A New Approach to Hydrogen Sulfide Removal

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Summary: Many separation processes are used to capture of hydrogen sulfide. Which of these techniques to choose depends on the location of the gas. Conventional gas cleaning processes have significant disadvantages such as considerable energy, maintenance costs and environmental concerns. Compared to conventional processes, membranes are light and compact and have a lower environmental impact, higher energy efficiency and ease of use. Although some rubber and glassy polymer membranes have been used for gas separation, there is an opportunity to reach a much larger potential market with newer and better membranes. In this study, H_2S was captured with copper chloride in the polymeric membrane. Copper chloride was added to the polymeric membrane by mechanical mixing. The present study had two main objectives. First, a water-based membrane was prepared, and its characterization was done. Second, a pilot experimental apparatus was built for hydrogen desulfurization. Next, the capture of hydrogen sulfide with the membrane was tested in a pilot experimental apparatus. This study highlights that a new model membrane can utilize the hydrogen sulfur capture performance.

FeS, iron (II) sulfide, and dilute HCl were used to obtain hydrogen sulfide in this study. The property of the membrane to hold H_2S gas was examined with the amount of gas released by passing the H_2S gas through the membrane.

SEM-EDS analysis confirmed the accumulation of copper and H_2S on the membrane surface. Also, no clogging and contamination problems were observed. The membrane retains its hydrophilic property even after use. The results obtained in the experimental study showed that the newly produced membrane captured 100 percent of H_2S.

The main object in this study, a new approach to H_2S capture. The new copper loaden membrane tested in this study has successfully removed H_2S and is expected to be a promising alternative to conventional desulphurization processes.

Introduction

The lack of clean fuel consumption causes many environmental problems. The increasing problem is the need to develop new methods to make fuels more efficient and cleaner. The use of fuels in gaseous form is one of these methods. This use of fuels helps to use hydrogen-rich and cleaner fuel. However, it is known that unwanted gases (CO, CO_2, SO_2 ve H_2S) exist in these fuels at different rates depending on the type and composition of the fuel used during the production of gaseous fuels. H_2S is an unwanted gas; therefore, it can cause significant risks. It is among these risks that it can cause serious security problems in transportation processes. It is also an extremely toxic and corrosive gas. Considering the presence of hydrogen sulfide in terms of processes, it is a gas that causes undesirable reactions in processes, corrosion in the process, and its presence is problematic. In addition, its toxicity requires the gases to be purified from H_2S before use [1]. Moreover, H_2S is the most prevalent contaminant that limits the direct use of raw biogas as fuel. This situation stems from that it may accelerate the corrosion of utilities and shorten the life of piping and other facilities [2, 3].

Hydrogen sulfide has also been responsible for environmental disasters. In the accident that took place in a gas drilling field in southwest China in 2003, natural gas was released into the atmosphere, and a hydrogen sulfide cloud formed in the mountainous area where many people resided. More than 200 people died, 9000 people were treated for injuries, and more than 40 000 people were evacuated. It is the most appropriate supportive care in the treatment of hydrogen sulfide poisoning. Treatment beyond supportive care has not been proven clinical benefit and antidotes [4]. When viewed from this angle, it is noteworthy that in the processes that will form hydrogen sulfide, the removal of hydrogen sulfide before the hydrogen sulfide is poisoned. Hydrogen sulfide can be determined in air concentrations below 0.1 µg / L [5]. Also, hydrogen sulfide is a smell gas that has an odor as ''rotten-egg''. This smell can be felt by most people as low as 0.0047 ppm. Even though no considerable harm may be produced in such a low

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amount, exposure to this gas can take to nausea, loss of appetite, and other negative effects [6]. The outdoors detection limit on a sample is approximate to 5 ppb and in close 2 ppb [7].

The amount that can be authorized to be present in the working environment of hydrogen sulfide (TWA) is specified as 10 ppm. (TWA: It is defined as the average concentration to which nearly all workers may be exposed during an 8 h shift or a 40-h workweek without known adverse effects) [8]. 1000 ppm and above; causes sudden death effect. There is a risk of exposure to hydrogen sulfide from industrial sources, such as pulp mills and oil refineries, and from the degradation of biological material in waste sites, sewers, and garbage storage areas [9, 10]. Therefore, in the light of all these data, it can be stated that the removal of hydrogen sulfide is an essential condition.

