

# Removal of Silica in Wastes With Methyl Cellulose Composite Membranes

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## Research Article

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# Abstract

In this study, experiments were carried out for composite membrane synthesis with m-phenylenediamine (MPD), hydroxyethyl methacrylate (HEMA) and methyl cellulose (MS) by changing process parameters (methyl cellulose ratio, synthesis temperature, stirring time, oven temperature). Taguchi Method, an optimization method for production, was applied to 4 levels 4 parameters. The silica solution was passed through the produced composite membrane, and the filtering property of the membrane for different periods was examined. Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) were used for characterization of composite membranes. Shore A test was performed to determine the mechanical strength of composite membranes. The amount of silica in membranes obtained because of the silica treatment was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis. As a result, it was seen that the composite membranes produced could be evaluated in the treatment of wastewater containing silica.

# Introduction

Membrane treatment processes were the primary wastewater treatment technologies (Yildiz et al., 2013). Researchers studied the preparation and characterization of polyurethane-based cation exchange membranes (Baig and Khan, 2015). Different researchers studied the pervaporation applications of interfacial polymerization by modifying thin film composite membrane (Yu et al., 2009). Also, the synthesis and characterization of o-phenylenediamine and xylylene copolymers were investigated (Li et al., 2001). In literature, researchers examined the oxidative copolymerization of p-phenylenediamine and 3-aminobenzene sulfonic acid (Amer et al., 2016). In a different study, oxidation polymerization of o-phenylenediamine and pyridinamine was evaluated (Huang et al., 2001). The manufacture of polyamide composite reverse osmosis membranes with unsupported interface polymerization was investigated (Park et al., 2017). Thin film composite reverse osmosis membranes combined with hydrophilic silicon dioxide nanoparticles were prepared by researchers (Peyki et al., 2015). Unlike the studies, thin film composite membranes with graphene oxide added for advanced osmosis applications were examined (Shen et al., 2016). Some researchers examined multilayer polyamide membranes with 2-stage interface polymerization (Tsuru et al., 2013). Other researchers studied polyamide interface composite membranes with Taguchi design (Khorshidi et al., 2015). In a study, reverse osmosis performance was investigated for synthesis, characterization, and desalination of polyamide thin film composite membranes (El-Aassar, 2012). A study was carried out on the removal of m-phenylenediamine from the aqueous solution (Raval et al., 2015). Different researchers studied the preparation of a thin-film composite nanofiltration membrane (Meihong et al., 2008). Also, many studies in literature investigated membrane structures for material properties (Roh et al., 2008; Sun et al., 2021).

In this study, unlike membranes used in the literature, m-phenylenediamine, hydroxyethyl methacrylate was used for membrane production with methyl cellulose. Characterization of produced membrane and its mechanical strength were determined by FT-IR, SEM, XRD, ICP-OES and Shore A test. Waste silica

solution was passed through the membrane, which was tested and produced under optimum conditions, and the synthesized membrane was found to have good filtering property for silica.

## Materials And Method

### Materials

M-phenylenediamine (Acros Organics), Hydroxyethyl methacrylate (Merck), Methyl cellulose (Sigma) were used as analytical purity in experimental study.

### Method

Taguchi Method was applied as 4 parameters and 4 levels of total 16 experiments. MS ratio, synthesis temperature, stirring time, oven temperature was 3.5-14% (w/w), 60-90°C, 10-40 min and 60-90°C, respectively. The determined amount of MPD was dissolved in ethanol. With the addition of HEMA and methyl cellulose, it was mixed at different temperatures in a heated magnetic stirrer. Then, the obtained mixture was poured into petri dish and kept in the oven for the determined times. FT-IR, XRD, ICP-OES analyzes were performed for characterization of membranes, and Shore A test was applied to measure the mechanical strength of membranes. At last step, the maximum amount of silica in the water was determined as 1000 mg/L. 0,5 gram of silica was dissolved in 500 ml of water. The 5 ml solution was passed over the membrane produced, and the measurement was taken every 5 minutes.

