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Research Article

Evaluation of the Durability of a New Water-Based Membrane Containing Copper Chloride

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Abstract: The durability of a new water-based membrane containing copper chloride, used to remove the toxic hydrogen sulfide (H_2S) gas, was evaluated. The pouring method was used to fabricate the membrane. The membrane contained water-based resin (15% polyamide), aluminum silicate, technosol, $CuCl_2.2H_2O$, distilled water and ethyl alcohol as the solvent. The resistance of the membrane against 1 M HCl, 1 M NH_3, 30% H_2O_2, 1 M HNO_3, 1 M NaOH, sunlight, and pure water was investigated. The changes in the surface morphology of the membrane treated under these conditions for over two weeks were examined using a scanning electron microscope (SEM) and a digital microscope. The Energy Distribution Spectroscopy (SEM-EDS) analysis was performed to confirm the gas capture ability of the membrane surface. The structural analysis of the membrane was performed by the X-ray diffractometry (XRD) analysis. Based on the results, the chemicals affecting the membrane morphology were identified. The results also showed that the water-based membrane was characterized by a certain adsorption capacity, and this membrane might be used as an eco-friendly alternative to the currently used materials.

Bakır Klorür İçeren Yeni Su Bazlı Membranın Dayanıklılığının Değerlendirilmesi

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Anahtar Kelimeler
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Membran

Öz: Bu çalışmada, toksik bir gaz olarak bilinen hidrojen sülfür (H_2S) gazının gideriminde kullanılan yeni bir alternatif olan bakır klorür içeren su bazlı membranın dayanıklılığı araştırılmıştır. Membran hazırlanırken dökme yöntemi kullanılmıştır. Membran su bazlı reçine (%15 poliamid), alüminyum silikat, teknosol, $CuCl_2.2H_2O$, çözücü olarak distile su ve etil alkol içermektedir. Membranın 1M HCl, 1M NH_3, %30 H_2O_2, 1M HNO_3, 1M NaOH, gün ışığı ve saf suya karşı dayanıklılığı incelenmiştir. Bu etkenlerle 2 hafta muamele edilen membranın taramalı elektron mikroskobu (SEM), dijital mikroskop ile yüzey morfolojisindeki değişimler incelenmiştir. Membran yüzeyindeki gaz adsorplamasını teyit etmek amacıyla Enerji Dağılım Spektroskopisi (SEM-EDS) analizi yapılmıştır. Membranın yapı analizi ise X-ışını kırınım difraktometresi (XRD) analizi ile yapılmıştır. Çalışmalar sonucunda elde edilen veriler, değerlendirilerek membran morfolojisini etkileyen kimyasallar tespit edilmiştir. Çalışma, su bazlı membranın belli bir adsorpsiyon kapasitesinin olduğunu ve bu membranın çevreci bir alternatif olarak kullanılabileceğini ortaya koymuştur.

1. Introduction

Sulfate (SO_4^{-2}) in domestic wastewater is converted to sulfur under anaerobic (absence of air) conditions (in the absence of oxygen and nitrate) facilitated by sulfate-reducing bacteria. The sulfur ion reacts with the hydrogen ion in the environment to form gaseous hydrogen sulfide. The rate of formation of the hydrogen sulfide gas under these conditions tends to increase in connection with an increase in the temperature in the summer. High levels of odor pollution occur under these conditions (Öztürk, 2017).

Hydrogen sulfide has a distinctive rotten egg odor, and humans can detect this at a minimum concentration of 0.0047 ppm (Guo et al., 2007). As gaseous hydrogen sulfide is 20% heavier than air, it accumulates in places and pits with poor ventilation. Thus, hydrogen sulfide accumulates in sewer systems. If the opening of the sewer manholes cannot be regulated, this accumulated toxic gas spreads to the environment and threatens the workers' health. If organic solids remain in the sewer system for a long time, the concentration of gaseous hydrogen sulfide may increase to 6,000 ppm in the channel (Öztürk, 2017). Because hydrogen sulfide causes sudden deaths when its concentration is 1,000 ppm, this situation might become very serious (Costigan, 2003; Bassindale & Hosking, 2011). The clinical techniques and antidotes used in treatment beyond supportive care for hydrogen sulfide poisoning need to be developed (Hoffman et al., 2008).

