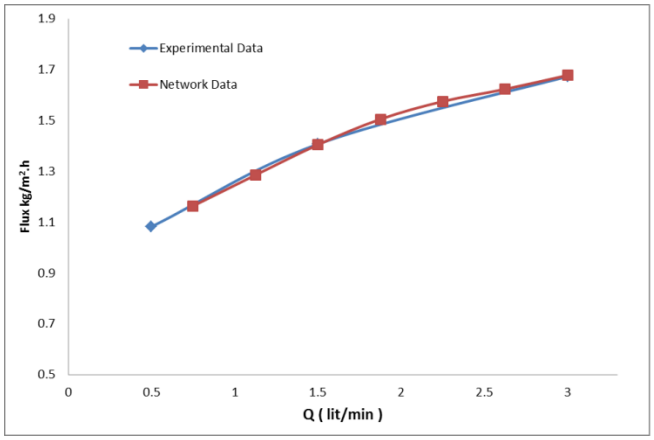

Figure 12: *Comparison of ANN model data and experimental data (volumetric flow parameter)*

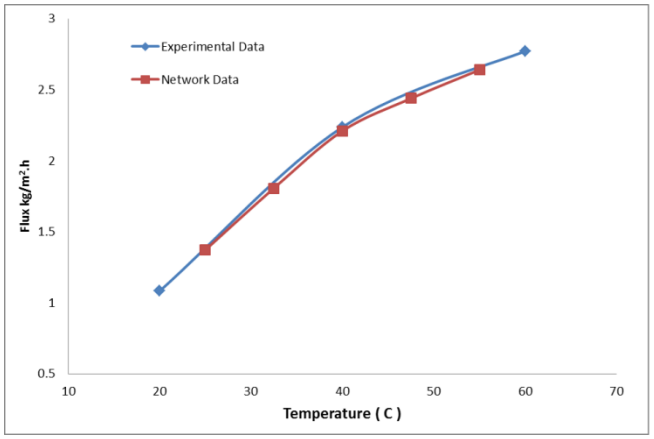

Figure 13: *Comparison of ANN model data and experimental data (temperature parameter)*

4.4. Pilot-scale pervaporation plant

This PV pilot plant was planned for multi-purpose dehydration of such as ethanol, IPA and methanol. This is the first large-scale commercial PV plant using NaA zeolite membranes in Iran. The whole plant view at site is shown in Fig 14.

Figure 14: *experimental Pilot-scale module*

The membrane of 14 mm-OD, 250 mm-length, 109.9 cm2-area (total area =1538 cm2) was used. The operating temperature was 70°C. The pilot plant design conditions are shown in Table 3. This plant produces 99.8 wt. % ethanol from 5 l/h, 90 wt. % waste ethanol feed at module inlet temperature of 75°C. This pilot plant is consisting of 1

module that compresses 14 pieces of NaA zeolite membrane. The module configuration and layout are shown in Figs 14 and 15. Experimental result of concentration of ethanol/water mixtures presented in table 3. Also, water flux verses ethanol concentration is shown in figure 16.

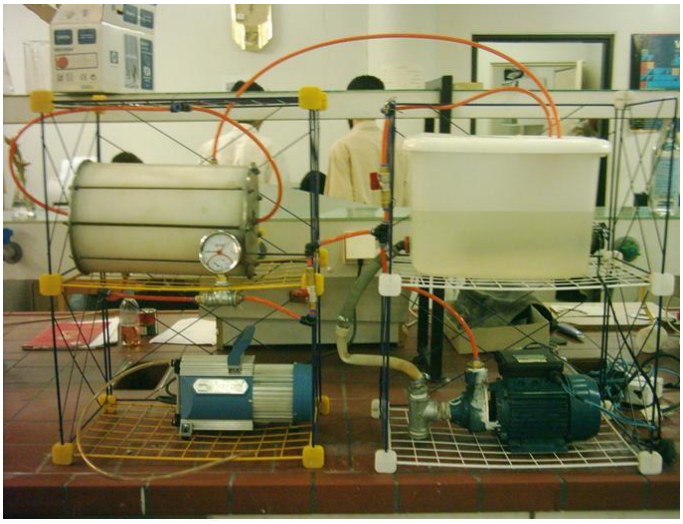

Figure 15: *experimental Pilot plant PV*

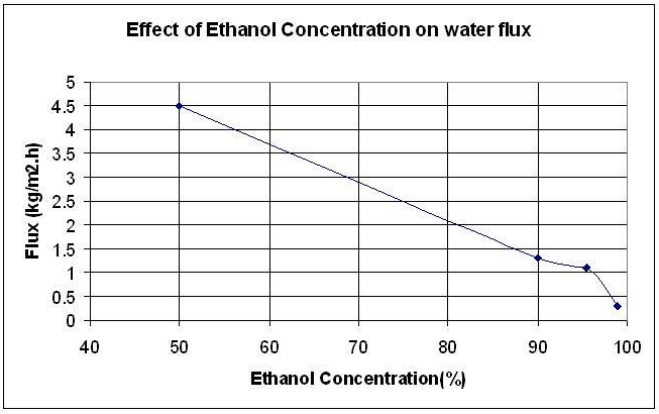

Figure 16: *water flux verses ethanol concentration*

Table 3: *experimental result of pilot-scale pervaporation test*

No	Ethanol Feed (lit)	Initial Feed Con (%)	Feed Pressure (bar)	Feed Temp.(^{0}C)	Duration Operation (h)	Flux (kg/m^2.h)	Final Feed Con. (%)	Sep. Factor
1	5	50	2	75	3	4.5	86	10000
2	5	90	2	75	2	1.3	97.8	10000
3	5	95.5	2	75	1	1.1	98.8	10000
4	5	99	2	75	1	0.31	99.8	10000

5. Conclusion

PV through a Nano pore NaA zeolite membrane is an effective technique to separate Organic component from water. These membranes showed very good membrane performance for separation of Ethanol /water mixtures. Effect of operating condition at pervaporation process show that increasing pressure, feed rate and temperature increases the flux linearly. Dehydration of water-ethanol by use of pervaporation process was modeled in ANN. the ANN in this study reflected the error suitably. We hope PV system with zeolite membrane becomes more popular through this successful result of the first pilot plant. It is expected that PV using these membranes can be a highly interesting tool for industry, provided they can be produced cheap at a large scale.

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