In the earlier studies were conducted some transition metal oxides such as Cu, Mn, Zn, Mo, Fe are used to purify hot gases from H_2S [11-13]. Metal oxides can also be used as mixtures to improve the performance of the metal oxides used. These mixtures can be sorbents containing carrier materials used in metallurgy [14], as well as membrane processes used in gas separation. Membrane processes are used as commonly because membrane processes present a number of advantages in terms of low energy consumption, low cost investment, simple and straightforward procedure, high mechanical resistance of polymers, and compact equipment [15, 16].

Tilahun *et al.,* [17] were carried out the novel gas-liquid polydimethylsiloxane membrane contactor tested in their study has performed well in selective removal of H_2S from biogas. They used a commercial tubular PDMS (polydimethylsiloxane) membrane. Tubular PDMS membrane could be used for selective removal of H_2S, but this process is costly.

The polymeric membrane separation process developed in recent years is predicted to be commercially competitive with conventional chemical gas absorption processes [18]. However, some limitations have been expressed, and these limits are permeability and selectivity. The combination of ionic liquids, particularly those that exhibit chemical affinity for acidic gases, with polymeric membranes has created new opportunities to overcome such limits in polymeric membranes. Although there are studies on this subject, studies on the adsorption of H_2S from gases using membrane are very scarce, owing to the high toxicity of H_2S [1].

In this study, the membrane prepared using copper chloride was used to purify hydrogen sulfide, and the capacity of hydrogen sulfide removal was investigated. Since H_2S is captured on the surface of the membrane designed in this study and it is done in a closed environment, it is thought that a solution to the problem of toxicity will be found.

According to the literature, for the sulfur removal process, metal oxides must have high sulfur retention ability, easy recoverability and thermal, rapid reaction kinetics, and mechanical strength [19, 20]. In this study, there is no need for metal oxide with these conditions, and the minimum amount of metal in the membrane shows that this study is advantageous compared to other methods.

In this study, a mechanism was designed. Membranes made within the scope of the study were placed in the mechanism that was designed. Thanks to the presence of multiple membranes in the device, a gradual capture process has been achieved, and at the same time, H_2S is wholly removed. The gas that cannot be trapped in the first membrane is transferred to the next membrane, and it is an essential advantage that the process can be continued until the gas is completely removed. In addition, the use of water-based resin in the formation of the membrane attracts attention in terms of being an environmentally sensitive process. This aspect of this process is vital in terms of being an alternative to many processes and providing advantages.

Experimental

Chemicals

Water-based resin (15% polyamide) (Teknomarin); anti-settling (Aluminum silicate) (Teknomarin); spreader (Teknasol) (Teknomarin); $CuCl_2.2H_2O$ (Merck); ethyl alcohol, 99.5% (Tekkim); FeS, Iron (II) sulfide (Sigma-Aldrich); 37% HCl (Merck) were used.

Preparation of the membrane

While preparing the membrane in the study, water-based resin (15% polyamide), anti-settling (Aluminum silicate), spreader (technasol), $CuCl_2.2H_2O$ and distilled water and ethyl alcohol as solvent were used. A water-based resin containing 15% polyamide was used as the polymer support. The spreader was used to outspread the polymer homogeneously. Aluminum Silicate (Al_2SiO_5) was used as an anti-settling agent to ensure the homogeneous dispersion of copper chloride into the resin. 2.5% Copper chloride, 15% water-based resin, 0.5% anti-settling, 2% technosol (spreader), 60% distilled water, 20% ethyl alcohol were used. Copper chloride was dissolved in distilled water and ethyl alcohol. In a separate beaker, the water-based resin was

dissolved in the spreader and anti-settling distilled water. Previously prepared copper chloride solution was added to this homogeneous mixture and mixed. The homogeneous mixture obtained was poured into the glass apparatus. One night the solvent was allowed to evaporate. The next day, the membrane was stripped from the glass with the help of distilled water. The membrane thickness obtained was measured as 147 μm with a digital micrometer (Salu Tron Combi-D3).