## Results And Discussion

The aim of Taguchi Method was to achieve the best result at minimum cost (Gökçe and Taşgetiren, 2009). Parameters were determined using orthogonal arrays and calculations were made with signal/noise (S/N). In this study, the graph of S/N values was given in Figure 1.

In Taguchi method, the 2-2-1-4 experiment, which corresponded to the experiment 6 with the “highest and best” selection, was chosen as the experiment obtained under optimum conditions.

As a result of FT-IR analysis, the FT-IR spectrum of HEMA hydrogel indicated the presence of functional groups. C=O stretching vibration peak, O-H stretching, and C-O stretching were obtained in the range of 1700-1750  $\text{cm}^{-1}$ , around 3550  $\text{cm}^{-1}$  in the range of 1150-1180  $\text{cm}^{-1}$ , respectively. FT-IR results for HEMA were observed to be compatible with literature (Figure 2) (Taleb et al., 2014). For MPD, a voltage peak of  $\text{NH}_2$  was observed in range of 3400-3450  $\text{cm}^{-1}$ . Aromatic C-H tension was observed in the range of 3000-3050  $\text{cm}^{-1}$ . After 1500  $\text{cm}^{-1}$ ,  $\text{NH}_2$  bond folds were seen as peaks. It showed that FT-IR results of MPD were compatible with literature (Oh et al., 2012). In produced sample, the peak of C-N bond was seen at a wavelength of 700-800  $\text{cm}^{-1}$ . FT-IR result of sample containing methylcellulose was given in Figure 2. The peak was C-O-C stretch in a peak anhydro glucose ring in the range of 1050-1100  $\text{cm}^{-1}$ . The 3452  $\text{cm}^{-1}$  peak was caused by O-H stress. In addition, the presence of  $\text{CH}_3$  groups in methyl cellulose formed

a peak in range of 2850-2900  $\text{cm}^{-1}$ . The peaks seen in 1400-1300-1100 and 900  $\text{cm}^{-1}$  intervals were the C-H stresses caused by the  $\text{CH}_2$  and  $\text{CH}_3$  groups. FT-IR results for methyl cellulose were found to be compatible with literature (Oliveira et al., 2015). The scanning electron microscope (SEM) gave information about the physical topography, crystal structure and electrical behavior of 1 micrometer (Vernon-Parry, 2000). When the membrane with methylcellulose was examined morphologically, it was seen that there were rod-shaped structures with an average length of 247.14  $\mu\text{m}$  and spherical structures with an average diameter of 65.712  $\mu\text{m}$  (Figure 2). The diffraction of waves with different wavelengths in XRD analysis showed the structure of a medium of different lengths. From this point, when the XRD analysis of the membrane sample obtained under optimum conditions was examined, it was understood that the characteristic peaks were seen at 18, 40, 45, 65 and 80  $\text{A}^\circ$  (Figure 2).

Silica was a compound that was difficult to remove during water treatment. It formed lime on the surface of industrial equipment and reverse osmosis membranes.

Silica was generally present in surface and groundwater concentrations ranging from 1-30 mg/L. However, depending on water source, it could exceed 100 mg/L concentrations (Sims, 2015).

The studies showed that it was over 1000 mg/L in some salt waters and sea waters. For silica treatment results, a measurement was taken every 5 minutes from the silica solution passed through a membrane with a diameter of 9,7 cm (experiment 6) and the flux calculation was given in Table 1.

ICP-OES was one of the popular analytical tools for identifying trace elements in countless sample types (Hou and Jones, 2000). In the study, ICP-OES analysis was performed on samples taken every 5 minutes for silica treatment and results were given in Table 1. According to the ICP-OES results, the best silica purification was seen after 30 minutes. Silica removal was calculated as 19.58%.

The most suitable mechanical strength test for materials in literature was Shore hardness test. The method contained indenting the sample using a specific geometry and strongly hardened steel indenter based on the selected measuring scale.

