# Measuring the dehumidification efficiency of zeolite nanostructured membrane with TiO<sub>2</sub> layer under different operating conditions in dehumidification of light gas mixture

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## **ABSTRACT:**

In this research,  $TiO_2$  zeolite nanocomposite membranes were first synthesized in order to remove moisture from the gas. Then, field tests were performed on the characteristics of the membrane, by performing several tests of gas selectivity and permeability in measuring different parameters and comparing the relevant graphs of membrane performance, it was obtained that It showed the separation of water from gas. A route for crystal transformation to prepare TiO2 at 70-110 °C under laboratory reflux conditions has been followed. The prepared titanium hydroxide gel crystallizes for 5 to 10 hours under reflux and stirring conditions. The formation of  $TiO_2$ Nano crystallites is confirmed by X-ray diffraction (XRD) study. The anatase phase transforms into  $TiO_2$ composite zeolite when crystallized at 700°C for 13 hours. Several experiments were also performed to verify both TiZ-V and NaA zeolites. Transmission electron microscopy (TEM) investigations showed that the average particle size for the TiZ-V phase was 10 nm, while for NaA it was 35 nm.. In order to further investigate the performance of the membrane under different operating conditions, the efficiency was measured. The tests of changing the relative humidity of the feed have shown better performance of the membrane at relative humidity lower than 80%, so that the selectivity of the membrane has increased under the condition of lower relative humidity of the feed. Next, the membrane was measured under different gas flow rates, which shows the stability of Esha under the tested high flows and the absence of a large drop in its selectivity. Also, in all these experiments, despite the increase in gas flow rate, the degree of superiority of the water component over the gas component in the percolation was evident to a high extent, which shows the high separation of water from gas even in the condition of high gas flow. Next, the membrane was measured under different flow rates of the gas flow, which shows the stability of the membrane under the tested high flows and the absence of a large drop in its selectivity. Also, in all these experiments, despite the increase in gas flow rate, the degree of superiority of the water component over the gas component in the percolation was evident to a high extent, which shows the high separation of water from gas even in the condition of high gas flow. At the end, in order to further increase the efficiency of the membrane, The sweeper gas was added from inside the membrane. which increased the water concentration gradient and decreased the gas concentration gradient on the sides of the membrane wall and as a result increased the selectivity of the membrane to the best level of 543.and also to check the stability of the membrane during operation, the test of increasing the operation time was performed. . In the results, there was no decrease in relative humidity, and its selectivity had little change, which shows the stability of the membrane performance increasing dehumidification operation time.

KEYWORDS: Dehumidification, natural gas, Nano composite membrane, TiO2 zeolite

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#### INTRODUCTION

The presence of water in natural gas can cause several problems, these problems include:

1- The presence of water with gas can cause the formation of hydrates in the gas transmission pipeline and block the passage of gas. Also, the presence of water drops causes various problems. Therefore, the dew point temperature of the gas must be lower than the lowest possible temperature of the pipeline so that water vapor does not condense.

2- In the presence of H2S and CO2, the corrosion of metal equipment increases.

3- Condensation of water vapor creates a two-phase condition, which reduces fluid transfer efficiency and vibration in the pipeline. Also, the life of the pipes is reduced due to wear.

4- The presence of water reduces the transmission capacity of the pipeline and also reduces the calorific value of the gas. [1]

In addition to liquid hydrocarbons, sulfur compounds, carbon dioxide, nitrogen, helium, fine solid particles; A significant amount of water is also extracted along with natural gas. There is water in the form of free water and saturated soluble water along with gas, free water in the well facilities (or close to the facilities) and also at the entrance of the refinery by flocculants up to the level of 25-120 Ib/MMscf. It is separated from the flow of natural gas.

To reach the desired conditions, 20-115 Ib/MMscf of water should be separated from the mentioned stream to reach the salable gas conditions, for this purpose, a process called dehydration is used. [2]

Due to the fact that no research has been done in this field so far, it is considered a new research, and on the other hand, zeolite membranes can be chosen as an alternative to conventional dehumidification processes due to their high chemical and thermal resistance as well as molecular sieve properties. . Rather, the use of zeolite membranes in the oil and gas refining industry leads to an increase in separation efficiency and a reduction in the amount of natural gas wastage, energy consumption, and harmful environmental effects compared to common gas refining processes. One of the most important features of membranes is controlling the speed of penetration and permeation of different models. Also, since membranes are materials that have the ability to be selectively selected for the purpose of permeating different types of materials, this property leads to the separation of different materials from each other. Among other properties of zeolite nanostructured membrane with layer index (TiO<sub>2</sub>), which shows the new aspect of the research. 1 .High surface area per unit volume; Result: occupying less space. 2 .simple operation without moving parts; Result: reducing the cost of repairs and stopping operations. 3 .less need for control during operation; Result: reducing the cost of control equipment and human errors

