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COMPOSITE HYDROXYL ETHYL CELLULOSE MEMBRANE FOR HYDROGEN PURIFICATION

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Abstract

Hydrogen is an important fuel production chemical that is used both for generating electrical energy in fuel cells and in which many chemicals can be produced. Hydrogen can be produced either by chemical methods from petrochemical products or from biomass by fermentation. However, in order to use hydrogen as a fuel source, it must be separated from other waste gases. Although there are many methods used for separation, the most efficient, clean and inexpensive method is membrane gas separation. The effectiveness of this process depends on the membrane produced. In this study, hydroxy ethyl cellulose (HEC) and polystyrene sulfonic acid (PSSA) membranes was synthesized for selective separation of hydrogen from carbon dioxide. In order to increase the hydrogen selectivity, natural zeolite was incorporated into polymer matrix. The effects of HEC/PSSA ratio, and zeolite content on gas permeability and hydrogen selectivity were investigated. As the PSSA ratio increased in HEC matrix, both the hydrogen permeability and selectivity increased. The content of zeolite also increased the hydrogen gas separation performance. The highest selectivity of 5.69 was achieved when the HEC/PSSA ratio was 1 and the zeolite content was 20% (w/w). The separation results showed that the PSSA and natural zeolite showed a positive effect on hydrogen purification and the membranes can be considered as a hydrogen purification material.

Key Words: Hydrogen purification, polystyrene sulfonic acid, hydroxyl ethyl cellulose, composite membrane.

1. Introduction

Hydrogen (H_2) is an important energy carrier to meet the “green energy” requirement and its energy content is higher than other clean energy sources (Rahman et al., 2015). It is known as a promising energy source for future zero-emission vehicles that will work with fuel cells. Hydrogen is either produced by petrochemical processes or produced by fermentation (biohydrogen) from waste. However, biohydrogen gases contain a lot of impurities that limits the use in fuel cell applications. After the fermentation process, the reactor contains hydrogen, carbon dioxide, carbon monoxide, unconverted methane, and hydrogen sulfides. It is necessary to use advanced separation techniques to obtain pure hydrogen from these gases. Membrane gas separation (MGS) is an advanced technology (Kumar et al., 2017) where the hydrogen or other gases can be purified using selective membranes. The driving force in MGS is the pressure difference between the sides of the membranes. Membrane gas separation is a promising technology in terms of ease of maintenance, modularity, environmental friendliness, cheapness, and efficient use of energy (Bakonyi et al., 2013). The performance of the system is directly related to the membrane as well as the process conditions. For this reason, scientific studies are focus on the production of more selective, more permeable and more durable membranes.

Non-porous membranes are used in the gas separation process (Abedini & Amir, 2010; Bernardo et al., 2009). Gases pass through the space between the membrane material molecules, which are often Angstrong size, and their transcription fields can be extended as required. Driving force is the pressure difference which is created between the sides of the membranes and chemical potential gradient (Ulbrich, 2006). Since a non-porous membrane is used in this system the separation process can be explained according to the dissolution-diffusion mechanism. According to this model, one of the components in the feed side, which is in high pressure, dissolves on the surface of the membrane, diffuses across the membrane and desorbs to the low-pressure side of the membrane (Sanders et al., 2013). The most important factors affecting the passage of the desired component in the diffusion step are the size of the structural gaps of the membrane, the size of the gas to pass through and the diffusion rate of the

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components. In case an inorganic material is used, the gas passes through the membrane occurs within the cage or holes of particles that do not change with the operating conditions. In case of a polymeric material usage, it is possible to change the gas permeability during the process since the transition occurs within the void spaces (free volume) between polymeric chains. The structural movement of the polymer varies depending on the operating conditions and the void volume changes with these movements. Gas separation with the polymeric membrane is a commercialized technique. Polymeric membranes are more widely available, low cost, and can be modified according to which gas is desired to be separated. Their lifetime is short, and their permeability values vary according to the operation conditions. In addition, an increase-decrease effect is generally observed between the permeability and selectivity of polymeric membranes (Han et al., 2010). In other words, when permeability increases, selectivity values decrease frequently. Blend membranes in which polymers are mixed with each other or mixed matrix membranes in which polymers are mixed with inorganic materials can be used to eliminate these disadvantages of polymers and increase their strength. In addition, it is possible to limit the gas transfer through the polymeric membrane by performing cross-linking (Yang & Chung, 2013; Sanders et al., 2013).

