RESEARCH ARTICLE

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Filtration Application with PVDF Membrane in the Removal of Natural Organic Matter Humic Acid from Surface Water

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ABSTRACT: Only 0.03% of water resources are used as drinking water in the world. The most important problem in drinking water is organic substances in surface waters. More than half of these organic substances are humic acid. Humic acid which is formed partially or completely by the decay of vegetation or animal waste, is a dark-colored substance. These substances enter surface waters with rainwater. In the chlorination process, which is a disinfection process applied to surface waters, chlorine reacts with humic acid and creates carcinogenic by-products such as trihalomethane and haloacetic acid. Trihalomethane and haloacetic acid are carcinogenic materials which are harmful to human health. Therefore, the removal of the humic acid from surface waters has critical importance. To develop alternative, economical and environmentally friendly processes against the classical methods has been inevitable for the removal of humic acid from surface waters. Membrane technology is an important alternative to traditional methods. It is possible to remove humic acid from surface waters by using membrane filtration technique. In this study, porous membranes were synthesized using polyvinylidene fluoride (PVDF) polymer by the phase inversion method. The removal of humic acid from surface water was investigated by using filtration technique with synthesized membranes. The separation performance of the membrane in different humic acid concentrations was tested and the effect of the change of the concentration on the removal of humic acid was determined.

Keywords: Filtration, Humic acid, Membrane, Polyvinylidene fluoride, Surface water.

INTRODUCTION

Organic substances are important factors to the affect the quality of water. Organic substances in surface and groundwater resources can cause many problems. The most important of these problems is the formed by-products during the chlorination process. By-products cause long-term problems in human health (Gümüş et al., 2013).

More than 50% of organic substances are humic substances. Humics are among the most critical pollutants (Gümüş et al., 2013). Humic acid is formed partially or completely as a result of the decay of vegetation or animal residues and is mixed by rainwater in surface water. There are three basic humic substances: completely insoluble humic acid, insoluble in water if the pH value is below 2, but soluble at higher pH values, and soluble fulvic acid at any pH value. Humic acids are in the dissolved organic carbon group. When the concentration of humic acid in water is above 5 mg/L, it affects the color of the water and become an aesthetic problem (Ateşli, 2006; Oğuz et al., 2008).

There are various treatment process for the removal of humic acid from water sources such as ozonation, biofiltration, adsorption, and membrane filtration. Membrane filtration technology is one of the advantageous water treatment processes in recent years (Gümüş et al., 2013). There are many advantages to using membrane technology. The most important advantages are good quality of the effluent, less area of the process, easy operation, consumption of less chemical substances in the process, and low cost (Aksu, 2019).

Membrane filtration process is used for the separation of liquids or gases containing particles in the range of 0.1-10 µm. The driving force is pressure in the membrane filtration process. The feed solution is fed to the top surface of the membrane as seen in Figure 1, particles or suspended solids are kept on the membrane surface and accumulate. This accumulation causes clogging in the pores of the membrane, and the formation of a film on the surface of it over time. This situation results in a decrement of the permeate flow. The decrease in flux means that separation does not occur and the membrane should be cleaned or replaced (Scott, 2006). Therefore, membrane synthesis should be controlled to achieve the desired results by optimizing the parameters.

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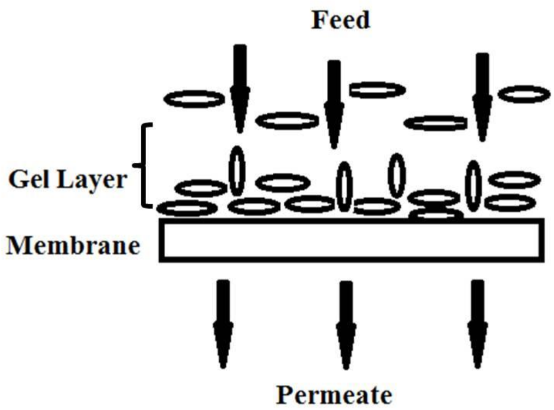

Figure 1. *Vertical directional flow model in membrane filtration method (Naharcı, 2007)*