Hardness values were used between 0 and 100 as a mathematical scale. This method was generally used to evaluate the properties of materials such as elastomer, porous, gel-like etc. (Zhao et al., 2015).

In this study, the mechanical strength test was performed on the sample produced for the mechanical strength test and the result was recorded as 48 Shore A. The device scale was in the range of 0-100. This test was repeated 3 times for each sample (Table 1).

Table 1

Test parameters, flux calculation for silica treatment, ICP-OES analysis and mechanical strength test data (Dağidir, 2017)

| Parameters                 | Level 1                     | Level 2   | Level 3              | Level 4 |
|----------------------------|-----------------------------|-----------|----------------------|---------|
| Methyl cellulose (%)       | 3,5                         | 7         | 10,5                 | 14      |
| Synthesis temperature (°C) | 60                          | 70        | 80                   | 90      |
| Stirring time (min)        | 10                          | 20        | 30                   | 40      |
| Oven temperature (°C)      | 60                          | 70        | 80                   | 90      |
| Time (min)                 | Flux (kg/m <sup>2</sup> .s) | Si (ppm)  | Silica treatment (%) |         |
| 0                          | -                           | 3,83±0,13 | -                    |         |
| 5                          | 1,714                       | 3,68±0,12 | 3,92                 |         |
| 10                         | 1,776                       | 3,67±0,12 | 4,18                 |         |
| 15                         | 1,835                       | 3,62±0,12 | 5,48                 |         |
| 20                         | 1,570                       | 3,64±0,12 | 4,97                 |         |
| 25                         | 1,767                       | 3,13±0,11 | 18,28                |         |
| 30                         | 1,369                       | 3,08±0,10 | 19,58                |         |
| 35                         | 1,703                       | 3,11±0,10 | 18,80                |         |
| 40                         | 1,786                       | -         | -                    |         |
| No                         | Shore A                     |           |                      |         |
| 1                          | 37                          | 32        | 40                   |         |
| 2                          | 38                          | 33        | 41                   |         |
| 3                          | 40                          | 36        | 43                   |         |
| 4                          | 43                          | 39        | 47                   |         |
| 5                          | 45                          | 41        | 50                   |         |
| 6                          | 49                          | 43        | 52                   |         |
| 7                          | 47                          | 43        | 51                   |         |
| 8                          | 46                          | 40        | 51                   |         |
| 9                          | 43                          | 39        | 48                   |         |
| 10                         | 42                          | 37        | 46                   |         |
| 11                         | 41                          | 35        | 47                   |         |

| Parameters | Level 1 | Level 2 | Level 3 | Level 4 |
|------------|---------|---------|---------|---------|
| 12         | 38      | 34      | 43      |         |
| 13         | 35      | 32      | 42      |         |
| 14         | 35      | 30      | 40      |         |
| 15         | 33      | 30      | 38      |         |
| 16         | 31      | 28      | 37      |         |

## Conclusion

As a result, composite membrane synthesis was achieved by using MPD, HEMA and methyl cellulose with good filtering property for silica. According to the Taguchi method, the experiment 6 with parameters 2-2-1-4 (7-70°C-10 min-90°C) was chosen optimally. In terms of industrial applications, it was observed that optimal composite membrane material could be produced with high mechanical strength, uniform physical morphology, high quality, low cost, and positive results can be obtained in the treatment of silica wastes.

## Declarations

### Acknowledgements

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### Availability of data and materials

All data generated or analyzed during this study are included in this article.

### Author contribution

Demet Dağdır: experiment, writing— original draft preparation.

Nil Acaralı: writing— original draft preparation, supervision.

### Data availability

All data is provided in full in the results section of this manuscript.