In this study hydroxyl ethyl cellulose and polystyrene sulfonic acid blend membranes have been synthesized and used for hydrogen separation from carbon dioxide as a model gas stream. The kinetic diameter of hydrogen gas (2.89 Angstroms) is less than that of carbon dioxide (3.30 Angstroms). Therefore, it is expected to obtain high hydrogen selectivity. Both the hydroxy ethyl cellulose (HEC) and polystyrene sulfonic acid (PSSA) polymers are hydrogen selective polymers due to the acid and hydroxyl groups in its structure. Therefore, blend membrane tends to solve hydrogen in its structure rather than carbon dioxide. In order to increase the diffusion selectivity, inorganic particle (natural zeolite) addition have been applied. The effect of zeolite addition and HEC/PSSA ratio on gas separation have been investigated in terms of the permeability (Barrer) and H2/CO2 ideal selectivity results.

2. Materials and Methods

Hydroxy ethyl cellulose (HEC), glutaraldehyde (vol%50), polystyrene sulfonic acid were purchased from Sigma Aldrich, Turkey. Natural zeolites were kindly supplied from Rota Madencilik, Gebze. Acetone (98% of purity) and hydrochloric acid (37% of purity) were purchased from Merck Chemical, Turkey

2.1. Membrane preparation

For the preparation of the pristine HEC membrane, the aqueous solution containing 1.5% (by weight) was stirred at room temperature for 24 hours until to obtain a homogeneous solution. The solution was poured onto a polymethyl methacrylate (PMMA) surface and dried at 40 °C for two days. For the preparation of blend membranes, varying ratio of PSSA and HEC polymers are solved in water and stirred at room temperature for 24 hours until to obtain a homogeneous solution. The solution was poured onto a polymethyl methacrylate (PMMA) surface and dried at 40 °C for two days. HEC/PSSA weight ratio was changed from 0.5 to 2 and the membranes were identified according to the ratio of polymers (HEC/PSSA:2, HEC/PSSA:1.5, HEC/PSSA:1, HEC/PSSA:0.5). For the preparation of zeolite loaded HEC/PSSA membranes, equal weight of PSSA and HEC was solved in water and 5-20% of zeolite by weight were added to the solution according to the total polymer's weight. The solution stirred at room temperature for 24 hours until to obtain a homogeneous solution. The solution was poured onto a polymethyl methacrylate (PMMA) surface and dried at 40 °C for two days. In order to increase the membrane rigidity membranes were also crosslinked with glutaraldehyde (GA) in a crosslinking bath containing 1% of GA, 1% of HCl, 23% of water and 75 % of acetone (by volume). The crosslinking procedure had been applied for two hours, then membranes had been taken from the bath, washed with water and kept within filter paper until they were used in gas separation process.

2.2. Gas separation

The single gas permeability of the pristine and grapheme-nanoplate (GNP) incorporated membranes were measured by using membrane gas separation apparatus which is shown in Figure 1 (Nigiz, 2020). The single gas permeation apparatus consists of a stainless-steel membrane cell, pressure controller and a digital flowmeter.

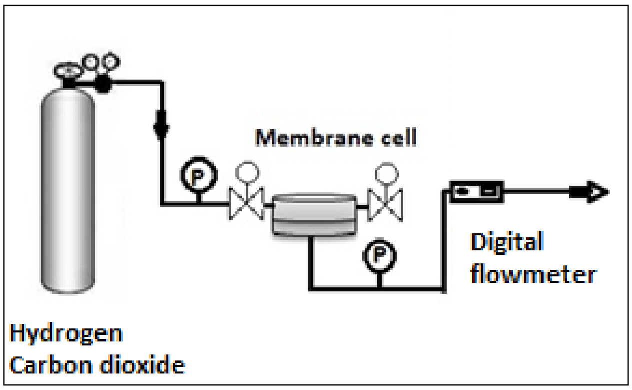

Figure 1. Single-gas membrane separation test unit (Converted from Nigiz, 2020).