Instrumental

In determining the surface characterization of the membrane; Scanning Electron Microscope (SEM) (Geol) and Surface Profilometer (KLA Tencor-P6) were used. Measurements were made in the form of service procurement from Sakarya University Research Development Application and Research Center (SARGEM). Contact angle measurements were measured with the Dataphysics brand wet angle device.

TG / DTA analysis was performed with the DSC200F3 NAIA brand (STA 449 F1 Jupiter) thermal analysis device. The membrane thickness was measured with the digital micrometer (Salu Tron Combi-D3) after calibration of the device.

At the end of the process, the amount of sulfur gas exiting from the outlet of the device; measured as ppm with the combined metering device (Sewerin EX-TEC HS 680) with an integrated ethane detector.

Method

Due to the high toxicity of H_2S, studies on H_2S adsorption from gases using membranes are limited. Liu *et al.,*'s work is one of the few studies [16]. They stated that the solubility of H_2S in the membrane was increased since this polar gas interacts with the polar part of the membrane. It was noticed that in the polymeric network, with the increase of hydrogen sulfide pressure, the gap between the chains increases, increasing the mobility gap and permeability of some parts of the polymer chain, leading to plasticization of the membrane. It is known that the membrane plasticization phenomenon damages the membrane structure and quality [21, 22]. In the studies of Liu *et al.,*., the permeability of hydrogen sulfide and natural gas increased due to increased pressure, but the selectivity of hydrogen sulfide over natural gas decreased due to membrane deterioration [16]. In order to avoid this problem, the pressure of hydrogen sulfide was not increased in this study, and the use of sequential membranes was preferred. The primary purpose of this study is to examine the characterization of the membrane that prepared and its performance in the

capture of hydrogen sulfide. Therefore, an experimental setup was designed that apparatus consists of two columns and a 4.5 cm diameter membrane holder in each column, and the membrane was placed in the designed experimental setup. In order to examine the performance of the membrane obtained in the study in capturing hydrogen sulfide, the feed solution was sent to the membrane placed in the experimental setup. It has been observed that hydrogen sulfide is retained in the membranes of the columns. The gas output from the column at the end of the trap was detected by a combined meter with an integrated ethane detector.

Experimental

In work, FeS, iron (II) sulfur, and dilute HCl were used to obtain hydrogen sulfide, and the feed was prepared by the following reaction.

Feed:

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S \qquad (1)$$
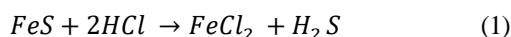
The prepared feed was sent into the membrane that within the designed experimental apparatus. The experiment apparatus consists of two 60 cm long, 5 cm diameter glass columns and a 4.5 cm diameter membrane holder in each column. Each column consists of 6 teflon membrane holders and a 3.4 cm diameter membrane, which is made of teflon, which can be moved round and which has a telfon lock to secure the membrane. The sulfur gas obtained by the reaction in Equation 1 was sent to the first column of the device with the help of a hose. Then gas retention of the membranes was examined with characterization methods such as SEM-EDS. Gas output from the mechanism was measured in ppm with a gas measuring device.

