Change Of Pvdf Ultrafiltration Membranes For Humus Acid Removal Applications In Water By Adding Fe2o3/Zeolite Additives

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Abstract. One of the most often used polymers as the primary component of membranes is polyvinylidene fluoride or PVDF. Nonetheless, its hydrophobic characteristic remains a significant barrier to this material's utilization. This study aims to reduce the likelihood of fouling by adding Fe2O3/Zeolite additions to the PVDF membrane. Fe2O3/Zeolite was used to modify the membrane through surface coating. Compared to the pure PVDF membrane, the results demonstrated that adding additives to the membrane polymer solution increased the purified water and humic acid fluxes. The best results in this study were obtained by modifying the PVDF membrane and adding Fe2O3/Zeolite additions in a ratio of 1 gr: 0.5 gr (M2). Based on these findings, it can be said that.

1 Introduction

Due to its strong chemical resistance, thermal stability, and capacity for membrane production, PVDF is a frequently employed material [1]. PVDF membranes have extensive application in ultrafiltration and microfiltration procedures[2]. However, PVDF membranes are more prone to clogging and have fewer uses since they are a semi-crystalline polymer with –CH2-CF2– repeating units that produce a hydrophobic structure[3]. Fluids containing hydrophobic species are the source of blockages because they reduce membrane permeability and lead to the formation of activated sludge, which can shorten membrane life and raise operating expenses[4]. Both reversible and irreversible blockages are possible[5]. Foulants that adhere firmly to the membrane pores induce irreversible fouling, whereas foulants that stick to the membrane surface cause reversible fouling[6]. Antifouling membranes must be

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developed and modified for more effective MBR applications by adding compounds to improve their hydrophilic qualities[2].

By engineering the membrane surface to be more hydrophilic, the membrane modification technique seeks to improve the membrane's hydrophilicity, antibacterial qualities, and performance while producing more effective wastewater treatment outcomes[7]. Grafting, covalent coupling, irradiation, plasma treatment, layer adsorption, and coating are a few alteration procedures[8]. The coating technology is the most adaptable, has a less complicated process and is reasonably priced[7]. The dip-coating method involves applying a liquid phase coating solution to the substrate's surface, allowing the solution to cover the surface before it dries [9]. The most excellent permeate flow readings and a hydrophilic surface on PVDF were achieved using the dip-coating technique. The dip-coating method doesn't require particular conditions (high pressure and temperature), is simple to use, and is highly efficient for industrial applications [8].

Iron oxide nanoparticles can be added to PES and CA membranes to lessen their poor flux [10]. Iron oxide is biocompatible, has low toxicity, and functions as an adsorbent for ionic pollutants while also improving the mechanical stability of membranes [11]. Compared to a pure PVDF membrane, the mixed matrix membrane has more holes and is more apparent with the addition of Fe2O3 [12]. Higher flux and FRR are produced when Fe2O3 is added to PVC instead of when it is not [13]. Zeolite is an inorganic crystal with high adsorption qualities that contains silica, oxygen, and aluminum. It also enhances the surface area available to produce biofilms [14]. Zeolites are extensively employed in industry to eliminate heavy metals, lessen surplus ammonium, adsorb gas, separate linear from non-linear hydrocarbons, and soften water [15]. One alternative for creating membranes with superoleophobicity and influential heavy metal ion adsorption is natural zeolite, a porous aluminosilicate mineral with high hydrophilicity and ion exchange capabilities [16]. Compared to when 4A zeolite is not added, the PSf matrix with 4A zeolite added yields flux, F7RR, RIrr, and RRev [17]. The present work aimed to investigate the impact of surface modification on PVDF membranes by adding Fe2O3/Zeolite via dip-coating. Functional group, hydrophilicity, morphological, and hydrophilicity tests are used to characterize membranes and tested humus acid selectivity and pure water flow of humus acid to assess membrane performance.

2. Methods of research

Distilled water, 70% alcohol, Fe2O3, hollow fiber membrane (PVDF), and zeolite are the materials employed in this study.

We weighed 0.15 grams of PVA and got 100 milliliters of purified water ready. PVA is a substance that dissolves in water, is environmentally friendly, and is frequently used in producing membranes [18]. Next, at a temperature of 120 C and a speed of 200–300 rpm, the ingredients are combined and stirred with a hot plate stirrer until they are homogenous [19]. Added 0.3 grams of Fe2O3 and Zeolite were added to the solution and mixed using a hot plate stirrer for 30 minutes. The solution was sonicated for 30 minutes using an ultrasonicator to obtain a homogeneous Fe2O3/Zeolite suspension [3]. After soaking in the dope solution for five hours, the membrane was allowed to dry at ambient temperature. The steps for membrane preparation are shown in Figure 1. Table 1 displays the composition of the membrane.