To protect the health of workers, a membrane is used in sewage systems where hydrogen sulfide accumulates, and in various industries (such as paper mills, oil refineries, and waste fields) where it is generated (Costigan, 2003; Bassindale & Hosking, 2011). Various membranes (e.g. tubular polydimethylsiloxane (PDMS) membrane, supported liquid membranes, etc.) and metal oxides (such as the oxides of Cu, Mn, Zn, Mo, and Fe) are also used (Swisher & Schwerdtfeger, 1992a; Swisher & Schwerdtfeger, 1992b; Elseviers & Verelst, 1999; Zhang et al., 2017; Tilahun et al., 2018).

In the European Union countries, some chemicals are injected into the canal to prevent the formation of hydrogen sulfide in sewage systems (Öztürk, 2017).

Gas accumulation can be prevented by placing the water-based membrane containing copper chloride, designed by Yildiz (2022), in certain areas of the sewerage systems. It can also be prevented by confining the gas inside the membrane (Yildiz, 2022). For this reason, it aimed to investigate the resistance of a water-based membrane containing copper chloride designed to remove hydrogen sulfide gas in the presence of 1M HNO_3, 1M NaOH, 1M HCl, 1M NH_3, 30% H_2O_2, sunlight and pure water.

2. Materials and Methods

Water-based resin (15% polyamide) (Technomarin), anti-collapse (Aluminum silicate) (Technomarin), distributor (Teknasol) (Technomarin), copper(II) chloride dihydrate (Merck), ethyl alcohol 99.5 %; (Tekkim), nitric acid (Sigma -Aldrich), sodium hydroxide (Merck), hydrochloric acid (Merck), ammonia (Merck), and 30% peroxide (Sigma -Aldrich) were used in this study. Additionally, 2.5% Copper(II) chloride dihydrate, 15% Polyamide, 0.5% Aluminum silicate, 2% technosol, 60% distilled water, and 20% ethyl alcohol were used (Yildiz, 2022). The membrane was prepared by dissolving the water-based resin, anti-slump, and dispersant in water, and copper chloride was dissolved in water and ethyl alcohol and mixed to form a homogeneous solution. The resulting homogeneous solution was poured into a Petri dish. The following day, it was removed from the petri dish using distilled water.

Yildiz investigated the hydrogen sulfide retention ability of the membrane fabricated by her research group (Yildiz, 2022).

The X-ray diffraction (XRD, Rigaku) technique was used to study the structure of the membrane, using an X-ray diffractometer. CuKα rays were used for the analysis (λ = 1.54059Å Cu/K-alpha1, 40kV,30mA). The scanning angle range (2θ) was 5- 90°, and the scanning speed was 0.02° per minute.

The characteristics and morphology of the polymeric membranes were studied using a scanning electron microscope (SEM, Jeol JSM-6060LV). Before testing, the sample membranes were frozen using liquid nitrogen and broken. Then, they were mounted on sample stubs using double-sided tape. The prepared samples were covered with a thin layer of gold. The morphological characteristics were studied using the SEM technique by observing the cross-sections of the samples and their surface (an optical microscope was used for sample observation). The surfaces of the membranes were analyzed after immersing them in different solutions. The images were captured using a Huvitz brand digital microscope.

The resistance of the membrane to chemicals such as acids and bases was investigated to determine the applicability of the membrane in sewage systems. Samples with dimensions of 100 mm×100 mm were used to evaluate the durability of the membranes. The samples were kept in an air-tight bottle containing 1 M hydrochloric acid, 1 M ammonia, 1M sodium hydroxide, 1M nitric acid, and 30% peroxide solutions in the dark at 20-25 ºC. They were irradiated with sunlight and treated with distilled water for two weeks. At the end of the waiting period, the changes in the membranes were examined using an SEM and an optical microscope. The Energy Distribution Spectroscopy (SEM-EDS) technique was used to confirm the gas-capture property at the membrane surface.

3. Results and Discussion

In this study, hydrogen sulfide was obtained using FeS, iron (II) sulfur, and dilute HCl as the feed solution (Yildiz, 2022). The prepared feed solution was added to the membranes in the experimental setup used in the method (Yildiz, 2022). The test setup consisted of glass columns holding the membranes. There were 12 membranes in total in the glass columns. H_2S gas was sent to the device, and the gas adsorption on the membranes was determined in ppm using a combined meter with an integrated ethane detector. When gas adsorption was completed, the membranes in the assembly were removed from the assembly, the image is shown in Figure 1. At the end of the process, 6 out of 12 membranes adsorbed the gas, while the other six membranes remained empty. The hydrogen sulfide adsorption capacity of the membranes, which was approximately 100% was determined by showing zero ppm of the gas measuring device located at the gas outlet of the assembly (Yildiz, 2022). Gas adsorption of these membranes was investigated by characterization methods such as SEM-EDS.

