

PREPARATION OF COPPER SULFATE LOADED MEMBRANE AND REMOVAL OF HYDROGEN SULFIDE

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Abstract— Hydrogen sulfide is a highly toxic gas and must be removed from where it is found or formed. A promising technique to achieve this is chosen. The aim of this study was to develop a membrane that holds the gas in processes and places where H₂S can occur and in order to prevent possible threats. The membrane was prepared by loading copper sulfate into a polymeric resin with mechanical mixing. The copper as CuS retained hydrogen sulfide gas in the membrane. At the end of the measurements made with the gas measuring device, results showed that the membrane captured 97 percent of H₂S in the feed. Without the need for additional steps, gas capture was encouraging, so it may be a preferable process. Additionally, an environmentally friendly membrane was obtained in terms of polymer ratio and solvent type in the membrane.

The stability of the membrane in acid, base, and effect of UV investigated. The characterization of the membranes was carried out by SEM and contact angle measurements. The contact angle of the membrane was 51.8 before the procedure and 88.9 at the end of the procedure. Even if the prepared membrane gets dirty, it has not lost its hydrophilic feature.

The success of the membrane that has been obtained in capturing hydrogen sulfide encourages the membrane to be recommended to local governments.

Keywords— pyrite; purification; capture; toxic gas; natural gas; biogas.

I. INTRODUCTION

H₂S is an acid pollutant of natural gas and biogas that must be removed because it causes corrosion and undesirable reactions in places where it is transported and stored. Besides, removing hydrogen sulfide from processes can avoid its release to the environment, reducing toxic effects. Also, when used to generate heat and electricity from biogas, it is necessary to lower concentration to reduce corrosion (Awe *et al.*, 2017). Besides all these effects, it is imperative to capture H₂S from natural gas to maintain economic growth. Adsorption, cryogenic process, absorption, and membrane technology are technologies used to remove H₂S from the gas mixtures (Harrigan *et al.*, 2020). On the other hand, these techniques (adsorption, cryogenic process, absorption, and membrane technology) are expensive and cause problems such as flooding and foaming. Membrane technologies are a fresh alternative for gas separations. Hollow-fiber membrane contactor (HFMC) is one of the different

membrane technologies in recent research subjects in ten years. Here, the membrane is a barrier between gas and liquid (Mirfendereski *et al.*, 2019). Also, metal oxides are used to separate H₂S from hot gases (Slimane and Abbasian, 2000; Li and King, 2006; Swisher and Schwerdtfeger, 1992a; Swisher and Schwerdtfeger, 1992b; Elseviers and Verelst, 1999, Girard *et al.*, 2015; Yoon *et al.*, 2003). Examples of these oxides are manganese oxides, zinc oxide, calcium oxide, copper oxide. However, metal oxides with high sulfur retention, easy recovery, and thermal, fast reaction kinetics, and mechanical strength can achieve high sulfur retention (Bakker, *et al.*, 2003; Meng, *et al.*, 2010). For this reason, it has been investigated different types of adsorbents for the adsorption of H₂S. For example, metal-organic frameworks (MOFs) have shown high adsorption capacity and selectivity toward H₂S removal. Besides, for H₂S removal from gaseous mixtures, several processes such as absorption in which acid gases are removed by a physical solution like Purisol™ and Selexol™ processes or chemical reactions with MEA and DEA (Oliveira, *et al.*, 2019). However, due to high energy efficiency and low operating and investment costs, membrane separation is more suitable for removing acidic gases than gas absorption. Polymeric membranes have low cost, easy manufacturing, and high mechanical strength of polymers, which has led to their extensive research for use in gas separation. However, it has some limits on permeability and selectivity. When polymeric membranes are combined with ionic liquids, it allows commerce relation in PIMs. The process of mixing these ionic liquids has also been studied in supported liquid membranes. However, due to the high toxicity of H₂S, studies on the separation of H₂S with SILMs (supported ionic liquid membranes) are minimal. The H₂S permeability and selectivity currently reported remain low, making it financially inconvenient for processes (Zhang *et al.*, 2017).

Membrane processes for H₂S removal have been more poorly investigated than for other gas removal. A review of the use of polymeric membranes for simultaneous removal of CO₂ and H₂S from natural gas and providing a comprehensive overview of reported membrane performance are among the highlights (George *et al.*, 2016). The gas transport properties of various polymeric membranes used for the removal of acid gas from natural gas are given. It is assumed that the use of selective CO₂ and H₂S polymer membranes can reduce the cost of membrane technology. However, a balance between costs and separation efficiency has not yet been

determined. A large number of studies have demonstrated polymer membrane routes for natural gas purification that are feasible, economic, and environmentally friendly alternatives to existing technologies. Research on this aspect continues in various academic and industrial laboratories to improve existing membranes or to invent new polymer membranes that are highly efficient for gas purification or capture while also reducing the overall cost of the separation process.