There are important parameters that affect the separation performance of the membranes in the filtration system. The type of material to be used in membrane synthesis, the membrane's pore size and pore distribution, surface charge, hydrophobic or hydrophilic property and membrane thickness are significant points for the filtration processes. In this study, PVDF polymer was used to membrane synthesis. The narrow pore size distribution of PVDF membrane provides good separation efficiency (Bayar, 2017). The hydrophobic property of PVDF prevents the entering the aqueous solution into the membrane pores. Therefore, it is expected that a membrane with high permeate flux under a high rejection performance will show better hydrophobic properties and have a larger pore volume (Kuo et al., 2008). There are many chemical materials commonly used in membrane synthesis. Material selection should be made in consideration of the separation rate, membrane morphology and system conditions. However, chemical, mechanical and thermal resistance and high permeability and selectivity should be among the expected properties (Su ve Çevre Teknolojileri, 2018). Having these features is an important factor for the selection of PVDF.

Microfiltration is a membrane supported filtration process with pore sizes ranging from 0.1 to 1.4 µm, where the driving force is pressure. It is used to separate particles in liquids and gases. The used membrane allows particles in the range of 0.1 to 1.4 µm to pass through the membrane, while allowing larger particles to retain onto the membrane surface. Thus, the separation process is completed according to the particle size. The particle holding capacity of the filter per membrane area is between 100-300 g / m^2 (Aslan, 2016).

In this study, it is aimed to synthesize porous membranes with phase inversion method using Polyvinylidenefluoride (PVDF) polymer and to remove humic acid from surface waters by microfiltration technique with these synthesized membranes. The separation performance of the membrane was tested in different humic acid concentrations. The structural morphology of the membranes has been characterized using SEM analysis.

MATERIALS AND METHOD

Materials

Polyvinylidene fluoride used in membrane synthesis was obtained from Solvay. Dimethylformamide and humic acid were purchased from Sigma Aldrich. Distilled water was also used in experimental studies

PVDF Membrane Synthesis

5 wt % PVDF was dissolved in dimethylformamide for preparation membrane solution. The homogeneous solution was prepared in room temperature. The obtained solution was coated on the nonwoven surface thinly and immersed in the water bath and phase change was achieved. After the water bath treatment, the membranes were allowed to dry at room temperature.

Preparation of Humic Acid Solution

Humic acid solution was prepared in different humic acid concentrations and the effect of feed concentration on humic acid removal was investigated. 2.5, 5 and 15 ppm of feed humic acid concentration was used for the separation experiments.

Separation Experiments With Membrane Filtration System

Membrane filtration experiments have been carried out for the removal of humic acid from water sources. The used experimental setup is shown in Figure 2.

Figure 2. *Membrane filtration test system*

In the membrane filtration method, humic acid is retained on the membrane filter surface. The filtration is carried out over the membrane filter by vacuum pump in membrane filtration system. While the water is separated from the membrane, the organic substance humic acid is removed by retain on the membrane filter surface. The humic acid concentration in the permeate was determined using a UV-Vis spectrophotometer (Agilent-Cary60) at 254 nm. The humic acid rejection was calculated by the Equation 1. In Equation 1, R is the humic acid rejection, c_f is the humic acid concentration on the feed stream side, and c_p is the humic acid concentration on the permeate side.

$$R = \frac{c_f - c_p}{c_f} \times 100 \qquad (1)$$

Membrane Surface Morphology Characterization

The morphological structure of the membrane was determined by Carl Zeiss / Gemini 300 scanning electron microscopy (SEM). The pore structure and distribution of membrane was observed by SEM analysis.

RESULTS and DISCUSSION

Membrane Morphology

The structural morphology of PVDF membranes was determined by SEM analysis. SEM images of membranes in different magnifications are given in Figure 3.

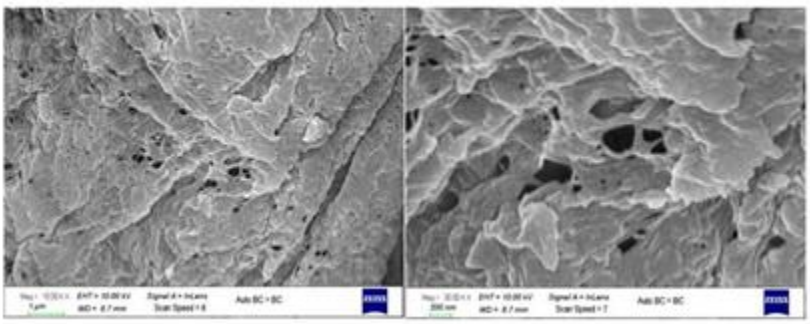

Figure 3. *SEM image of PVDF membrane*

SEM images show that the membrane has porous structure. It was observed that the pore distribution was more intense in some regions and no pore formation was seen in some regions. It was concluded that the synthesized membrane should be developed to obtain a more homogeneous pore distribution.