Figure 1. The image of the membrane recorded after gas adsorption (Yildiz, 2022).

From the SEM-EDS graph in Figure 2, it was confirmed that the $CuCl_2$-containing membrane, recorded after adsorption, adsorbed hydrogen sulfide.

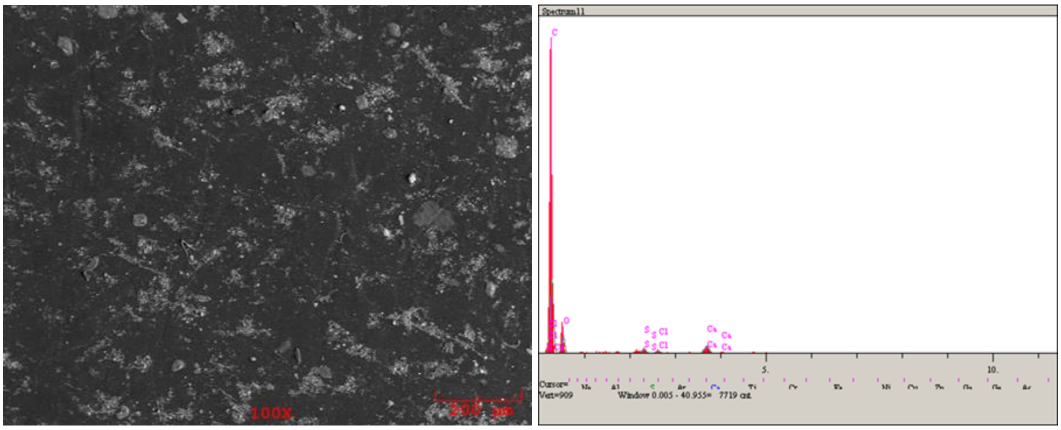


Figure 2. The SEM-EDS image of the membrane containing $CuCl_2$ recorded after gas adsorption.

The membranes that were kept in a closed glass bottle containing 1 M hydrochloric acid, 1 M ammonia, 30% peroxide solution, sunlight and distilled water for two weeks did not rupture or fragment at the end of the period.

In acidic conditions, the membrane remained stable for two weeks. Based on the structure of the resin, the membrane is expected to be highly resistant to hydrolysis under extremely basic or acidic conditions. The intramolecular forces are predominantly expressed in interactions. These forces explain their resistance toward hydrolysis. Based on the nature of the chemicals in the membrane, these forces were inferred to be hydrogen bonds and polar interactions.

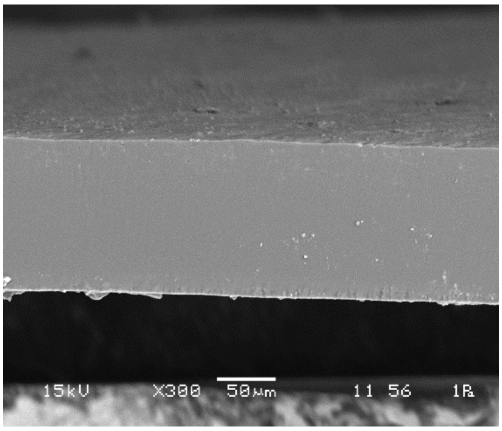
The results showed that when treated with certain chemicals (1 M NH_3 and 30% H_2O_2) and exposed to sunlight, the surface morphology of the membrane samples changed after 15 days. However, the membrane did not fragment or rupture. No changes were observed in the membranes treated with pure water. The results were similar to those reported by Chin et al. (2006). The resistance of the membrane was closely related to the membrane structure.

The SEM images showed the changes in the surface morphology of the membrane (Figures 3). When the SEM sections of the membranes were examined after exposure to sunlight for two weeks, the surface morphology was different.

