Surface modification of nanofibrous membranes for water purification

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Water covers approximately 70% of the earth's surface and is important for all living things. Yet, there is a serious lack of drinking water in many countries. Water treatment is becoming more important for world countries to tackle water scarcity by strengthening their infrastructure with the increase in global freshwater consumption. The aim of the project is to obtain nanofibrous membranes, which provide high fouling resistance and antibacterial properties for water purification.

Key words: nanofiber, membrane, surface, alkaline, modification

Introduction

One of the biggest problems in membrane technology is membrane foulingwhich causes a decrease in membrane flow and increase cost. Hydrophilic membranes are good candidates to reduce the membrane fouling against hydrophobic foulants.

Herein, PVDF membranes were modified by alkaline agents such as KOH, NaOH, ethanoloamine and diethylenotriamine. Alkaline treatment degrade the PVDF and defluorization increase hydrophilicity, that reduce fouling [1]. It is well known that, some of nanoparticles, such as AgNPs, ZnO, CuO, TiO_2, have antiseptical properties [2]. They may reduce growth ability of bacteria present in water, casue their irreversible damages in cells and disrupt cellular membrane structure [3]. In this research tried to remove fluoride from PVDF chain and add -OH and -NH_2 groups, which in next step will be used to bound covalently nanoparticles.

Methods

Preparation of membranes

2,65 g/m^2 PVDF has been binded on a nonwoven support using various adhesive web (coPET, coPA, polyurethane) using lamination proces.

Alkaline treatment with NaOH, KOH, ethanolamine (ETA) and diethylenetriamine (DETA)

Membrane surfaces were washed in isopropanol and rinsed with deionized water, and dried at a of 40°C in an oven. Sodium hydroxide was dissolved in ethanol whereas potassium hydroxide was dissolved in isopropanol. KOH and NaOH solutions were prepared as 0.025M and 2M, respectively. The reaction was conducted at room temperature at various time: 10, 15, 20, 30 minutes, 1,2 hours. The aqueous solutions of ethanolamine and diethylenetriamine were prepared in 4M and 2M in concentration. The reactions were performed for various times: 1,3 and 5 h at 80°C. After chemical treatment, the membranes were washed with deionized water and stored in DI water at 25°C.

Membrane characterization

Vega 3SB scanning electron microscope (SEM; TESCAN VEGA) was used to observe nanofibers surface. The diameter of nanofibers was measured by ImageJ program. The samples were analyzed by Nicolet iZ10 Fourier transform infrared spectroscope (FTIR, Thermo Scientific) to detect changes in chemical structure. The water contact angle was determined by Drop Shape Analyzer DS4 (Krüss GmbH). Membrane pore size was determined by by bubble point method using Porometer 3G through a pore size analyzer (Quantachrome Instruments, Anton Paar GmbH).

Results and discussion

Increased concentration and alkaline treatment time destroyed the adhesive web. FTIR results are shown in Figures 1 and 2.

The presents of -OH, -CF, -C=C and C=O groups were checked in FTIR analysis to estaminate the changes in surface sturcture. In range 1050-1250 cm^{-1} appears two sharp peaks from the vibrations of bihalide. The results shown that amount of C-F groups is reduced after alkaline treatment.

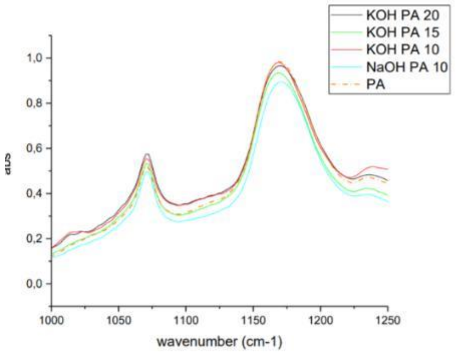

Figure 1: The FTIR spectrum in range 1000-1250 cm^{-1} for KOH treatment for membranes with PA adhesive web.

The -OH groups shown near 3400 cm^{-1} , the radical forms of -OH groups may occurs either in dissociation (3580-3650 cm^{-1}) or in association (3200-3400 cm^{-1}) as shown in Figure 3.

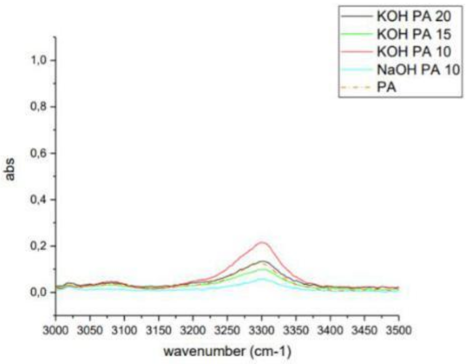

Figure 2: The FTIR spectrum in range 3000-3500 cm^{-1} for KOH treatment for membranes with PA adhesive web.

The -OH groups appeared in FTIR spectrum after alkaline modification occasionaly. The intensivity of peaks after modification were close to results for pristine membrane. However, it could be noticed that intensivity of peaks for -C=O, -C=C was higher than for not modified membrane. It means, that reaction of defluorization was initiated, but not completed. After DETA treatment in FTIR spectrum appeared peaks for - NH_2 groups. Alkaline treatment increased the fiber diameter from 198 nm up to 300 nm. Similarly, membrane pore size reduced from 0.7 µm to 0.3-0.4 µm.

Modificaton improve membrane hydrophilicity (Figure 3) The contact angle in KOH modification decreased gradually whereas in others alkaline treatrments reached 0°C.

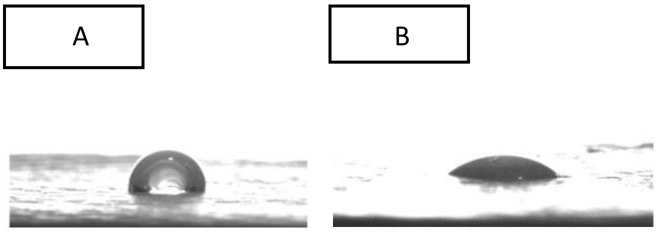

Figure 3. The contact angle for pristine and KOH-1h modified PVDF.

Conclusion

According to obtained results, alkaline treatment by KOH and NaOH does not provide sufficent amount of -OH groups into surface of nano PVDF membranes. The high concentration of alkaline agent causes damage of adhesive webs. The small concentration of modified agent initiate reaction of defluorization, but not completed it.. As future work, it is planned to decrease maximum concentration of amine agent, but increase reaction time. The alkaline modification by DETA provided small amount of - NH_2 gropus. However, it is essential to optimize reaction conditions.

Acknowledgements

This work was supported by the Student Grant Competition (SGS) project at the Technical University of Liberec in 2021. The authors acknowledge the assistance provided by the Research Infrastructures NanoEnviCz (Project No. LM2018124), which is supported by the Ministry of Education, Youth and Sports of the Czech Republic.

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