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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## Figures

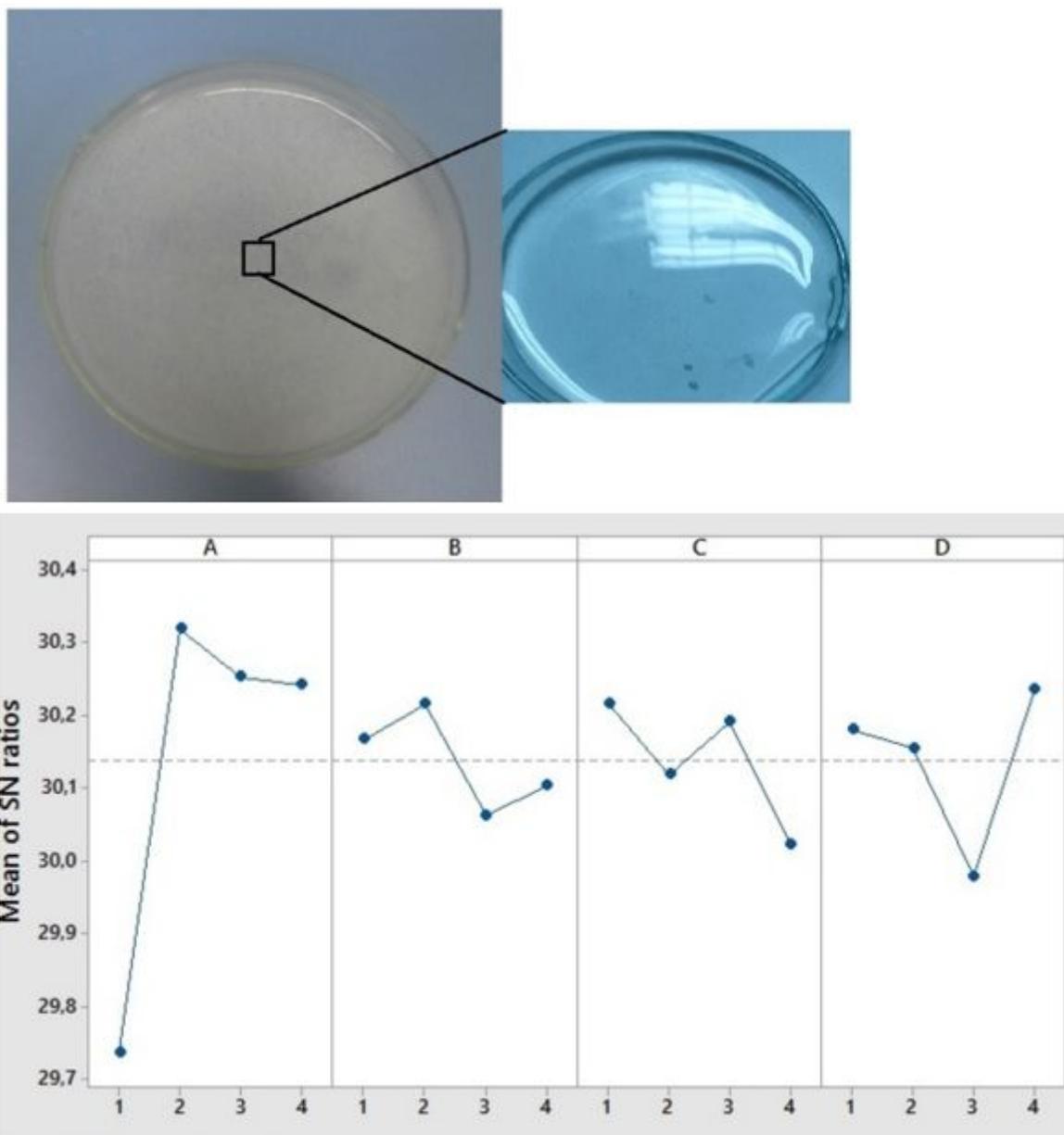


Figure 1