Results and Discussion

Surface Roughness

The surface roughness value of the prepared membrane is given in Fig. 1. The surface roughness value of the membrane changes 0.1 ± 0.56 μm. In general, it is known that the adsorption property of the membrane also increases as the increased surface roughness increases. Increased surface roughness ensures excellent conditions for adsorption. In addition, the membrane with a more rough surface can offer more surface area and, therefore, more active areas for adsorption. Therefore, it is desirable for the membrane to have a rough surface [23].
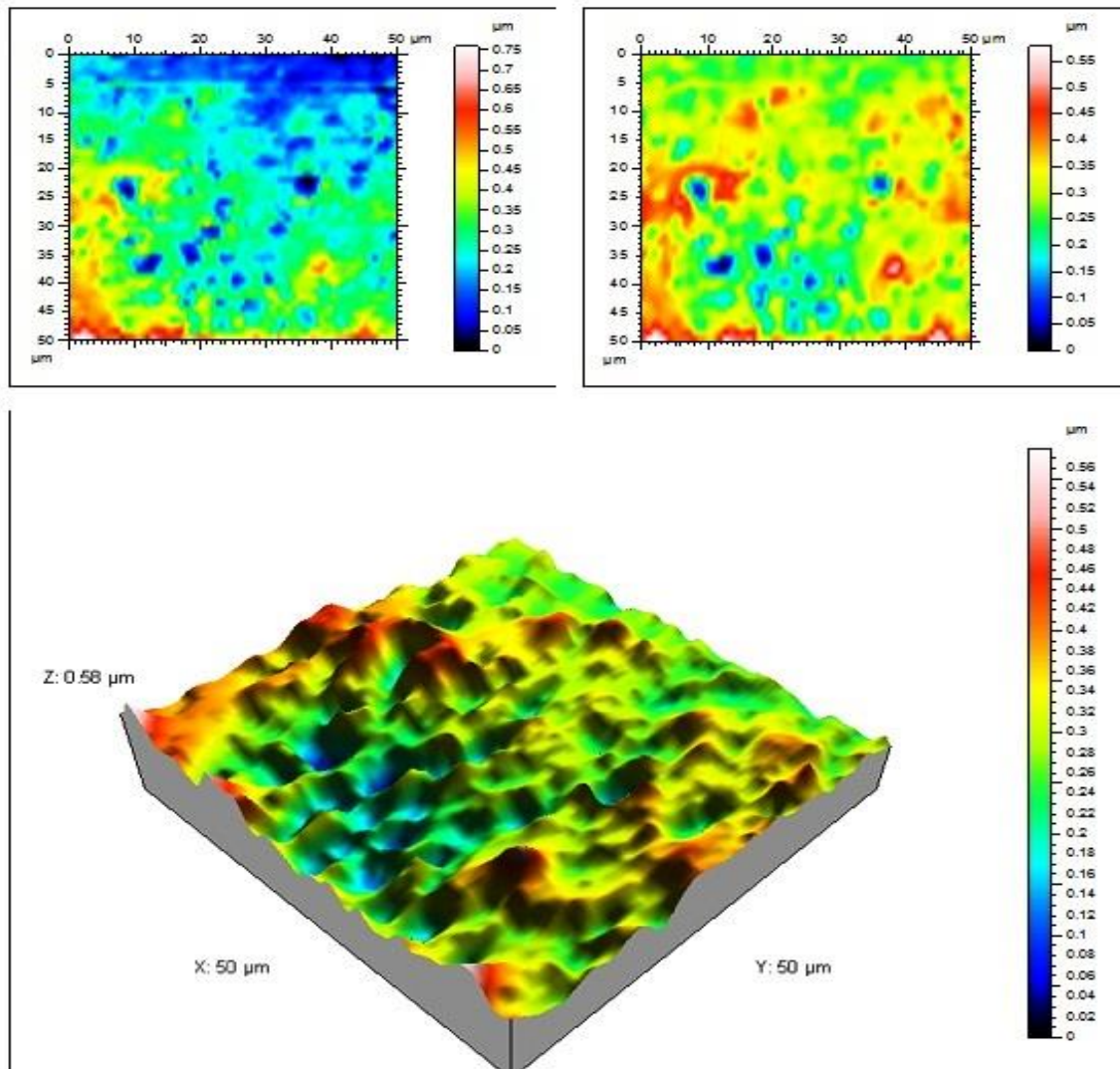
Fig. 1: Image of surface roughness before procedure.

SEM Analysis

Before SEM analysis, the membrane was covered with a thin layer of a conductive material such as gold, chrome, or carbon, and care was taken to keep the membrane dry. SEM-EDS image before the procedure and surface SEM image of the membrane before the procedure is shown in Fig 2 and 3, respectively. The SEM image shows that copper chloride is loaded on the membrane. In addition, the peak seen before chlorine, which is not mentioned in SEM-EDS images, is the Aluminum Silicate peak that uses as an anti-settling agent in Fig 2. As a cross-section of the membrane is taken for SEM-EDS analysis, the ratio of copper is 1%, and this indicates that the ratio of copper in certain areas of the membrane is low and that homogeneous distribution is not fully achieved. In addition, a surface without homogeneous distribution is seen in Fig 3. Despite this, a very successful result was obtained in gas retention.