4 . The effect of membrane modules in reducing weight and size; Result: saving investment cost. 5 .No phase shift is required to achieve separation; Result: high and competitive energy efficiency. 6 -Membrane systems are generally very environmentally friendly technologies[3,4]

As we know, the humidity in the raw materials and products of various industries lowers their real value and causes the products to be unusable. Therefore, it is important to choose the most appropriate additive which, in addition to being cheap and available, should have the ability to recycle and waste little zinc, and also should not have a destructive effect on the process and fluid. In this research, by using nano technology in natural gas dehumidification, while nano-structure synthesizing membrane and determining its crystallinity characteristics as moisture absorbers, optimization of the properties of this synthesized absorber is done in order to select the influencing variables in the use of It should be used as a substitute for common materials.

The National Gas Company and gas purification institutions/refineries can use the results of this plan.

In recent years, membranes and membrane separation techniques have grown and expanded from laboratory scale to industrial processes. Today, membranes are used to produce drinking water from sea water using the phenomenon of reverse osmosis, cleaning and recycling valuable substances from the effluents of industrial factories by electro dialysis and Nano filtration, industrial wastewater treatment using filtration processes (micro-ultra and Nano filtration). and the process of membrane bioreactors for separating macromolecule solutions in the food and pharmaceutical industries with ultrafiltration, removing urea and other toxic substances from the blood system with the help of dialysis, separating gases to produce nitrogen, sweetening natural gas, producing gases that are useful in the production processes of petrochemical industries, is used [5].

The membrane is a permeable or semi-permeable phase that selectively blocks the passage of some particles, or in other words, selectively allows the passage of particles. Membrane processes are processes in which food, which is a mixture of two or more components, is divided into different components using a membrane. In this case, the basis of separation is based on the principle that one or more components pass through this substrate faster than other components. In this method, the phases do not change and the products can be mixed together with each other. In other words, the membrane is selective towards one of the components. In this case, its transfer from one phase to another phase will be done by the membrane. In this way, one of the phases rich in that component and the other is depleted of it. A membrane is defined as a phase through which nutrients selectively pass. In other words, the membrane acts as a phase that allows some separated components to pass through it at different speeds and prevents others. As shown in (Fig 1), the feed is separated by the membrane into two flows, including the passing flow, that is, A part of the feed that does not prevent it from passing through the membrane and the remaining flow. That is, a part of the feed that cannot pass through the membrane is divided, and based on the purpose of separation, each of them can be considered as a product. In general, membrane methods are directly related to concentration and can be used well when the concentration of substances is low. [6].

The performance of a membrane is determined by two main factors, which are the flux and selectivity or return of the membrane. Flux or intensity of permeation is the intensity of volumetric flow (molar or mass) that passes through the membrane surface per unit of time. The selectivity or the separation factor, which is discussed in the case of a mixture of miscible liquids or gases, is defined as the permeability ratio of the desired components [7].



Fig 1: Basic principles of membrane process [6].

Structurally, membranes fall into two main categories. Symmetric membranes and asymmetric membranes. In asymmetric membranes (unlike symmetrical membranes), the porosity, pore size, or composition of the membrane changes from the top to the bottom of the membrane. Asymmetric membranes are usually layered structures that have a selective thin layer on a much thicker and highly permeable microporous substrate. Since the selective layer is very thin, its membrane fluxes are high. The microporous substrate also provides the required strength for membrane performance. The outline of an asymmetric membrane is shown in (Fig 2). Membranes made by the Loeb and Sir-Irian processes contain a single membrane material, where the level of porosity and the size of the pores are different on different levels of the membrane. Asymmetric membranes that are fabricated in other ways and used on a large scale are often composed of layers of different materials that perform different functions. [8,9]

1. Phase separation membranes: This category includes membranes made by the Loeb and Srirajan method, which involves the deposition of a casting solution by immersion in a bath (water) without solvent. It also includes a variety of related methods such as deposition by solvent evaporation, deposition by water absorption from the vapor phase, and deposition by cooling.

2. Solution-coated composite membranes: To prepare these membranes, one or more thin and dense polymer layers are coated on the surface of a microporous support.

3. Interfacial polymerization membranes: This type of asymmetric membrane is made by polymerizing a very thin layer of polymer on the surface of a microporous polymer support.



Fig 2: Outline of an asymmetric membrane [9].

Membrane processes with advantages such as reduced energy consumption due to no phase change, small volume and no need for much space, diversity in shape and size, low pressure drop and high mass transfer, high separation performance for dilute solutions, low need to additives and solvents, the simplicity of membrane design and the ease of their use in industrial scales are also distinguished from other separation methods because they are environmentally friendly. Nonetheless, this method has disadvantages such as concentration polarization (difference in permeability of particles of different sizes) that those particles pass relatively slowly, accumulate in the vicinity of membrane and thus concentration distribution in feed flow is changed. If this phenomenon continues, it is one of the most important reasons for membrane's blockage. Other disadvantages of membranes include short membrane life, selectivity and low flow rate passing through membranes, and high manufacturing cost [10].