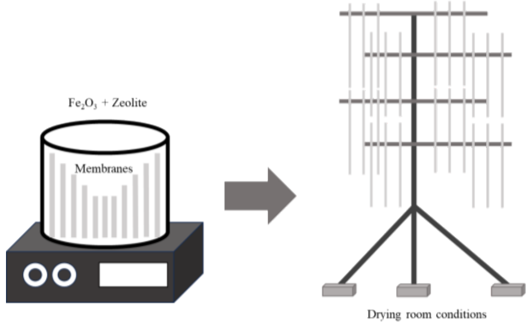

Fig. 1. Procedures for preparing membranes.

Table 1. Fe2O3/Zeolite Composition.

Membrane Type	Membrane Name	Ratio	
		Fe_2O_3	Zeolit
PVDF	P0	0	0
PVDF/ Fe_2O_3-Zeolit	P1	1.0	0.5
PVDF/ Fe_2O_3-Zeolit	P2	0.5	1.0
PVDF/ Fe_2O_3-Zeolit	P3	1.0	1.0

The functional groups of the membrane were tested using an FTIR Spectrophotometer both before and after modification. Attenuated Total Reflection (ATR-FTIR) Thermo Scientific iD5 ATR-Nicolet iS5 Japan is the apparatus's specs. The membrane is dried for a few hours before being placed in the sample holder. Infrared spectra were recorded between 400 and 4000 cm-1 in the wavenumber range.

Test for Contact Angle, The Drop Master 300 from Kyowa Interface Science Co. in Japan, was used to assess the degree of hydrophilicity of the membrane. Data is recorded at least five times for each membrane sample, and the average value is utilized.

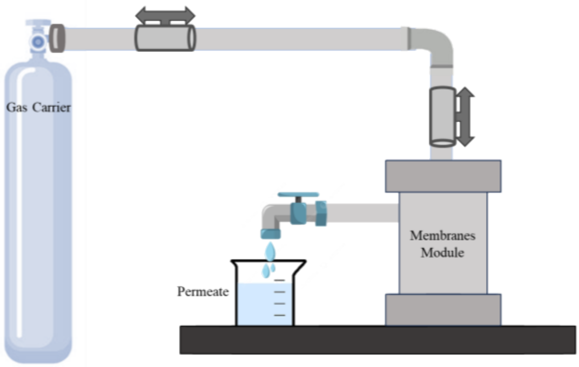

Fig. 2. Tool Kit for Ultrafiltration.

Water and humic acid flux in a performance test experiment to examine the impact of change on membrane performance. The filtration test was employed using a set of ultrafiltration cells at a pressure of 1.5 bar. The experiment used two kinds of bait: humic acid (50 ppm) and pure water (aquadest). With a dead-end ultrafiltration module powered by gas pressure, the amount of feed that flows through the membrane may be detected. In Figure 2, the ultrafiltration apparatus is displayed. A volume of pure water (for measuring the flow of pure water) or humic acid solution (for evaluating the rejection and flux of humic acid) is fed into the ultrafiltration module, which is equipped with a membrane that varies in pressure relief to perform the measurements. Retentate is the solution that remains on the membrane surface, and permeate is the fluid that gets through the membrane. The permeability coefficient (Lp) for pure water, selectivity tests for humic acid samples, and flux (J) for pure water are all determined by the membrane's permeability.

3. Results and discussion

3.1 Membrane Chemical Structure

The results of an FTIR examination show changes in the chemical composition of the PVDF membrane following treatment with Fe2O3/Zeolite. The PVDF membrane combined with Fe2O3/Zeolite and the pure PVDF membrane are very different, as Figure 3 illustrates. The presence of asymmetric C=O, C-C, and C-H groups, which signify the presence of Fe2O3/Zeolite bound to the membrane surface, characterizes this distinction. Because of their strong affinity for water, these two groups make Fe2O3/Zeolite very hydrophilic. It is clear from the FTIR data in Figure 3 that the Fe2O3/Zeolite change in the membrane system was effective.

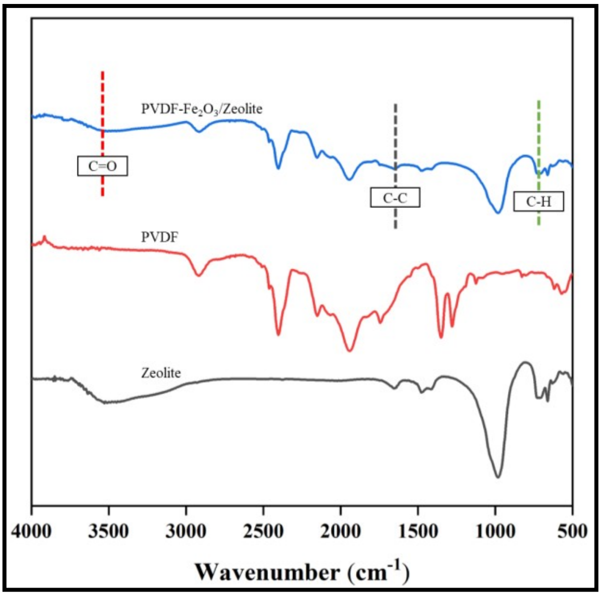

Fig. 3. PVDF Membrane Infrared Spectra with and Without Modification.

