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Preparation of a Hollow Fiber Membrane Made of Antifouling PVDF/Zeolite using the Dip-Coating Technique

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Abstract. The practical technique for membrane modification is dip coating. This study coats a PVDF hollow fiber membrane-based composite with a zeolite coating. The composite is made of a polyvinylidene fluoride (PVDF) membrane. The separation capabilities and propensities of composite membranes for organic impurities were examined during water filtering. Fourier-transform infrared spectroscopy analysis of the findings demonstrated that the Zeolite coating was successfully deposited on the PVDF membrane. The flux recovery ratio increases from 69% to 80% while the relative flux drop decreases from 63% to 50%. A composite PVDF membrane dip-coating of Zeolite with a GA and H₂SO₄ ratio of 1:2 is needed to remove about 75% of humic compounds from effluent. This study's results show that adding Zeolite with a GA and H₂SO₄ layer can significantly improve the PVDF hollow fiber membrane's hydrophilicity, selectivity, and anti-organic fouling.

Keywords: *fouling, PVDF, dip-coating, membrane performance.*

1. Introduction

The industry has grown exponentially due to rising population growth, creating environmental issues, and driving up demand for clean water [1], [2]. Water supply and waste management shortages are the biggest obstacles to sustainable growth in the 21st century. According to projections, the world's water consumption will rise from 4600 km³/year to 6000 km³/year by 2050, likely generating more wastewater [3]. The membrane bioreactor is a substitute for conventional wastewater purification technology. (MBR). Microfiltration (MF) and ultrafiltration (UF) are two common membrane filtration techniques used in MBR [2][4][5].

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MBR eliminates pathogens, organic matter, and suspended solids, and removal of COD (up to 90%) and TOC (more than 80%) while producing effluent with high effluent and biomass concentration, a minor environmental impact, less reactor volume, and less sludge production [6][7].

Due to its excellent thermal stability, chemical resilience, and membrane-forming capacity, PVDF is a widely used material [8][9][10]. In microfiltration and ultrafiltration, PVDF membranes are frequently employed [11]. On the other hand, the semi-crystalline polymer PVDF has repetitive units of -CH₂-CF₂, which can produce hydrophobic structures that make the membrane more prone to fouling [8][11]. Hydrophobic species in fluids cause blockage, which lowers membrane permeability. A buildup of activated sludge can also shorten the lifespan of the membrane and increase running costs [8][12]. Blockages may be both reversible and permanent [5][13]. Reversible fouling is caused by contaminants that adhere to the membrane's surface, but persistent fouling is brought on by pollutants that securely attach to the membrane's pores [14]. Therefore, more effective antifouling membranes for MBR applications must be developed, and changes must be made with the addition of hydrophilic component enhancements [11][12].

The membrane modification method aims to engineer the membrane's surface to make it more hydrophilic, increasing the hydrophilicity, antibacterial properties, and performance of the membrane and producing more effective wastewater treatment results [15][16]. A few modification techniques include coating, grafting, covalent coupling, irradiation, plasma treatment, coating adsorption, and coating [16]. The coating approach, which has a straightforward procedure and is less expensive, is the most adaptable method [15]. The substrate surface is coated with a coating solution (liquid phase) using the dip-coating technique, which is then applied to another surface and dried [17]. The dip-coating method allowed the PVDF surface to have a maximum permeate flow and hydrophilic qualities. The dip-coating method is easy to use, has high efficiency for industrial applications, and does not require special conditions (high pressure and temperature) [15][18]. In some earlier studies, coating techniques employing polydopamine (PDA), titanium dioxide and silver nanoparticles (TiO₂-NP and Ag-NP), thin-film nanofibrous composite-cellulose nanofiber (TFNC-CNF), and other materials were also employed [8][16][19]. One of the most well-liked and effective methods is the inclusion of inorganic nano- and micro-particles, such as Al₂O₃, SiO₂, and several compounds with polar groups [15][9][20][21].