The most of membranes are polymers or biopolymers, mostly cellulose derivatives or engineering synthetic polymers that are used for specific purposes. The first application of polymer membrane in the 60s by Loeb and Sourirajaun was reported for water purification by RO reverse osmosis method [11].

Material transmission through membrane can be due to concentration difference, pressure difference or electric field difference on both sides of membrane. Based on the porosity characteristics, membranes can be classified according to Table 1 [12].

For non-porous membranes, the mechanism of material transmission through membrane is described by the permeation dissolution model. But in porous membranes, transfer speed and selectivity are influenced by factors such as particle size and fluid viscosity.

Table 1: Classification of porous properties of membranes

Membrane	Motive force (Driving for			
structure	Pressure	Concentration		
Non-Porous	Reverse osmosis (RO)	Pervaporation (PV)		
Micro- Porous pore diameter dp<2nm	Nano filtration (NF)	Dialysis		
Meso- Porous pore diameter 2 <dp<50nm< td=""><td>Ultra filtration (UF)</td><td></td></dp<50nm<>	Ultra filtration (UF)			
Macro- Porous pore diameter 50 <dp<500nm< td=""><td>Micro filtration (MF)</td><td></td></dp<500nm<>	Micro filtration (MF)			

Structurally, membranes fall into two main categories: Symmetric and asymmetric membranes. In asymmetric membranes (unlike symmetrical membranes), the porosity, pore size, or composition of membrane are changed from the top to the bottom of membrane [13, 14].

Two models of describing the penetration mechanism are shown in (Fig 3). In the solutionpermeation model, the penetrant is dissolved in membrane materials and then permeates through membrane towards the lower concentration gradient. Penetrants are separated due to the difference in the solubility of the materials and the difference in the penetration rates of the materials in membrane [15, 16,].



Fig 3: Molecular transmission through membranes [14].

The basics of membrane separation in relation to the removal of moisture from natural gas can be stated as follows; The steady state permeability of a polymer for gas i (P<sub>i</sub>) is determined as follows [17]:

$$P_{i} = \frac{N_{i}.l}{A.(p_{2} - p_{1})}$$
(1)

For thin film composite membranes, due to the difficulty of accurately measuring the thickness (l) of the selective layer, the permeability  $(P_i/l)$  has been used to describe the gas flux through membranes.

$$\frac{P_i}{l} = \frac{N_i}{A.(p_2 - p_1)}$$
(2)

The selectivity of a membrane for component i over j is:

$$\alpha_{i/j} = \frac{P_i}{p_j} = \frac{P_{i/l}}{P_{j/l}}$$
(3)

During the last 20 years, membrane processes have made great progress compared to other common separation methods such as distillation, absorption, desorption, extraction, etc. Membranes are classified based on different parameters. These parameters are: Driving force, type of membrane, geometric shape of membrane, structure of membrane [18].

Membrane processes, whose driving force is pressure difference, are used to separate insoluble and suspended particles of different sizes. These processes according to the small size of the holes are called reverse osmosis (RO), Nano filtration (NF), ultrafiltration (UF) and microfiltration (MF) respectively [19, 20, 21].

To achieve a dew point of 40 to 140°F in large gas volumes, liquid absorption systems are more economical. But if a dew point above 180°F is of interest, membrane absorption technology is more suitable. Considering the problems caused by water in the system, a lot of research has been done on the effect of various parameters such as the type of absorbing material, the amount of incoming feed flow, temperature and pressure of the process on the moisture absorption performance of the gas flow. Therefore. temperature, pressure, moisture concentration in feed, intensity of feed flow (independent variable) are investigated as variables affecting the performance of moisture absorption in a nanostructured membrane system.. Due to the increase in problems caused by old methods of dehumidification, the need to conduct research in relation to promising technologies such as nanomembranes is getting more attention. [22,23]

In this research, the separation of water from gas by membrane technology and by zeolite nanostructured membrane with  $TiO_2$  layer is investigated, in this context the following points can be mentioned:

In this research, eutectic or hydrothermal method is used for Nano synthesis, then the size of the Nano hole on the surface of the membrane is determined by FTIR test or SEM or TM technique.[24]

In the next step, two methods are used for nanostructure membrane analysis.

The first method is experimental, where a filling or spraying tower is built to direct Wet Gas into this tower, and then from the tank exiting from the tower, the amount of moisture with the gas is detected and measured by a head sensor.

A wide range of separation problems can be solved by changing and modifying the membrane structure. Membranes have fundamental differences in terms of structure and function. Many efforts have been made to find the relationship between the membrane structure and the transfer phenomenon through the membrane. In order to determine the type of membrane application in separation, the characteristics of the membrane must be determined and identified. A small change in one of the membrane manufacturing parameters can have changes in the structure and subsequently the performance of the membrane. Among the most important parameters that are needed to relate the membrane properties with the separation properties, the following can be mentioned.