3.2 Hydrophilicity of Membranes

Using a contact angle meter to measure the angle of contact between the membrane surface and the water droplets, the hydrophilicity of the membrane was examined. The hydrophilicity of a membrane is positively correlated with its contact angle with water. Figure 4 illustrates how the degree of hydrophilicity of the membrane printing fluid changes when additives are added. Figure 4 shows how adding Fe2O3/Zeolite results in a more hydrophilic PVDF membrane with a reduced contact angle [20].

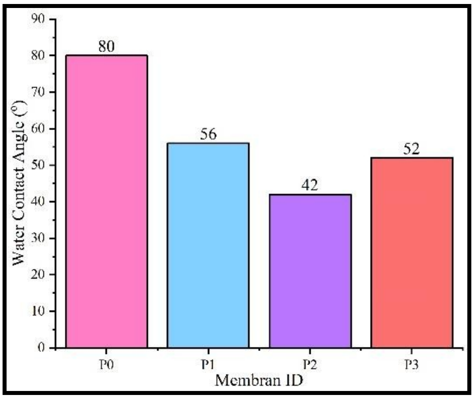

Fig. 4. PVDF membrane contact angle before and after modification.

3.3 Pure Water Flux and Humic Acid Flux

The pure water flow values from pure PVDF and PVDF modified with Fe2O3/Zeolite are displayed in Figure 5. The purified water flux a virgin PVDF membrane (P0) generates is just 9.96 L/m2.h. In the meantime, the pure water flow values generated by the modified membranes (P1, P2, and P3) reached 15.77, 38.16, and 21.98 L/m2.h. Following alteration, the membrane's hydrophilic characteristics and pore size both increased, increasing the membrane's pure water flux value [21].

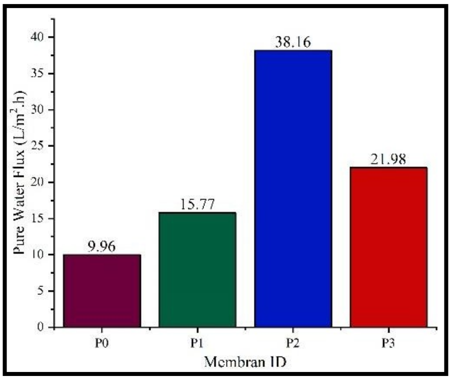

Fig. 5. Pure Water Flux of PVDF membrane before and after modification.

Figure 6 illustrates this same tendency in the flow performance of filtration employing humic acid solution as input. With Fe2O3/Zeolite-modified membranes, the amount of humic acid the membrane can hold increases. The size of the membrane pore increases with an increase in the additive concentration. The P2 membrane yielded the most flux. Figure 7 displays the humus acid selectivity test findings. This graphic also shows how adding the Fe2O3/Zeolite additive influences the humus acid rejection. The selectivity value is generally inversely related to all membranes measured humic acid flow value. This is because of the membrane's pore size. Water may flow through the membrane more quickly due to the larger pore size, increasing the permeate.

Conversely, selectivity will diminish due to more humus acid particles entering the permeate due to the presence of pores, especially those with larger diameters. Because the PVDF membrane's surface is covered in relatively dense, small-sized, and few-numbered holes, it possesses the highest selectivity of any membrane, measuring 89.15%. Pure PVDF's surface properties allow water ions and humus acid particles to flow through, resulting in a meager flux value [22].

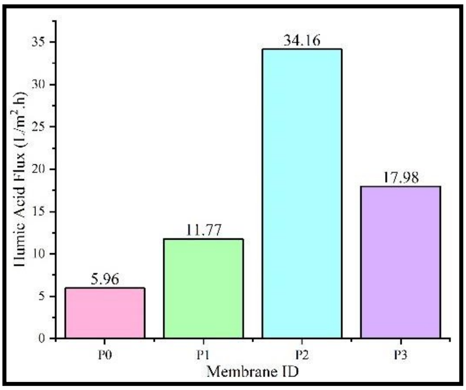

Fig. 6. Humic Acid Flux of PVDF membrane before and after modification.

4. Conclusion

Fe2O3/Zeolite additions improve the hydraulic characteristics and overall performance of PVDF-based membranes. Pure water and humic acid flux increase when Fe2O3/Zeolite is added to the membrane because it increases pore size and hydrophilicity. Based on the overall results, Fe2O3/Zeolite is a suitable additive that may be utilized to improve the properties of PVDF-based membranes, particularly regarding hydrophilicity, which directly affects the membrane's filtration performance.

Acknowledgement

The author would like to thank the Institute for Research and Community Service at Jember University.

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