SEM image and SEM-EDS image of the membrane are given at the end of the procedure, in Fig 4 and Fig 5, respectively. At the end of the procedure, sulfur retain was detected in the membrane, as can be seen in the SEM-EDS image. This evidence supports the measurement made with the gas measuring device. In the light of SEM-EDS analysis at the end of the membrane, it is thought that the membrane retains sulfur gas and that HCl is not kept on the membrane surface and remains in an aqueous environment (Equation 2).
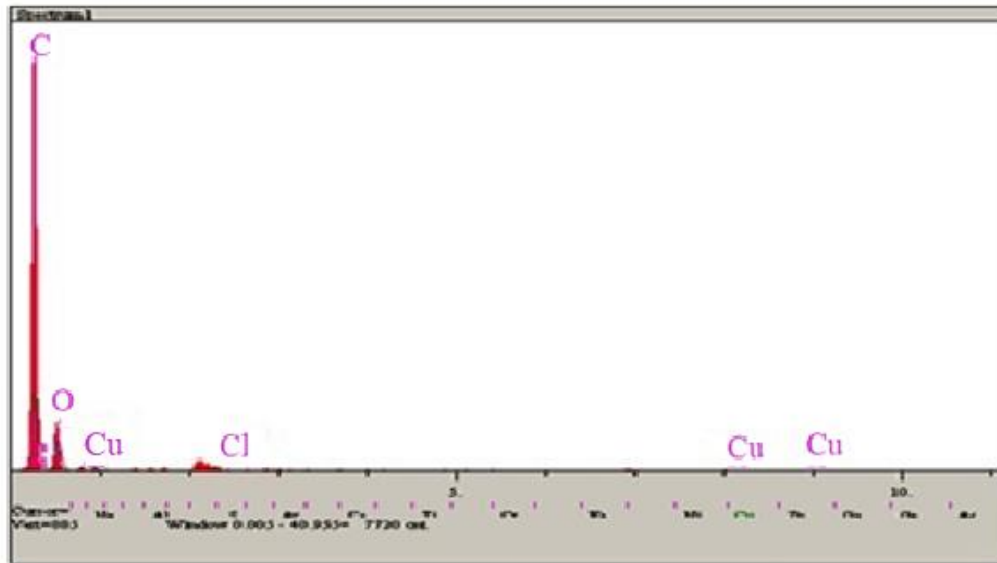
E lt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units	
C	Ka	140.56	7.497	53.186	wt.%	
O	Ka	51.00	4.516	45.299	wt.%	
Cl	Ka	1.73	0.833	0.414	wt.%	
Cu	Ka	0.64	0.507	1.101	wt.%	
				100.000	wt.%	Total

kV 15.0
Takeoff Angle 35.0°
Elapsed Livetime 10.0

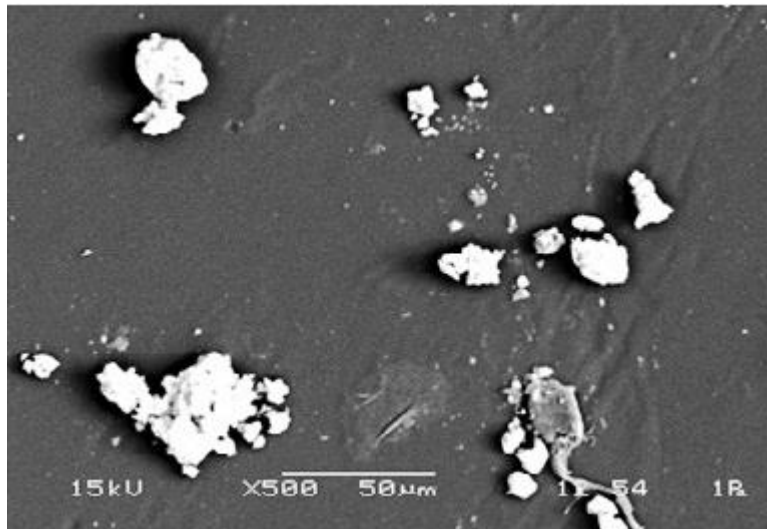Fig. 2:   SEM-EDS image of the membrane before the procedure.