- Hole size (diameter)
- Hole size distribution
- Membrane void volume
- Crystallization

To identify these characteristics, several methods have been presented and developed. The most important of these methods are mentioned below, separating porous and non-porous membranes. Methods are used to know the properties of porous membranes, which are briefly presented below [25]

## Atomic force microscope

This method is one of the newest methods in identifying the surface of membranes. In this method, a very sharp rod with an approximate diameter of 100 angstroms is used to photograph the desired surface. While this rod is in contact with the surface with a constant force, the Landen-Andro-Wales interactions created between the atoms of the rod and the surface are measured by special detectors.

By photographing the surface, a straight line or a curve is created from the structure of the tested surface. The constant and uniform force on the rod, which is very small (1 nano-newton), is provided by means of micro levers. As a result, this method can be used to identify soft surfaces such as polymer membrane surfaces [26].

#### Scanning electron microscope

One of the common and common methods to identify membranes is the use of electron microscopes. Electron microscope methods work in two ways:

scanning electron microscope (SEM)

transmission electron microscope (TEM)

The basis of the work of the SEM method is electron irradiation to the surface of the membrane and detection of the electrons produced from the surface. A beam of electrons with a kinetic energy of about 1-25 kv hits the membrane sample and heats it up. Electrons hitting the sample are called primary (high-energy) electrons, and electrons that go from the surface to the detector are called secondary electrons [27].

Secondary electrons are not caused by reflection, but are separated from the surface of the object itself. These electrons form the same image that can be seen on the screen or micrograph. Due to the high heat caused by the impact of electrons on the sample, a special protective layer is used to prepare the sample. When a membrane (or polymer) is exposed to electron radiation, depending on the type of polymer and the accelerating voltage used, the said sample may burn or be damaged. To avoid this, the sample is of particular importance. The basis of the TEM method is similar to SEM, with the difference that in the TEM method, a higher voltage is used to accelerate the electrons, which creates higher quality images. Therefore, by using the TEM method, it is possible to study the structure of very fine membranes and membranes that are used in ultrafiltration or gas separation.

In this method, high precision should be used to prepare the sample to be tested. This method is also used to identify the properties of asymmetric nonporous membranes [28].

## MATERIALS AND METHODS

## Synthesis of preparation of titanium dioxide nanowire by eutectic method

In this research, due to the cheap and availability of devices and devices and safety and environmental factors, such as the research of Fouladi et al. [29], it is used for membrane synthesis and coating. In this research, the tectic method is used to make titanium oxide nanocomposite.

To prepare one-dimensional nanostructures (nanowires), titanium dioxide from the tectic method, a mixture of disodium phosphate salts (Na<sub>2</sub> HPO<sub>4</sub>) and sodium chloride (NaCl) and the raw material titanium dioxide (TiO<sub>2</sub>) with specific weight ratios (1: 4:1) was prepared and ground in a mortar. [29] (Fig 4).



Fig 4: Different stages of synthesis by Eutectic method

#### Nano porous TiO2

As shown in (Fig 5), the X-ray test results of the TiO<sub>2</sub> sample crystallized at 300°C for 5 hours. The peaks were relatively sharp, indicating relatively high crystallinity.



Fig 5: X-ray diffraction image of TiO<sub>2</sub> calcined at 300°C for 5 hours

A test TEM image of TiO<sub>2</sub> crystallized at 300 °C for 5 h, (Fig 6(a)), shows a crystal structure with a Nano-size of 7-15 nm. The SAED pattern (inset of Fig. 6(a)) and TEM image (Fig. 6(b)) showed that

the nanoparticles were composed of anatase phase.



Fig 6:TEM SAED, and HRTEM image of the prepared metal oxides

In (Fig 7(a)), a representative SEM image of the 50 mol% TiO<sub>2</sub> Nano powder is shown. TiO<sub>2</sub> systems with other composition gave SEM images similar to the mixed oxides of the 50 mol% TiO<sub>2</sub> system. TEM (Fig 7(b)) and HRTEM (Fig 7(c)) images of the same powders also show Nano porous structure in mixed oxides system



Fig 7:SEM(a), TEM (b), SAED (inset of b), HRTEM (c) images of the 50 mol% TiO<sub>2</sub> calcined at 300 °C for 5 h

(Fig 8) shows the XRD for the sample after refluxing at 110°C. The sample for the first sample is X-ray

amorphous and no distinct peak is observed. After digestion, the powders showed a crystalline pattern and the observed d lines correspond to the values reported for the TiZ-V membrane. The calculated lattice parameters for TiZ-V are a=3.872 Ű and c=9.605 Ű. It should be noted that the molarity of the solution must be > 0.15 M of TiO<sub>2</sub> to achieve crystallization in this process. Otherwise, it takes a long time to form a crystalline product at 100°C. Calcination of the sample at 750°C for 13 hours leads to rutile phase.