Developing new membrane materials, it is the key element in the success of membrane separation. So, in this study, H₂S retention was investigated by adding metal to a polymeric membrane.

II. METHODS

A. Materials and Methods

The chemicals used in the study were CuSO₄·5H₂O (Merck); ethyl alcohol, 99.5% (Tekkim); FeS₂, pyrite, Iron disulfide (Sigma-Aldrich); 37% HCl (Merck), water-based resin (15% polyamide) (Teknomarin); anti-settling (Aluminum silicate) (Teknomarin); spreader (Teknasol) (Teknomarin).

The membrane was prepared in a laboratory environment with a water-based resin using minimum metal. It was also designed in a setup to be used in the experiment. Membranes were placed in the device, and the number of membranes can increase according to need. The presence of more than one membrane in the device allows for a gradual purification process. That is useful in that it allows the process to continue until the gas is completely removed. The gas was removed by trapping it with metal in the membranes. Thus, the gas sent to the device remained in the membrane and was removed from the environment. The advantage of the process over other separation techniques is that the membrane is prepared with a water-based resin, and the gas remains in the membrane in this way without additional costs. This study aims to present a membrane process used in H₂S separation.

The feed prepared by the following reaction,

Feed:



During the production of hydrogen sulfide in the gas phase will fly vapors of hydrochloric acid and chlorine (obtained by Eq. 1), and the purification of the gas mixture is not carried out before feeding to the membrane apparatus.

4.76 g pyrite was used. 1,526 kg/m³ H₂S was obtained. Feed was sent to the experiment device with a hose. It was formed of two 60 cm long, 5 cm diameter glass columns and a 4.5 cm diameter membrane holder in each column. There is a space made of Teflon that was prepared to place six membranes in each of the columns in the experimental setup. Membrane (3.4 cm diameter) was placed in this void that can be moved around and has a Teflon lock to secure the membrane. The retention of the gas in the membranes in the column was examined with SEM-EDS images. Gas output from the test apparatus

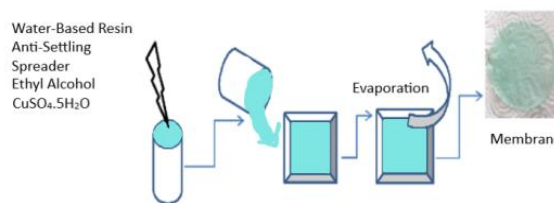


Figure 1. The preparation of the membrane

was measured as ppm with a gas measuring device. At the end of the process, the gas from the test apparatus was measured: 0.041 kg/m³. In other words, 1.526 kg/m³ gas was reduced to 0.041 kg/m³.

B. Preparation of the Membrane

The membrane was obtained using water-based resin (6.18% polyamide), anti-settling (Aluminum silicate), spreader (Technasol), CuSO₄·5H₂O, distilled water, and ethyl alcohol as a solvent. A water-based resin provided polymer support in the membrane.

The homogeneous dispersion of copper sulfate to the resin was realized by Aluminum Silicate (Al₂SiO₅). 6.46 % Copper sulfate, 6.18 % water-based resin, 0.21 % anti-settling, 0.62 % technosol (spreader), 32.45 % distilled water, 54.08 % ethyl alcohol were used. CuSO₄·5H₂O was dissolved in distilled water and ethyl alcohol. The water-based resin spreader and anti-settling are also dissolved in a separate container in distilled water. To this homogeneous mixture, pre-prepared copper chloride solution was added and mixed. This homogeneous mixture is poured into the glass apparatus. The solution was left to room temperature overnight to evaporate the solvent. The next day, the membrane was removed from the glass apparatus using distilled water. The preparation of the membrane is given schematically in Fig. 1. The membrane thickness obtained was measured as 149 μm with a digital micrometer (Salu Tron Combi-D3).

C. Instrumental

The surface characterization of the membrane was determined with the help of a Scanning Electron Microscope (SEM) (Geol). These analyzes were made with the purchase service from Sakarya University Faculty of Engineering, Metallurgical and Materials Engineering. Contact angle measurements were taken with a Dataphysics brand wet angle device. Membrane thickness was determined by the digital micrometer (Salu Tron Combi-D3). The amount of sulfur gas at the end of the experiment was detected as ppm with the help of a combined measuring device with an integrated ethane detector (Sewerin EX-TEC HS 680).