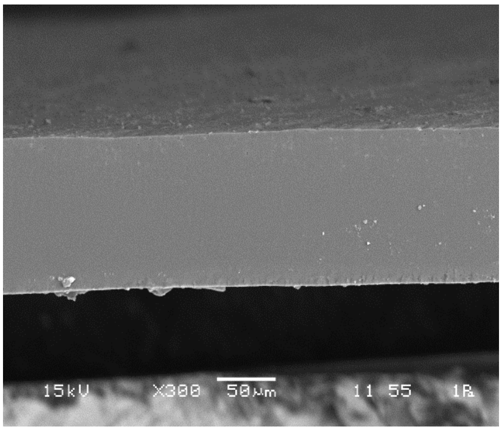
The surface morphology of the membrane did not change when the membrane was treated with pure water. When the membrane was treated with 1 M NH_3, the surface morphology of the membrane was relatively altered, but this change was reasonable compared to that after treatment with other chemicals. When the SEM image of the membrane containing $CuCl_2$ was examined after the gas was adsorbed, the changes in these membranes were acceptable for an adsorption membrane, compared to the changes in the membranes exposed to chemicals. This indicated that the membrane was stable in other solvents. It also revealed that the fabricated membrane could be used for gas separation and in various processes. Based on structural defect observed in the cross-section and the images of the surface obtained via SEM, it was found that the effect of 30% H_2O_2 on the membrane was considerably higher than the effect of other chemicals.

The optical microscope image of the membrane before and after the gas was adsorbed is shown in Figure 4. The most significant difference between the two images was the color difference seen in Figure 1. Additionally, the changes observed on the surface of the membrane before and after gas adsorption were similar to those found in the SEM images in Figure 3.

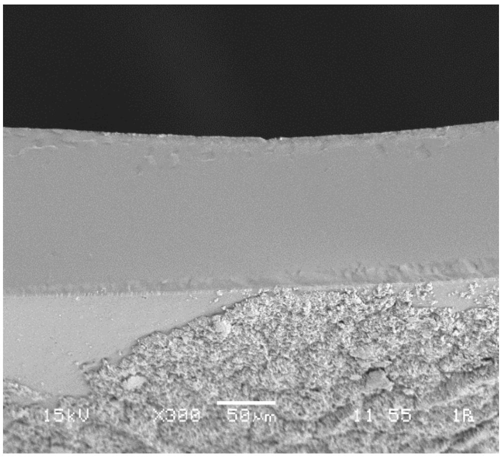
The effect of HNO_3, NaOH and HCl on the membrane was also investigated using an optical microscope (Figure 5). The images showed that the chemicals that caused the most changes on the membrane surface were HNO_3, H_2O_2, NaOH, and NH_3. Although these results were similar to those of the SEM analysis, no analysis for nitric acid and sodium hydroxide was conducted via SEM. Hydrochloric acid slightly altered the membrane surface. Additionally, the optical microscope images showed that daylight changed the membrane surface.



(a)



(b)



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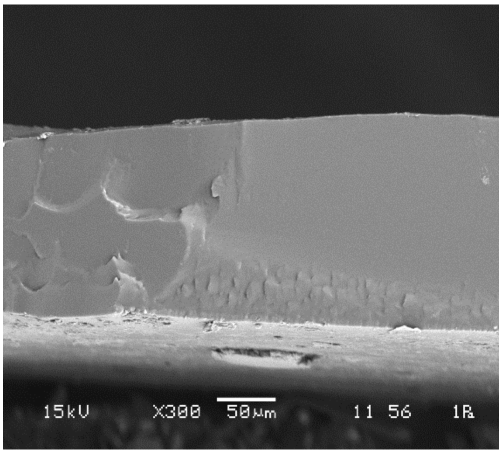