The effective separation area of the membrane was 19.6 cm^2. The trans-membrane pressure was 2 bar at the ambient temperature conditions. Gas permeability (P) was calculated using Equation 1;

$$P = \frac{F.l}{\Delta p.A} \tag{1}$$

where F (cm^3/s) is the volumetric flow rate of the single gas, Δp (cmHg) is the trans-membrane pressure, A is the effective membrane area (cm^2), l is the membrane thickness (cm). The unit of permeability (P) is Barrer (1 Barrer=10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)).The ideal selectivity of the component H_2/CO_2 was calculated from the ratio of permeability of the hydrogen (P_{H2}) to carbon dioxide (P_{CO2}) using Equation 2;

$$\propto_{H2/CO2} \frac{P_{H2}}{P_{CO2}} \tag{2}$$

3. Results and Discussion

3.1. Characterization

In Figure 2, FTIR analysis of HEC/PSSA polymers containing different proportions of PSSA polymer can be seen. The peak appeared in 3250 cm^{-1} is corresponding to the -OH stretching vibration. The intensity of the -OH peaks is slightly decreasing when the amount of PSSA increased in the HEC matrix. The peaks seen in the 2912 cm^{-1} and 2850 cm^{-1} regions can be attributed to the asymmetric and symmetric -CH2 bending vibration in the HEC matrix. The intensity of these peaks is also decreasing with the increasing ratio of PSSA. The stretching vibration peaks of C-C in aromatic structure of PSSA is observed in the 1410 cm^{-1} region and the intensity of the peak increases when PSSA ratio is increased. The characteristic O=S=O stretching vibration of PSSA is also seen at 1120 cm^{-1} (Kandeel et al., 2018).

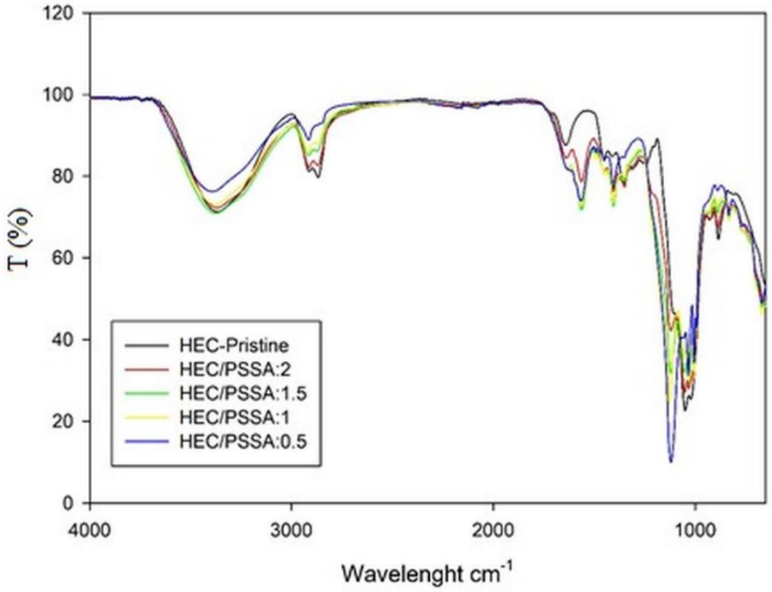

Figure 2. FTIR spectra of the pristine and HEC/PSSA blend membranes.

In Figure 3, FTIR spectra of the equal weight ratio of HEC and PSSA and different weight ratio of natural zeolite are seen. The region seen in the 3254 cm^{-1} band is due to the -OH stretching vibration and the intensity of this peak decreased as the zeolite content is increased from 5wt.% to 20wt.%. The peaks seen in the 2912 cm^{-1} and 2850 cm^{-1} regions are asymmetrical and symmetrical -CH_2 bending peaks. It is observed that the intensities of these peaks also decreased as the zeolite ratio is increased. The characteristic Si-O-Al peaks of zeolites are seen at around 600 cm^{-1}.