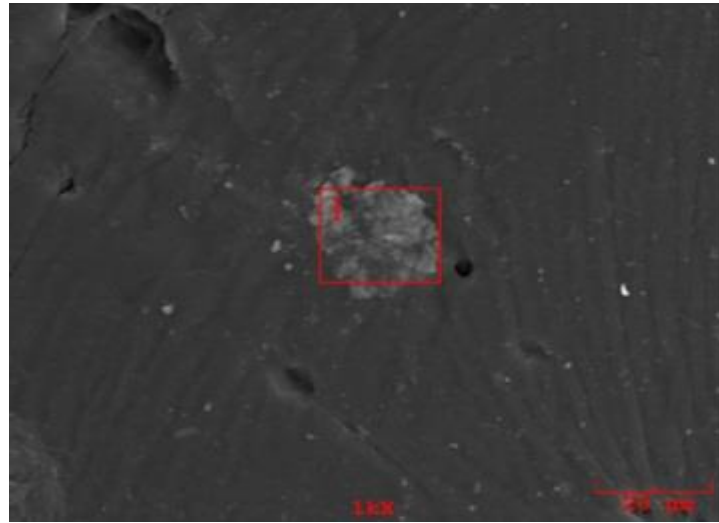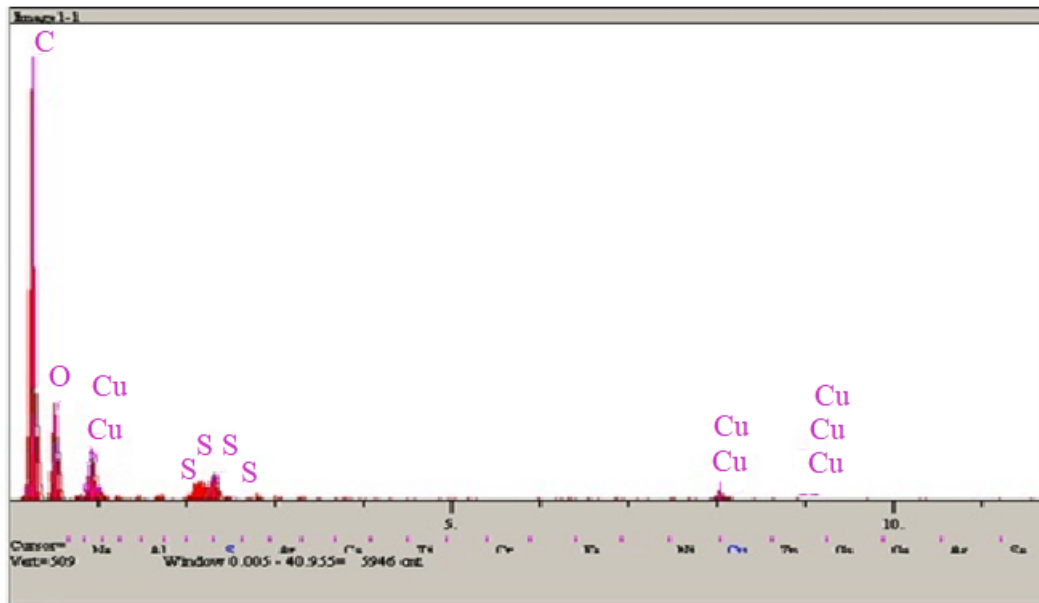Fig. 3:   Surface SEM image of the membrane before the procedure

Fig. 4: SEM image of the membrane at the end of the process.

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units	
C	Ka	111.30	6.670	49.278	wt.%	
O	Ka	58.52	4.837	43.393	wt.%	
S	Ka	31.56	3.552	3.296	wt.%	
Cu	Ka	9.55	1.954	4.033	wt.%	
				100.000	wt.%	Total

kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 10.0
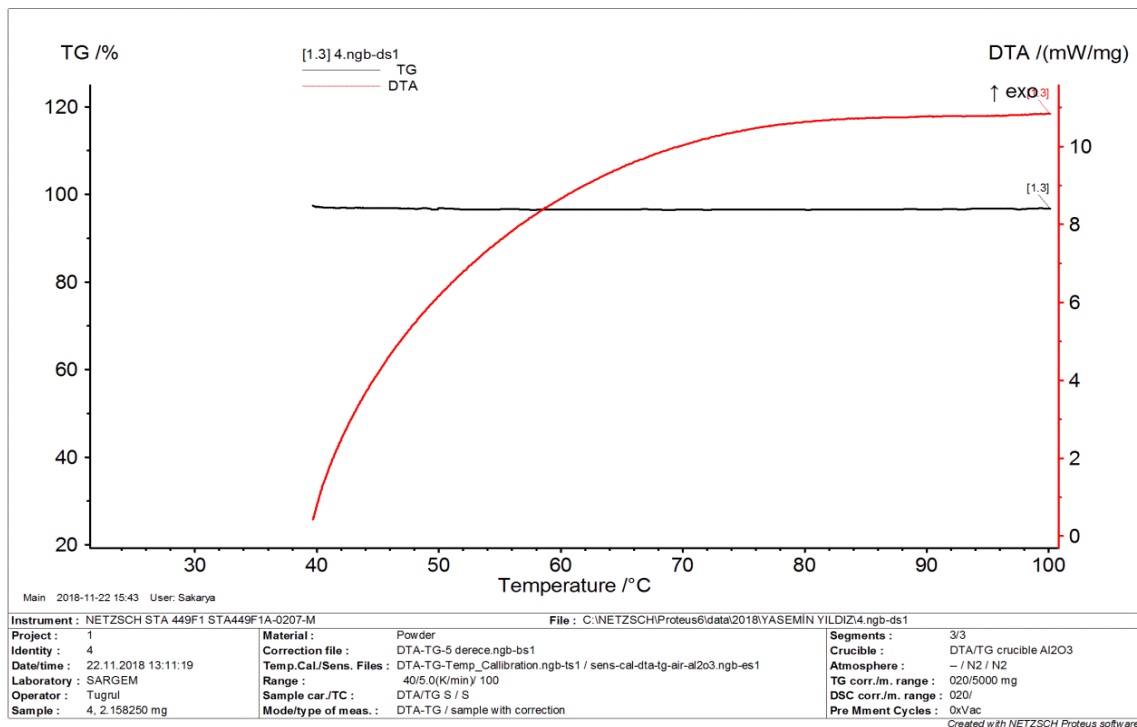
Fig. 5: SEM-EDS image at the end of the membrane.

Fig. 6:   TG / DTA analysis of the membrane.

Thermal Analysis

Changes in the properties of the membrane as a result of physical and chemical reactions were measured against temperature change by thermal analysis. The change in the mass of the sample was examined as a function of temperature by Thermo Gravimetry (TG). When the measurement is examined, there is no mass change, as seen in Fig 6. With the differential thermal analysis (DTA), the same temperature program was applied to the sample and the reference material thermally inert (α-Al$_2$O$_3$). When thermal stability was evaluated by TG / DTA analysis, the membrane was found to be stable. Since the ignition temperature (water-based emitter) of some chemicals that make up the membrane is low (200°C), its high temperature has not been raised.

Contact angle

Contact angle measurement was carried out using distilled water with a microsyringe, and the drop volume was 5 μl. Contact angle measurements were made at specific time intervals for a single drop by recording 10-15 in 5 seconds. At the end of the procedure, no significant difference was observed in the contact angle of the membrane, as can be seen from Fig 7 and Fig 8. The contact angle of the membrane before the procedure was measured as 78.7, and the membrane is determined to be hydrophilic. The contact angle of the membrane used at the end of the procedure is; it was measured as 79.7. It also did not acquire hydrophobic properties when the membrane got dirty.
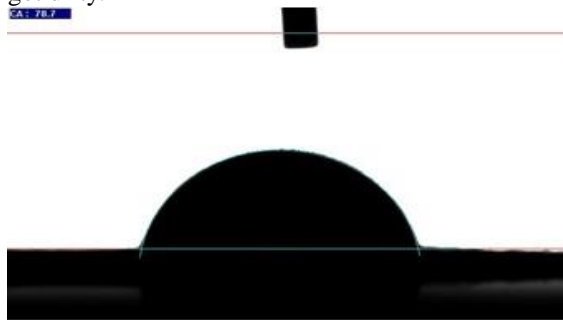

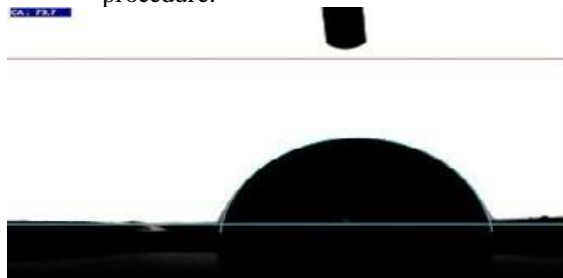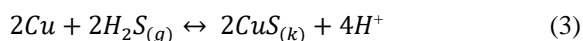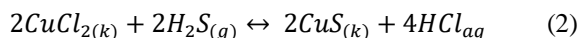Fig. 7:   Contact angle of the membrane before the procedure.