Fig 8: XRD of (a) as dried gel (b) after digestion at 110°C for 5 h (anatase) and (c) after annealing at 750°C for 13 h (rutile).

Expansive heating above 550 °C indicates the formation of NaA membrane. The surface area of TiZ-V powders was 60 square meters/gram. The average size of TiZ-V membrane particles is 10 nm and the particles are observed as agglomerates (Fig 9)



Fig9: TEM pictures of (a) TiZ-V and (b) NaA

(Fig 10) represents the results of field emission scanning electron micrograms (FESEM) in order to investigate the particle size and morphology of the  $TiO_2$  nanocomposite. The FESEM of catalyst shows nanoparticles with small sizes.



Fig 10: SEM image of the TiO<sub>2</sub> nanocomposite

## SiO2 deposition on TiO2

For the synthesis of di-titanium nano wire and the synthesis of NaA zeolite membrane, as well as  $SiO_2$  coating on  $TiO_2$  and coating of P-TiS with NAA zeolite, the research of Fuladi et al., 2023 was used [29] (Fig 11,12).



Fig 11: Design of gas test device of the hollow fiber membrane.

$$A\left\lfloor m^2 \right\rfloor = \pi \times d \times L \tag{4}$$

The pressure in Pascal is obtained as follows;

$$p[pa] = p.[bar] \times 100000$$
 (5)

Then the average pressure of the ambient ratio is calculated to be used in permeability diagrams according to pressure:

$$p_{avg}[pa] = \frac{(p+101325)+101325}{2} \tag{6}$$

We consider the volume in the bubble flow meter in cubic meters:

$$V\left[m^3\right] = \frac{V.}{10^6} \tag{7}$$

Next, the amount of moles (n) of gas per unit of time is obtained as follows:

$$n\left[\frac{mol}{s}\right] = \frac{p.V}{R.T} = \frac{101325 \times \left(\frac{V}{t}\right)}{8.313 \times 298} \tag{8}$$

Finally, gas permeability is obtained as follows:

$$\left[\frac{mol}{s.m^2.pa}\right] = \frac{n}{A \times p}P$$
(9)

In order to investigate the water permeability of hollow fiber membranes, a water test is performed.



Fig 12: Image of the constructed gas dehumidification membrane device.

#### FINDINGS

#### Investigation of NaA zeolite membrane

#### Gas test

(Table 2) shows the results of a sample of performed gas tests on NaA zeolite membrane.

Table 2: NaA zeolite membrane gas test results

P(bar)	$P_{avg}(pa)$	n(mol)	P(mol /m².s.pa)
0.1	106325	2.2442E-06	1.766E-06
0.3	116325	6.7191E-06	1.762E-06
0.5	126325	1.1174E-05	1.758E-06
0.7	136325	1.56294E-05	1.757E-06
0.9	146325	2.00279E-05	1.751E-06
1.2	161325	2.66429E-05	1.747E-06
1.6	181325	3.54392E-05	1.743E-06
2	201325	4.4189E-05	1.738E-06
3	251325	6.61227E-05	1.734E-06
5	351325	0.000109702	1.726E-06
7	451325	0.000153287	1.723E-06



Fig 13: Mole-pressure diagram of NaA zeolite membrane gas test

As can be seen in (Fig 13), increasing the amount of moles of output penetrant gas from membrane is done by increasing feed gas pressure. According to the diagram in (Fig 14), the data related to the permeability in terms of feed gas pressure has a very small decreasing trend, so that with the increase of 70 times of the gas pressure from 0.1 to 7 bar, it has changed equal to  $4.6 \times 10^{-8} (mol / m^2.s.pa)$  and in the investigated pressure range, NaA zeolite membrane has an average gas permeability results of NaA zeolite membrane will be used to compare with TiZ–V membranes made by vapor phase carrier.



Fig 14: Diagram of NaA zeolite membrane gas test results

#### Water test

(Fig 15), shows the results of adsorbed water on NaA zeolite membrane. In the constant flow rate of feed water, due to the increase in pressure, the flux of penetrant water has increased. Average flux of NaA zeolite membrane in the investigated pressure range was equal to 24.4[L/m<sup>2</sup>.h], which will be used to compare with water flux of TiZ–V membranes.



Fig 15: Diagram of NaA zeolite membrane water test results

#### Investigation of TiZ-V membrane

#### Gas test

The data obtained from TiZ–V membrane gas test are presented in (Fig 16).



Fig 16: Mole-pressure diagram of TiZ-V zeolite membrane gas test

The comparison of the mole values of permeating gas of NaA zeolite membrane relative to the T i Z - V membrane is presented in (Fig 16). This figure shows the average reduction of 50 times of the permeating gas moles for membrane T i Z - V.