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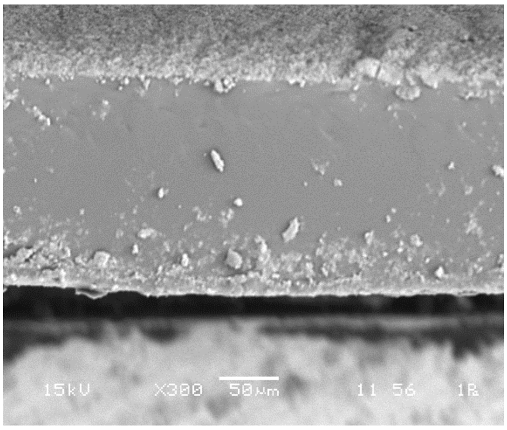
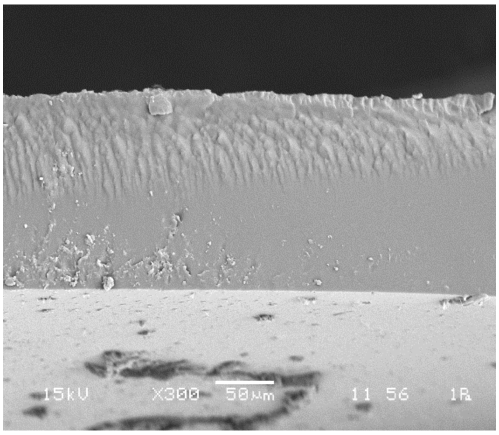
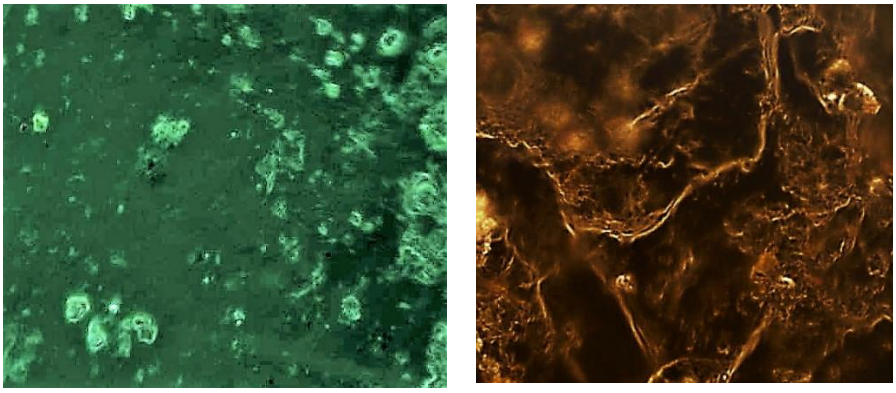


(e)



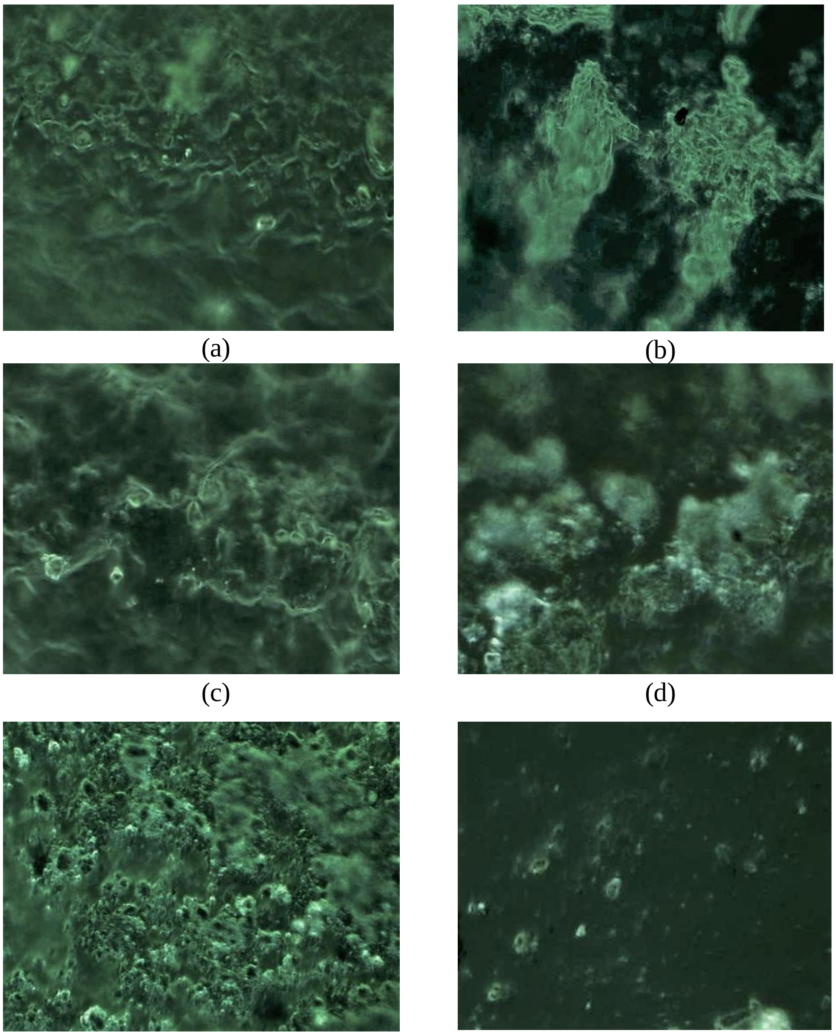
(f)

Figure 3. The SEM cross-sectional images (a: $CuCl_2$-containing membrane before gas adsorption; b: the effect of pure water on the membrane; c: the effect of NH_3 on the membrane; d: the effect of sunlight on the membrane; e: the effect of H_2O_2 on the membrane; f: the SEM image of the $CuCl_2$-containing membrane after gas adsorption;) (time: 15 days).