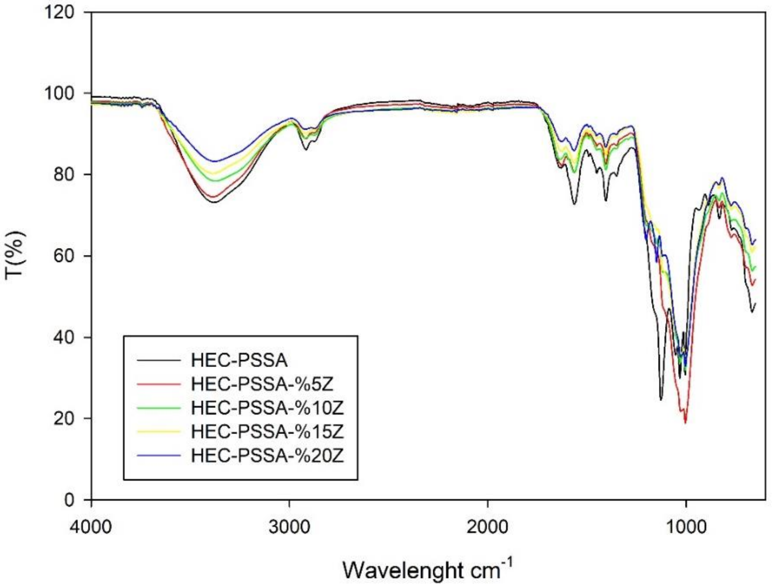

Figure 3. FTIR spectra of the HEC-PSSA blend and HEC-PSSA-zeolite mixed matrix membranes.

Gas passage in non-porous membranes occurs according to the dissolution-diffusion model. According to this model, there are two important factors affecting the gas permeability and selectivity in the membrane. The solubility selectivity of gases in the membrane, and the diffusion selectivity across the membrane. For solubility selectivity, the membrane must have an affinity for the substance to be separated. The close solubility parameters of the membrane and gas, their close polarities, and the appropriate chemical bond structure increase their solubility. The solubility values of the hydroxy ethyl cellulose for hydrogen and carbon dioxide are not much different. Cellulose derivatives are known to be selective to hydrogen (Phair & Badwal, 2006). In the present study, PSSA has been added to the membrane matrix in order to increase the hydrogen permeability of the membrane. The permeability results of the gasses are shown in Figure 4.

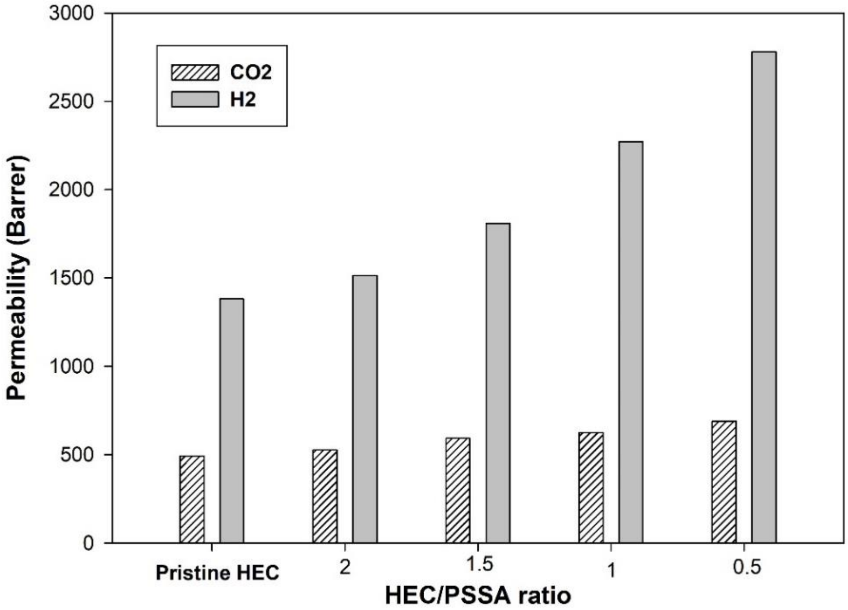

Figure 4. Permeability results of HEC-PSSA blend membranes.