III. RESULTS

A. SEM Analysis

Increasing surface roughness provides obtaining suitable conditions for adsorption. In other words, the membrane with a more rough surface contains more active sites for adsorption due to its greater surface area. For this reason, it is preferred that the membrane has a rough surface (Salehi and Madaeni, 2014). The SEM image before treatment that a surface without homogeneous distribu-

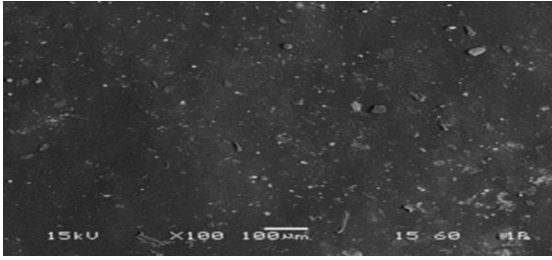


Figure 2. Surface SEM image of the membrane before the procedure

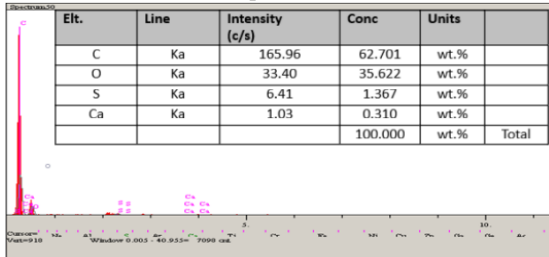


Figure 3. SEM-EDS image at the end of the procedure of the membrane

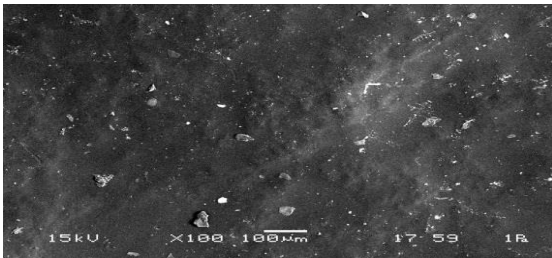


Figure 4. SEM image of membrane in micro-pure water for a week

tion is seen in Fig. 2. The obtained membrane gas retention was also successful.

The SEM-EDS image of the membrane at the end of the process is shown in Fig. 3. Sulfur gas retains stated in the membrane, as can be seen in the SEM-EDS image. This gas retention is also supported by measuring with a gas measuring device. Calcium in SEM-EDS images was evaluated as the impurity in the pyrite due to the feed being obtained from pyrite (Fig. 3).

Studies have been conducted to evaluate the effect of water on absorption capacity and selectivity. In these studies, there are findings showing that the selectivity of H_2S/CH_4 decreases in the presence of moisture (Zhang *et al.*, 2019). The humidity that will reach the membrane together with the H_2S gas during the experiment is not in the amount that will cause any adverse effect on the membrane in this work. Because these membranes have partially lost their hydrophilic character due to contamination, as shown by the contact angle measurements at the end of the experiment. In addition, there was no change in membrane performance when the membranes were kept in micro-pure water for a week (Fig. 4).

Membrane stability was characterized by changes in pure water, 1M HCl, 1 M NH_3 , the effect of UV, and then scanning electron microscope (SEM) morphology analysis. Also, it was found that the membrane is suitable to be exposed to %30 H_2O_2 . SEM images are respectively Fig. 5 to Fig. 8.