Membrane Filtration Results

In order to examine the effect of feed concentration on humic acid removal from surface waters, different concentrations of humic acid solutions were prepared and filtration processes were carried out.

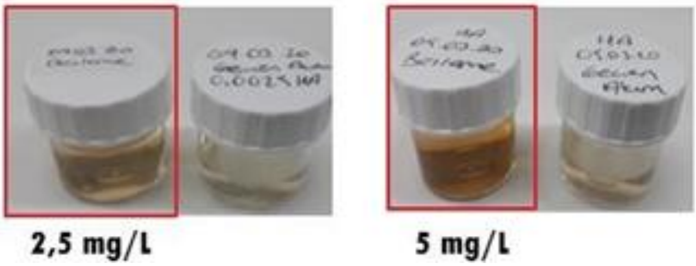

Figure 4. *Feed and permeate samples of humic acid solutions*

As can be seen in Figure 4, a visible color difference in samples was observed after the membrane filtration process. It can be said that the pure water permeability of PVDF membrane is high in the membrane filtration process.

During the filtration process, water flux is one of the most important parameters for evaluating membrane performance. The fouling properties of the membranes can be examined by decrease in flux values. It can be said that the decrement of flux in filtration processes is mainly related to membrane fouling caused by membrane clogging, cake formation and concentration polarization. Figure 5 shows the used membranes in the filtration process.

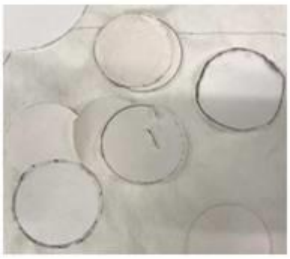

Figure 5. *PVDF membranes used in filtration process*

In order to evaluate the humic acid removal by using the prepared PVDF membrane, water samples were taken from the feed solution and permeate side. Samples were analyzed with UV at 254 nm. UV_{254} generally represents humic-like fractions, which is a type of organic matter with aromatic structure, carbonyls or olefins. These components are more easily rejected by the PVDF membrane due to their hydrophobic and relatively high molecular weight. The percentage values of humic acid removal obtained as a result of this analysis are shown in Table 1.

Table 1. *The effect of feed concentration on humic acid removal*

Feed concentration (ppm)	Humic acid removal percentage (%)
2.5	33
5	53
15	75

Table 1. shows the effect of feed concentration on humic acid removal. The experiments were conducted by humic acid solutions of 2.5, 5 and 15 mg/L feed concentrations. As can be seen in Figure 6, as the feed humic acid concentration increased, the removal ratio of humic acid increased. This is an expected result. Humic acid is a negatively charged chemical component. PVDF membrane is also negatively charged material (Kakihana et al., 2017). Since both of them have the same charge, the force of repelling each other increases and humic acid is pushed from the membrane surface. This causes an increase in the percentage of removal of humic acid.

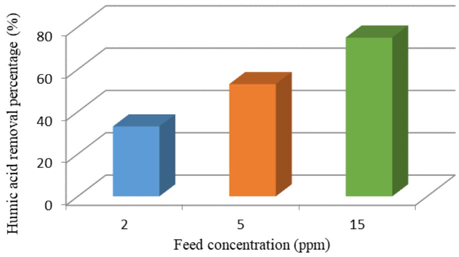

Figure 6. *Influence of feed concentration on percentage of humic acid removal*

CONCLUSION

The effect of feed concentration on the humic acid removal was investigated in this study. As the concentration of the humic acid increased, the removal ratio of humic acid increased. The best removal efficiency was obtained as 75% by using 15 mg / L humic acid containing solution. In this study, it was determined that humic acid can be successfully removed from the water by membrane filtration, and it was concluded that it was possible to obtain the desired purity water by using suitable membranes. It is possible to obtain higher separation performance by optimizing the membrane synthesis conditions. It is considered that more better separaton performance will be obtained by changing the operation parameters.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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