Fig 17: Permeability-pressure diagram of TiZ-V membrane

Comparison of the gas permeability values of NaA zeolite membrane relative to TiZ–V in (Fig 17), shows the reduction of gas permeability of TiZ–V membrane. Reduction of the gas permeability of TiZ-V membrane is due to the formation of a cross-linking selective layer, which is the result of the reaction of the silicate phase containing SiO<sub>2</sub>. The resulting selective layer is permeable to water molecules.

#### Water test

The results of the performed water test on TiZ-V membrane are presented in (Fig 18). In the constant flow rate of feed water, due to the increase in pressure, the flux of penetrant water has increased. Average flux of NaA zeolite membrane in the investigated pressure range was equal to 4256[L/m<sup>2</sup>.h], which has increased relative to water flux of NaA zeolite membrane on average. Increasing water flux of TiZ-V membrane was due to the formation of hydrophilic amide layer resulting from the reaction and the penetration of the interfacial polymerization solution in the pores of NaA zeolite membrane.



Fig 18: Results of water test performed on TiZ-V membrane

#### **PERFORMANCE TEST**

The result obtained from the comparison of gas and water tests on NaA and TiZ-V zeolite membranes shows the separation of water from gas. The primary NaA zeolite membrane was permeable to gas and water, while membrane TiZ-V, which is made by conducting vapor phase carrier with certain materials and conditions, has lower permeability than gas and more permeability than water, and this means separating gas from water.

In this section, the dehumidification performance of TiZ-V membrane in mixed gas conditions has been investigated. (Fig 19), shows the amount of reduction in relative humidity obtained compared to wet feed gas, only during one membrane phase. Reduction is due to the hydrophilicity of the silicate layer that created in TiZ-V membrane.



Fig 19: Dehumidification performance of TiZ-V membrane in mixed gas conditions

The status obtained for gas test and water test is similar to the selectivity of TiZ-V membrane shown in (Fig 20). When wet gaseous feed is in contact with the surface of TiZ-V membrane, nitrogen is not able to pass through the most of pores of the cross-linking selective network, as a result, nitrogen gas exits from the residue side. Whereas, when wet feed gas is in contact with the surface of TiZ-V membrane, due to the possibility of water molecules passing through the pores of the cross-linking selective layer, and in addition, due to the hydrophilicity of the silicate selective layer, the moisture in the gas passes through membrane from the residue side and consequently, the gas with decreased moisture content exits from the residue side, and small amounts of gas with saturated moisture also exits from the residue side. As shown in (Fig 21), water component in penetrant decreases with increasing pressure and correspondingly gas component increases in penetrant. This situation means an increase in gas loss in the form of wet gas. The value of penetrant mole (np) is given in (Table 3), and in contrast, the state of penetrant mole is determined by the water and gas components. This trend is drawn in (Fig 21), and whatever the intersection of the YW and YG graphs occurs at higher pressures, it is more desirable and means that water component is more in the water.

Table	3:	Perf	orma	ince	test	results	of	TiZ-	V
			m	emb	rane	?			

P(bar)	n <sub>f</sub>	n <sub>p</sub>	Y <sup>W</sup>	Y <sup>G</sup>	а
2	5.845E- 04	1.601E-05	0.667	0.333	0.77
3	5.863E- 04	1.78722E- 05	0.621	0.379	5.62
4	5.902E- 04	2.17654E- 05	0.521	0.479	2.41
5	5.958E- 04	2.73018E- 05	0.433	0.567	0.29
6	5.063E- 04	3.78423E- 05	0.325	0.675	1.18



Fig 20: Pressure-selectivity diagram in TiZ-V membrane performance test



Fig 21: Diagram of penetrant state of TiZ-V membrane (nf and np)

(Fig 22) The diagram shows the gas and water permeability values of the membrane and their corresponding selectivity (a) for each pressure. As it can be seen, only higher water permeability or lower gas permeability does not lead to better membrane performance, but the highest selectivity value is the result of the highest ratio of water permeability difference to gas, which means the greatest separation of water from gas, or in other words, the best dehumidification condition. Since this concept is obtained in the form of selectivity data and indicates the performance of membrane, therefore, the improvement of membrane condition is determined by the improvement of the selectivity values. In the case of membranes used in the dehumidification tests, the output product is actually the output dry gas from the residue side, and not the permeated output from membrane, which is considered as actual residue of the operation due to

its high humidity. Anyway, in order to know the amounts of water and gas on the penetrant side, its

diagram is presented in (Fig 22).



Fig 22: Diagram of gas and water permeability values of membrane and their corresponding selectivity(a)

#### CONCIUSION

As it was observed, The original NaA zeolite membrane was permeable to gas and water, while the TiZ-V membrane, which was made by using the vapor phase carrier with certain materials and conditions, was less permeable to gas and more permeable to water. And this is in the sense of separating gas from water.