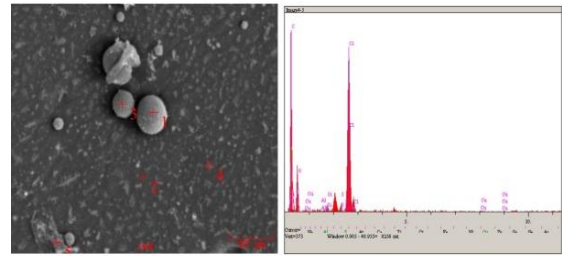


Figure 5. SEM image of membrane in 1M HCl for a week

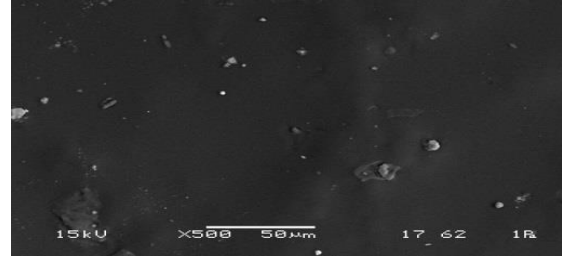


Figure 6. SEM image of membrane after 24 hours of exposure to UV

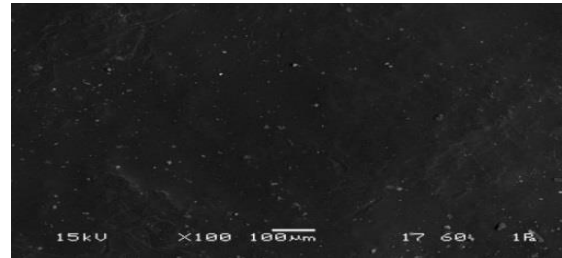


Figure 7. SEM image of membrane in 1 M NH_3 for a week

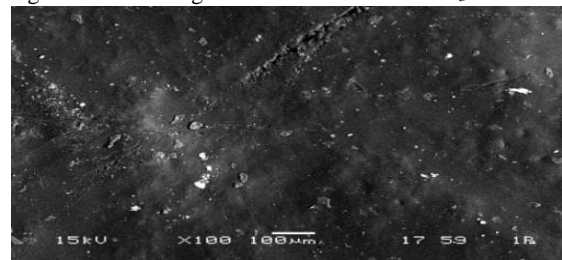


Figure 8. SEM image of membrane in %30 H_2O_2 for a week

Figure 5 as can be seen there, the effect of HCl on the membrane is obvious. If HCl and Cl^- vapors had affected membrane in this study, this could be clearly seen from the end-of-study SEM images.

After 24 hours of exposure to UV, some studies showed a decrease in the resistance of the membranes. This has been attributed to the fact that their membranes contain structures that are highly sensitive to UV light (Chin *et al.*, 2006).

In this study, there is no difference in surface morphology when the SEM images of the membranes are examined after one day of exposure to UV light (Fig. 6). The absence of any change in the membrane structure may mean that the resistance remains the same. This finding agrees with that of Chin *et al.*, (2006), that membrane resistance is closely related to the membrane structure. In this case, SEM images also give information about the resistance.

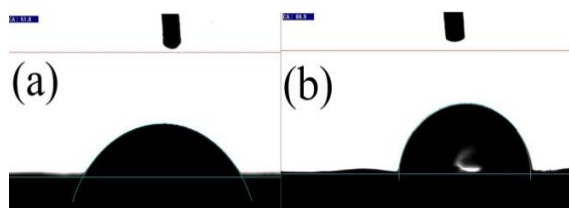


Figure 9 (a). The contact angle of the membrane before the procedure; (b)The contact angle of membrane after processing

It was observed that there was no change in the surface morphology of the membrane by keeping the membrane in micro pure water, 1 M NH₃ and 30% H₂O₂ for a week (Figs. 7 and 8). This shows the stability of the membrane in other solvents as well as the fact that it can use the obtained membrane not only in gas separation but also in different processes.

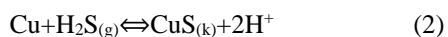
B. Contact Angle

Contact angle measurement was made with distilled water with a drop volume of 5 μl and a microsyringe. An increase in the contact angle at the end of the procedure was observed, as can be seen from Fig. 9a and Fig. 9b. The contact angle of the membrane before the procedure was measured as 51.8, and at the end of the procedure was measured as 88.9. In both cases, the membrane was determined to be hydrophilic. This increase in contact angle indicates contamination at the end of the process. However, it was not hydrophobic even when the membrane got dirty. This showed that the membrane does not lose its hydrophilic property even if it gets dirty.

C. Performance of the Membrane in the Removal of Hydrogen Sulfide

The membrane obtained by loading copper metal was used in the study. These membranes were placed in the experimental setup to remove hydrogen sulfide. 1.526 kg/m³ sulfur gas obtained in the study was sent to the test apparatus with a hose, as shown in Fig. 10a. Gas retention was carried out starting from the membranes in the first column of the mechanism to the last membrane. Figure 10b shows the sulfur gas trapped by copper during the process in black (CuS). The gas output from the test apparatus was detected with a combined measuring device (Sewerin EX-TEC HS 680) with an integrated ethane detector. The amount of sulfur gas released from the test apparatus was measured as 0.05 kg/m³. The sulfur gas sent to the device was held by 12 membranes as CuS. In this study, 4.02 g copper metal captured all 1.476 kg/m³ sulfur gas.

In this process, the reaction of copper sulfate in the membrane with hydrogen sulfide can be shown as follows:



It has been stated that the metal oxides of Fe, Zn, Mn, Mo, V, Ca, Sr, Ba, Co, Cu and W can be used for effective desulfurization (Meng *et al.*, 2010). Even assuming that the heat energy released during these reactions increases the oxidation kinetics of ZnS, this released heat energy is an industrial problem (Girard *et al.*, 2015).