Due to the styrene groups in the PSSA, it is seen that the permeability increases as this ratio increases (Phair & Badwal, 2006; Ockwig & Nenoff 2007). Though the carbon dioxide permeability increases in the figure, this increase is lower than hydrogen. Therefore, as seen in Figure 5, the hydrogen selectivity increased from 2.8 to 4 with the increase in PSSA ratio.

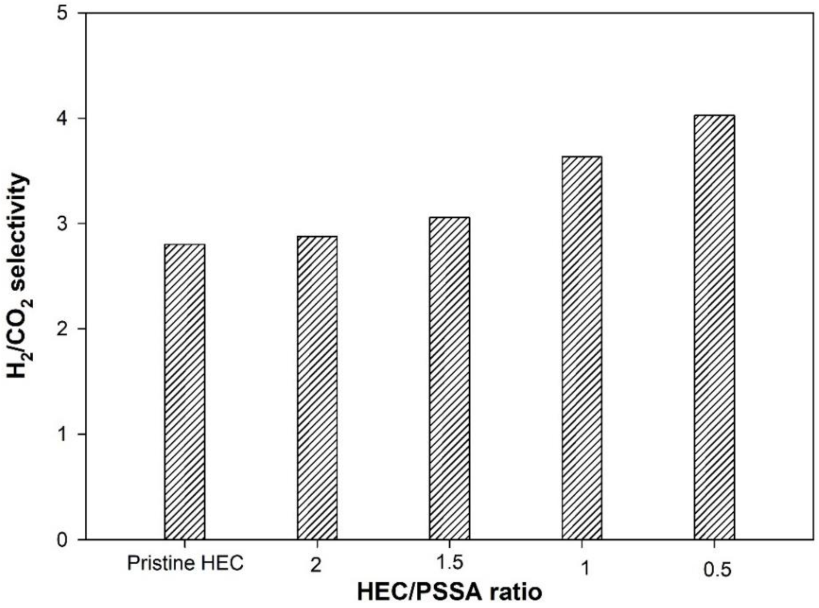

Figure 5. Selectivity results of HEC-PSSA blend membranes.

Figure 6 shows the effect of zeolite content on gas permeability. Natural zeolite was incorporated into HEC/PSSA:1 matrix. As seen in the figure, when the zeolite content increased from zero to 20wt.%, permeability values decreased. One of the most important factors in the increase of selectivity in gases is the diffusion selectivity. Diffusion selectivity occurs when the diffusion rate of the target gas is higher than those of the other gasses. In a polymer, if the ambient conditions and other effects are stable, the only way to increase the diffusion selectivity is to change the transition pathway. Since the kinetic diameter of hydrogen gas is lower than that of carbon dioxide, the hydrogen/carbon dioxide ideal selectivity becomes relatively high even the polymer is not selective for one of the gasses. The diffusion of carbon dioxide can be slowed down by incorporating inorganic materials into the polymeric matrix. Therefore, hydrogen selectivity enhances. If the inorganic material shows a molecular sieve effect (to pass hydrogen and retain carbon dioxide), then the transition gap is becoming prominent. Hence, both permeability and selectivity values increase for hydrogen according to the "molecular sieve" transition mechanism. In this study, natural zeolite (clinoptilolite) was added to the membrane to increase both the permeability and selectivity of hydrogen. However, as can be seen from the experimental results (Figure 6), the permeability values decreased as the zeolite content increased inside the HEC/PSSA matrix. The probable reason for this is that the permeability values of the polymeric materials (HEC and PSSA) are much higher than those of zeolite.