The result obtained regarding the comparison of gas and water tests of NaA and TiZ-V zeolite membranes indicates the occurrence of water separation from gas. The primary NaA zeolite membrane was permeable to gas and water, while the TiZ-V membrane, which was made by carrying out the vapor phase with certain materials and conditions, had 40 times lower permeability than gas and had less permeability than water. Permeability is 174 times higher and this means separating gas from water.

As it was observed, only the higher water permeability or the lower gas permeability did not lead to better membrane performance, but the highest selectivity value is the result of the highest ratio of the difference in water permeability to gas, which means the greatest separation of water from gas, or in other words, the best moisture condition. Degassing.

Is the hydrophilicity or hydrophobicity of the membrane surface effective on the separation of moisture from gas?

When wet gas feed is in contact with the surface of TiZ-V membrane, nitrogen is not able to pass through most of the pores of the cross-linking selective network, as a result, nitrogen gas exits from the residual side. This is despite the fact that when wet feed gas is in contact with the surface of the TiZ-V membrane, due to the possibility of water molecules passing through the pores of the cross-linking selective layer, and in addition, due to the hydrophilicity of the silicate selective layer, the moisture in the gas passes through the membrane wall. It exits from the pervious side, and as a result, the gas whose moisture content has decreased is exited from the waste side, and small amounts of gas with saturated moisture also exits from the pervious side.

In order to further investigate, the perormance of membrane was measured under differet operating conditions. As it was observed, only higher water permeability or lower gas permeability does not lead to better membrane performance, but the highest selectivity value is the result of the highest ratio of water permeability difference to gas, which means the greatest separation of water from gas, or in other words, the best dehumidification condition of is gas Since this concept was obtained in the form of selectivity data, it indicates the efficiency of the membrane, so the improvement of the membrane condition was determined by the improvement of the selectivity values. Next, membrane was measured under different flow rates of gas flow, which shows the stability of membrane under the tested high flows and no high loss of Its selectivity. Also, in all these tests, despite the increase in gas flow rate, the degree of superiority of water component over gas component in the penetrant was evident to a high extent, which shows the high separation of water from gas even in the condition of high gas flow.

At the end, in order to further increase the efficiency of the membrane, sweeper gas was injected into the membrane. Increasing The sweeper gas was added from inside the membrane. which increased the water concentration gradient and decreased the gas concentration gradient on the sides of the membrane wall and as a result increased the selectivity of the membrane to the best level of 543.

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#### REFERENCES

- [1] Liang CZ, Chung T-S. <u>Robust thin film composite PDMS/PAN hollow fiber membranes for water vapor</u> removal from humid air and gases. *Separation and Purification Technology*. 2018; 202:345-56.
- [2] Xu J, Zhang C, Ge T, Dai Y, Wang R. <u>Performance study of sodium alginate-nonwoven fabric composite</u> membranes for dehumidification. *Applied Thermal Engineering*. 2018; 128:214-24.
- [3] M. Hossein, b. Afsana Rafiei, K. Arash, and A. Hamid Abbasi, "<u>Using new technologies of gas and liquid two-phase contactors instead of trays in order to improve the performance of natural gas dehumidification unit,</u>" presented at the second process engineering scientific conference, 2013. [Online]. Available
- [4] K. Ali Asghar and Hossein, "<u>Modeling and simulation of absorption cycle of gas dehumidification unit of</u> <u>Parsian Refinery in order to optimize and improve performance and compare with real data</u>," presented at the 4th Process Engineering Scientific Conference, 2014. [Online]. Available
- [5] Cuo Z, Zhang J, Yu B, Peng S, Liu H, Chen Y. <u>Spherical Al2O3-coated mullite fibrous ceramic membrane</u> and its applications to high-efficiency gas filtration. *Separation and Purification Technology*. 2019; 215:368-77.
- [6] Hou L, Liu J, Li D, Gao Y, Wang Y, Hu R, et al. <u>Electrospinning Janus nanofibrous membrane for unidirectional liquid penetration and its applications</u>. *Chemical Research in Chinese Universities*. 2021;37(3):337-54.
- [7] Cheng J, Huang Q, Huang Y, Luo W, Hu Q, Xiao C. <u>Study on a novel PTFE membrane with regular geometric pore structures fabricated by near-field electrospinning, and its applications</u>. *Journal of Membrane Science*. 2020; 603:118014.
- [8] Pöyry S, Vattulainen I. <u>Role of charged lipids in membrane structures—insight given by simulations</u>. *Biochimica et Biophysica Acta (BBA)-Biomembranes*, 2016;1858(10):2322-33.
- [9]. Collins I, Hossain M, Dettmer W, Masters I. Flexible membrane structures for wave energy harvesting: A review of the developments, materials and computational modelling approaches. *Renewable and Sustainable Energy Reviews*. 2021;151:111478.
- [10] Lyu C, Zhao P, Xie J, Dong S, Liu J, Rao C, et al. <u>Electrospinning of Nanofibrous Membrane and Its</u> <u>Applications in Air Filtration</u>: *A Review. Nanomaterials.* 2021;11(6):1501.
- [11] Tu Y, Chen C, Li Y, Hou Y, Huang M, Zhang L. <u>Fabrication of nano-hydroxyapatite/chitosan membrane</u> with asymmetric structure and its applications in guided bone regeneration. *Bio-Medical Materials and Engineering*. 2017;28(3):223-33.
- [12] Sheng Z, Zhang J, Liu J, Zhang Y, Chen X, Hou X. Liquid-based porous membranes. *Chemical Society Reviews*. 2020;49(22):7907-28.
- [13] Pöyry S, Vattulainen I. <u>Role of charged lipids in membrane structures—insight given by simulations</u>. *Biochimica et Biophysica Acta (BBA)-Biomembranes*. 2016;1858(10):2322-33.
- [14] Collins I, Hossain M, Dettmer W, Masters I. <u>Flexible membrane structures for wave energy harvesting: A</u> review of the developments, materials and computational modelling approaches. *Renewable and Sustainable Energy Reviews*. 2021; 151:111478.
- [15] Du JR, Hsu LH, Xiao ES, Guo X, Zhang Y, Feng X. <u>Using genipin as a "green" crosslinker to fabricate chitosan membranes for pervaporative dehydration of isopropanol</u>. *Separation and Purification Technology*. 2020; 244:116843.
- [16]. Ding Y, Zhu J, Liu D. Separation performance and mechanism of the novel modified polyether sulfone composite nanofiltration membrane for the detection on dissolved organic nitrogen. Water Environment Research. 2021;93(9):1748-61..