Figure 10(a). Experiment start; (b) Image of the membranes at the end of the experiment

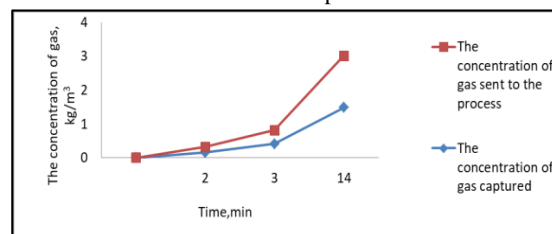


Figure 11. Comparison of the H₂S sent to the process and concentration of H₂S captured in the process

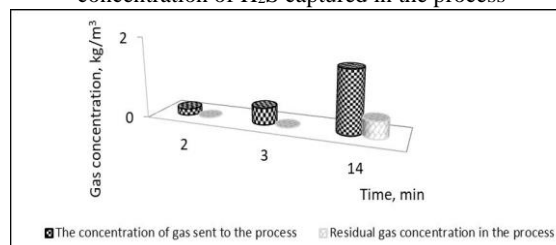


Figure 12. Comparison of the H₂S sent to the process and the remaining H₂S in the process

Table 1. The amount of H₂S sent and captured to the process

Process time, min	Sent to the process, kg/m ³	Residual H ₂ S concentration, kg/m ³	H ₂ S captured, kg/m ³
14	1.526	0.041	1.485
3	0.41	0	0.41
2	0.16	0	0.16

In this study, copper sulfate was added to the membrane instead of copper oxide for the desulfurization process. H₂S gas is retained in the membrane as CuS at the end of the process (Eq. 2). The black color of CuS can be seen from the experimental photos (Fig. 10b). Also, the amount of H₂S sent to the process and captured within the scope of this study and the processing time are shown in Table 1.

Figure 11 shows comparison of the H₂S sent to the process and concentration of H₂S captured in the process, and Fig. 12 shows the comparison of the H₂S sent to the process and the remaining H₂S in the process. When the gas concentration forwarded to the process is 0.41 kg/m³, the membrane retains all the sent gas. When the delivered gas concentration increased (to about 1.526 kg/m³), it was observed that approximately 97% of the gas was retained in the membrane. Given the toxicity of hydrogen sulfide gas, it will be noticed how serious the gas concentration is trapped in the membrane.

Membrane technology is promising for gas separation applications as it fulfills the main gas separation design requirements with simple design, while the use of a se-

quential membrane combines the advantages of the membrane separation with the advantages of continue processes.

Therefore, a consecutive membrane process is preferred to have basic and mobile design, easy arrangement and discharge, and renewal operations. In addition, the use of membranes prepared with water-based resin in this study caused it to be a preferred method in terms of environmental sensitivity.

A good combination of membrane materials and metal has been achieved (Fig.1 and 2), resulting in reliable and efficient long-term gas confinement.

The fact that the membrane was not hydrophobic even at the end of gas confinement showed that it did not lose its hydrophilic character (Fig. 9(b)). Being a hydrophilic membrane is also ecologically valuable. Hydrogen sulfide retention (CuS) by the copper loaded on the membrane during the process shows that the sulfur gas is not released again and is trapped in the membrane (Eq. 2). Considering the toxicity of hydrogen sulfide gas, the importance of not releasing this gas becomes evident.

Although successful applications of H₂S capture capability have been noted in recent studies (Zhang *et al.*, 2021; Xiong *et al.*, 2021), the prepared membrane in this study will find its place in the literature as a membrane with high H₂S capture capability.

Thanks to the design of the experimental setup, membrane replacement will be carried out very easily, and it is thought that this will increase the efficiency of gas retention.

V. CONCLUSIONS

The membrane was designed by lading copper sulfate into a polymeric resin. H₂S gas was kept as CuS with copper inside the membrane. That indicates that there is no need for additional processing during the capture of the gas. It may be preferable that the process does not require many steps in other purification processes. The results demonstrated that the membrane captured 97 percent of the H₂S in the feed. The membrane's ability to hold gas is highly promising. Moreover, by increasing the number of membranes, more gas can be trapped. When the process is considered in terms of the rate of polymer and type of solvent in the membrane used, it is also apparent that it is an environmentally friendly membrane. The present work has successfully ensured a protocol for H₂S capture. However, further research regarding the long-term hydrogen sulfide removal performance of this membrane is needed.

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