<p>Membrane and mean of S/N ratios (Karapınar and Acarali, 2017)</p>

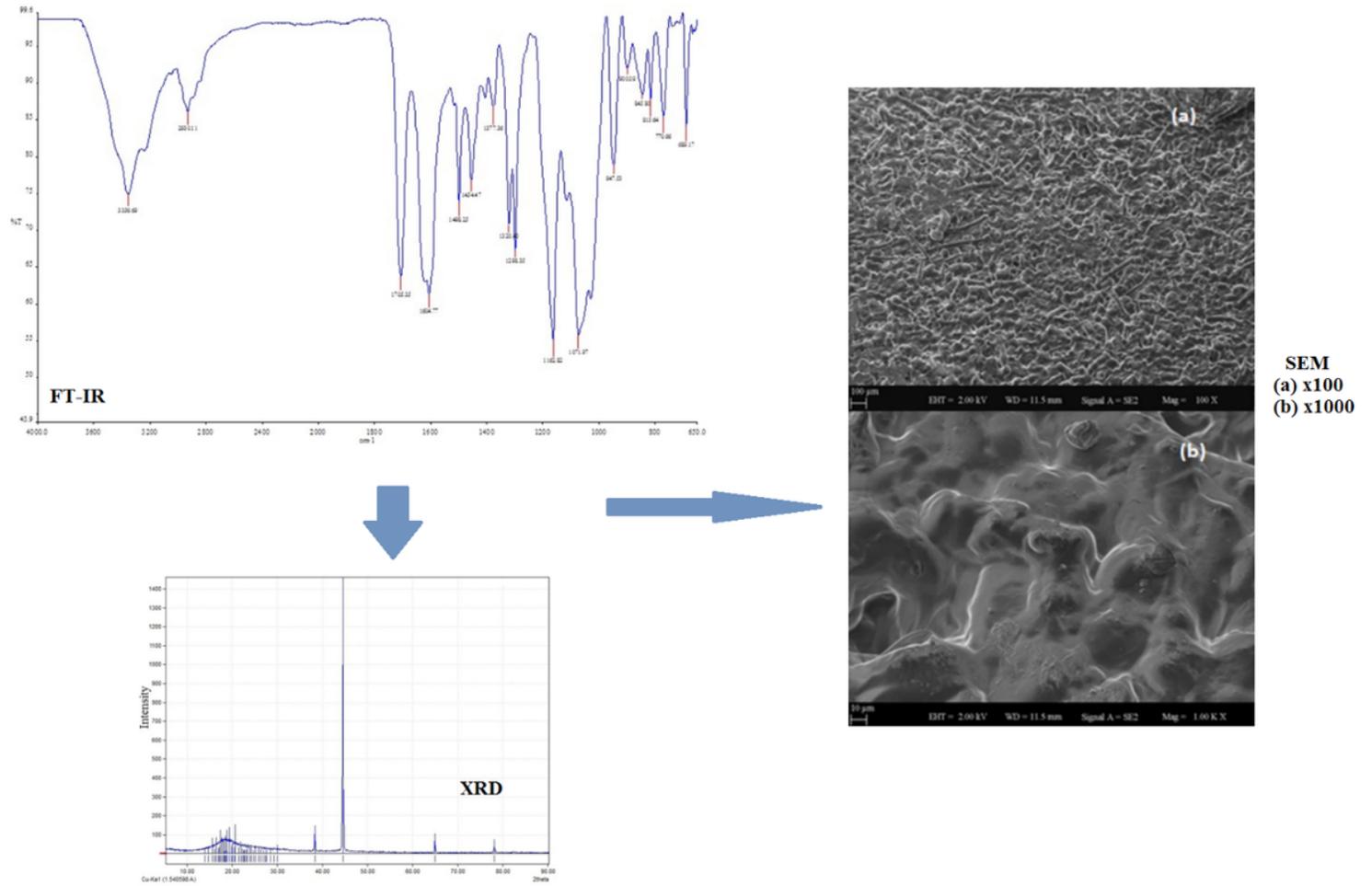


Figure 2

<p>FT-IR, SEM, XRD analysis of membrane</p>