- [17] Zhao J, Yang Y, Li C, Hou L-a. <u>Fabrication of GO modified PVDF membrane for dissolved organic matter</u> removal: Removal mechanism and antifouling property. *Separation and Purification Technology*. 2019; 209:482-90.
- [18] She Q, Wang R, Fane AG, Tang CY. <u>Membrane fouling in osmotically driven membrane processes: A review</u>. *Journal of Membrane Science*. 2016; 499:201-33.
- [19] Liao Y, Bokhary A, Maleki E, Liao B. <u>A review of membrane fouling and its control in algal-related</u> membrane processes. *Bioresource technology*. 2018; 264:343-58.
- [20] Ladewig B, Al-Shaeli MNZ. <u>Fundamentals of membrane processes. Fundamentals of membrane bioreactors:</u> Springer; 2017. p. 13-37.
- [21] Bazinet L, Doyen A. <u>Antioxidants, mechanisms, and recovery by membrane processes</u>. *Critical reviews in food science and nutrition*. 2017;57(4):677-700.
- [22] Shams K, Ahi H. Synthesis of 5A zeolite nanocrystals using kaolin via nanoemulsion-ultrasonic technique and study of its sorption using a known kerosene cut. *Microporous and mesoporous materials*. 2013; 180:61-70.
- [23] Matsukata M, Ogura M, Osaki T, Rao PRHP, Nomura M, Kikuchi E. <u>Conversion of dry gel to microporous</u> <u>crystals in gas phase</u>. *Topics in Catalysis*. 1999;9(1-2):77-92.
- [24] Liu X, Li Y, Chen B, Wang Y. <u>Cleaner process for synthesis of zeolite MCM- 22 by vapor- phase transport</u> <u>method.</u> *Asia- Pacific Journal of Chemical Engineering*. 2009;4(5):607-11.
- [25].Pirkin-Benameur J, Bouyer D, Quemener D. <u>Self-oscillating polymer-membranes with chemically fueled</u> pore size oscillation mediated by pH-responsive polymer. *Journal of Membrane* Science. 2022;658:120742.
- [26].Sutariya B, Karan S. <u>A realistic approach for determining the pore size distribution of nanofiltration</u> <u>membranes.</u> *Separation and Purification Technology*. 2022;293:121096.
- [27]. Iesako R, Yoshioka T, Nakagawa K, Shintani T, Matsuoka A, Kamio E, et al. Organic solvent permeation characteristics of TiO2-ZrO2 composite nanofiltration membranes prepared using organic chelating ligand to control pore size and surface property. Separation and Purification Technology. 2022;297:121458.
- [28]. He Q, Hu Y, Li X, Liu M, Yu S, Gao C. Pore size regulation of polyamide composite membrane via a sol-gel process confined within the selective layer. *Journal of Membrane Science*. 2022;655:120581.
- [29] Fouladi, G.R., Mazaheri, H. and Marjanib, A., Effect of SiO2 Concentration and Time on Stability of TiO2 Zeolite Nanocomposite Membrane in Light Gas Dehumidification. International Journal of Engineering.2023 vo37 No 02:365-376