(a) (b)

Figure 4. Optical microscopy images of the membrane containing $CuCl_2$ 1000x (a) before gas adsorption and (b) after gas adsorption.



(a) (b) (c) (d) (e) (f)

Figure 5. The $CuCl_2$ optical microscope images 1000x (a: the effect of HNO_3 on the membrane; b: the effect of sunlight on the membrane; c: the effect of H_2O_2 on the membrane; d: the effect of NaOH on the membrane; e: the effect of NH_3 on the membrane; f: the effect of HCl on the membrane) (time: 15 days).

The XRD technique was used to study the structure of the membrane (Figure 6). The results indicated that although the membrane was amorphous in the range of 2θ = 14-28°, an increase in the signal intensity in the XRD spectrum was observed as the crystal-like lattice was associated with the density of silica (2θ = 28-30°). The polyamide used in the membrane is a polymer that can be found in either semi-crystalline or amorphous structures (Tasdemir, 2016). Results of the study revealed the amorphous character in the 2θ range of 30°-90° in the membrane. The XRD patterns were similar to those reported for the numerous polymer-containing membranes. The XRD analysis also revealed that the polyamide in the membrane was a semi-crystalline or amorphous polymer.

The contact angle of the membrane measured before the treatment procedure was 78.7°, and the membrane was found to be hydrophilic. The contact angle of the membrane used at the end of the procedure was 79.7°. The dirty membranes did not exhibit hydrophobic properties (Yildiz, 2022).

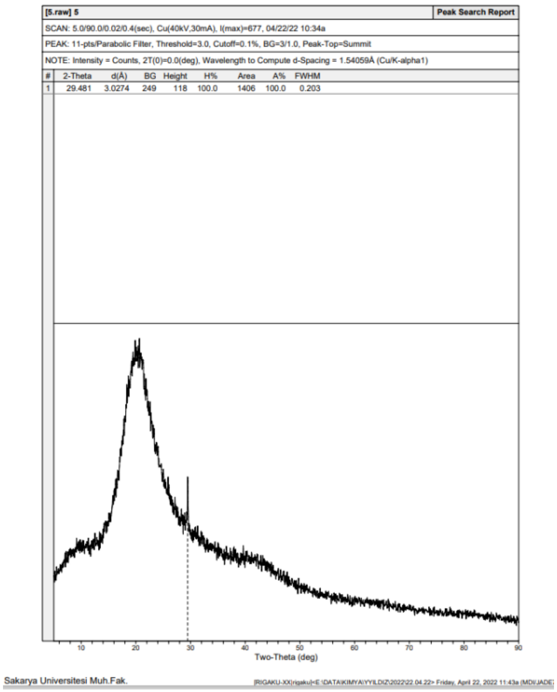


Figure 6. The XRD analysis of the $CuCl_2$-containing membrane before gas adsorption.

4. Conclusion

In this study, the durability and characteristics of a new water-based membrane containing copper chloride prepared for adsorbing H_2S gas were investigated. The SEM-EDS images and optical microscope images showed the ability of the membrane to adsorb H_2S gas. No noticeable difference in composition of the membranes was found from the SEM images of the membranes that were exposed to different chemicals for two weeks compared to the composition of the membranes synthesized in other studies (Yildiz, 2022), and the exposure time was determined as two weeks for the durability of the membrane. This indicated that the membranes can be used for up to 15 days and must be renewed after 15 days. The membrane surface was altered the most after exposure to HNO_3, H_2O_2, NaOH and NH_3, while it was altered the least by hydrochloric acid. Additionally, the SEM and optical microscope images images showed that daylight altered the membrane surface.

The fabricated membrane can be used in sewage systems and various industries in this study. It can improve the health conditions of individuals for workers in areas where sulfur gas occurs.

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