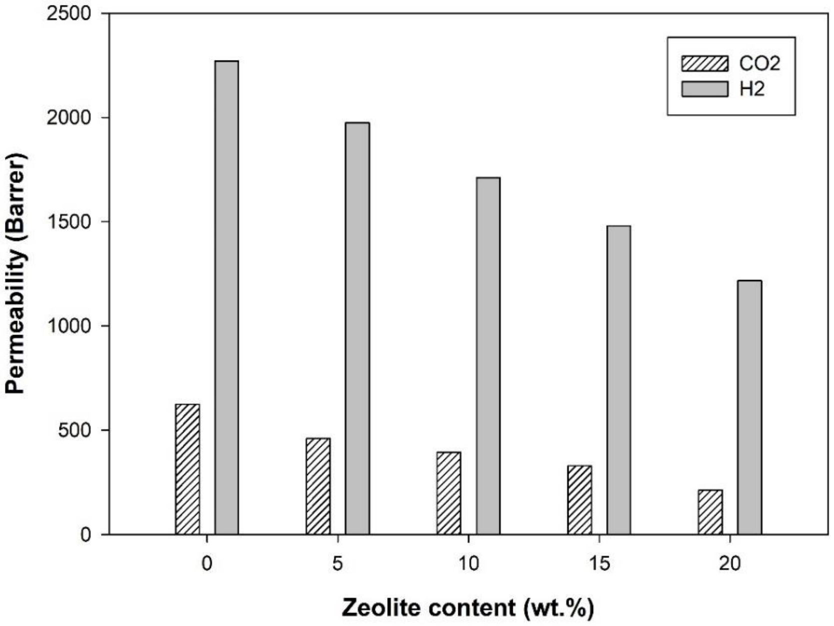

Figure 6. Permeability results of HEC-PSSA-zeolite mixed matrix membranes.

Figure 7 shows the effect of zeolite content on H_2/CO_2 selectivity. When the zeolite content increased from 0 wt.% to 20 wt.%, selectivity enhanced from 3.63 to 5.69 due to the restricted diffusion of carbon dioxide molecules through the membrane.

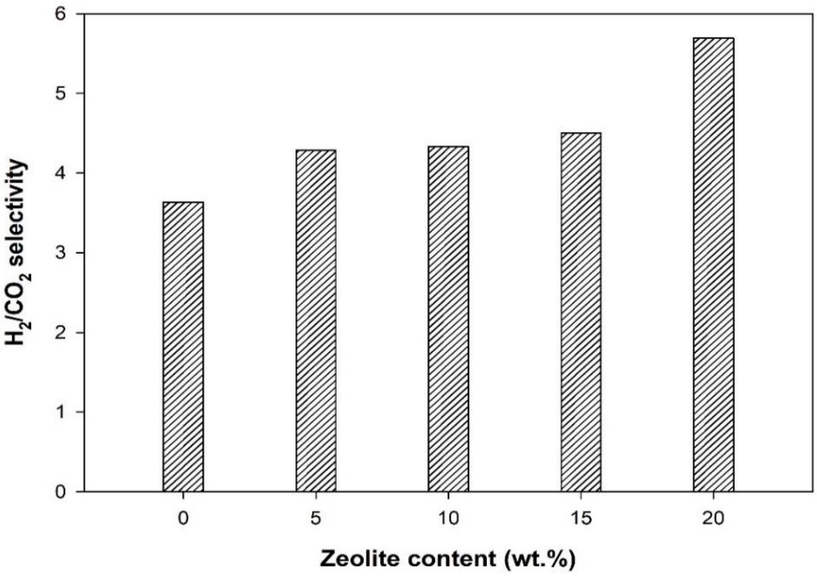

Figure 7. Selectivity results of HEC-PSSA-zeolite mixed matrix membranes.

4. Conclusions

In this study, cellulose-based hydroxyl ethyl cellulose membrane was modified to increase the hydrogen permeability and selectivity of the membrane. First, the blend membrane was made by adding the hydrogen selective PSSA polymer. In this way, the hydrogen selectivity and permeability of the membrane are increased. Then, the natural zeolite was added to increase the diffusion selectivity of the blend membrane. The selectivity of the zeolite incorporated membrane enhanced from 3.63 to 5.69. According to this study, it has been proven that the gas separation performance can be increased with the modifications made to the membrane and the commercial usability of the produced membranes.

Acknowledgement

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