Fig. 8:   The contact angle of the membrane after processing.

Performance of the membrane in the removal of hydrogen sulfide

The membranes prepared by loading copper to capture hydrogen sulfide were placed in the designed mechanism. Obtained 1473 ppm sulfur gas in this study was sent to the experimental apparatus with the help of a hose. Gas retention took place by the membranes in the first column. The process was continued until the H₂S, which could not be trapped in the first membrane, passed to the next membrane, and H₂S gas sent to the device at the last membrane was utterly captured. The gas output from the scheme was detected with a combined measuring device (Sewerin EX-TEC HS 680) with an integrated ethane detector. After the sulfur gas was retained entirely in the membranes, the combined measuring device showed the amount of sulfur gas exiting the device as zero ppm (Fig 9). This result showed that the membrane that prepared holds all the sulfur gas. As seen in the image of the membranes at the end of the experiment in Fig 10, it was observed that the seventh membrane in the mechanism remained clean. The 1473 sulfur gas sent to the apparatus was wholly captured by six membranes. The amount of copper metal per 1 cm² in the membrane was calculated as 0.07 g. (There are 2.5 grams of copper chloride on the entire membrane). Results show that the membrane captures 100 percent of H₂S in the feed (Fig 11).

In this process, the reaction of copper chloride in the membrane can be demonstrated as follows:

$$2CuCl_{2(k)} + 2H_2S_{(g)} \leftrightarrow 2CuS_{(k)} + 4HCl_{aq} \qquad (2)$$

$$2Cu + 2H_2S_{(g)} \leftrightarrow 2CuS_{(k)} + 4H^+ \qquad (3)$$

As seen from the reaction in Equations 2 and 3 at the end of the process, H₂S gas is retained in the membrane due to the sulfur bonding with the metal in the membrane. The membrane retained twice as much hydrogen sulfide as hydrogen sulfide, which copper chloride should hold according to Equations 2 and 3. The black color of CuS can be seen from the experimental photos (Fig 10). The SEM-EDS analysis at the end of the procedure shows that HCl is not kept on the membrane surface and can be expressed in an aqueous medium. Fig 11 shows how fast the hydrogen sulfide capture performance of the membrane is and the gas trapping feature of the membrane within minutes. In this case, it confirms the success of the obtained membrane, as can be seen in Figs 9 and 10.

Fig. 9:   Gas measurement at the end of the experiment.

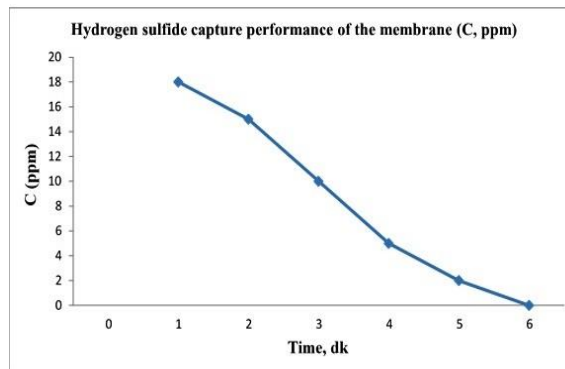Fig. 10: Image of the membranes at the end of the experiment.

Fig. 11: Hydrogen sulfide capture the performance of the membrane (C, ppm)

Conclusion

In many processes, the membrane needs to be renewed during gas purification and capture. In this study, H₂S gas passes through the membranes gradually without the need for renewal, and gas retention occurs on the next membrane. The progressive process also helps to capture completely H₂S gas. In addition, the use of water-based resin in the formation of the membrane attracts attention in terms of being an environmentally sensitive process. This aspect of this process is vital for being an alternative to many processes and providing advantages.

Although the focus is on hydrogen sulfide confinement, the resulting membrane will retain hydrogen sulfide in the presence of other gases.

Acknowledgment

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