Aluminum (AI), silica (Si), and oxygen are the molecular constituents of zeolite, an inorganic crystal. (O). It enhances the surface area for the development of biofilms and has high adsorption and ion exchange capacities, as well as the capacity to filter molecules and recycle waste [26][27]. Zeolites have many commercial applications, including separating linear from non-linear hydrocarbons, decreasing excess ammonium, gas adsorption, removing heavy metals, and softening water [28]. The material of choice for membranes with superior properties. The oleophobicity and heavy metal ion adsorption capabilities of natural zeolite, a porous aluminosilicate mineral with exceptional ion exchange capabilities [21]. The FRR, RIrr, and RRev flows were produced in the PSf matrix at rates of 8.4 L/m²h, 40%, 84%, and 2 L/m²h, 41%, 78%, and 19.5%, respectively [29]. Vatanpour et al. (2016) found that adding SAPO-34 to the PVDF membrane resulted in fluxes known as RRev (47 kg/m²h, 66.4%, 24.98%, and 7) and fluxes known as FRR, RIrr, and RRev (63.5 kg/m²h, 89.4%, 7%, and 19%) [30].

The surface of the PVDF hollow fiber membrane will be altered using a dip-coating of Zeolite in this research. In addition, analyses of the membrane's performance (flux and antifouling) and tests on the quality of the treated water were performed. The modified membrane is then applied to industrial and municipal wastewater treatment systems.

2. Materials and Methods

2.1 Materials

Materials used in this research included distilled water, 70% alcohol, glutaraldehyde (GA), 98% H₂SO₄, hollow fiber membrane (PVDF), poly (vinyl alcohol) (PVA), and zeolite. The tools used in this research included stir bars, glass funnels, beaker glasses, measuring cups, glassware, volumetric flasks, digital balances, ovens, glass plates, tongs, tweezers, pipettes, spatulas, and ultrasonicators ROHS-CSBJZQFS-150N0001V2.

2.2 Solvent Preparation for Coatings

One hundred milliliters of distilled water were prepared with 0.15 g of PVA. When homogeneous, the components were combined and stirred with a hot plate stirrer at 200 to 300 rpm [31][32]. The mixture was then stirred for 30 minutes using a hot plate stirrer before Zeolite was added to it in four amounts (0.1, 0.2, 0.3, and 0.4 g). Then the solution was ultrasonicated for 30 minutes to produce a consistent Zeolite dispersion [8]. The membranes were immersed in the dope solution for 5 hours and then desiccated at room temperature.

2.3 Crosslinking Solutions Creation

Use 0.5 g of GA, 100 ml of distilled water, and 5% prepared H₂SO₄ for each component. Once homogeneous, the mixture is stirred and mixed once more. To catalyze the reaction, H₂SO₄ is introduced in the f[33]. The cross-linking solution was made by mixing GA and H₂SO₄ according to the proportions. (1:1; 1:2; and 2:1). The desiccated membrane was immersed in the crosslinking solution for two minutes. The membrane was placed on a glass plate and dried in a 45 °C oven for two hours. Crosslinking solutions aim to maintain PVA's stability in the aqueous phase by incorporating elements that may reduce PVA's solubility in water (like GA) and increase the tensile strength of thin film composites [34].

2.4 Performance of Membranes

Flux Recovery Ratio (FRR) analysis:

$$FRR = \frac{Jr}{Jw} \times 100\%$$

Where (Jr) is water flux following a fouling test and (Jw) is pure water flux [25]. The FRR calculation aims to determine the membrane's antifouling capacity [29].

Analysis of Fouling Resistance:

$$R_{Rev} = \frac{(Jp - Jr)}{Jw} \times 100\%$$

Fouling resistance analysis was done by computing the total R, RRev, and RIrr. The reversible blockage fraction (RRev) is obtained from the following equation [30][32]. The irreversible blockage fraction (R_{Irr}), however, employs the following formula:

$$R_{Irr} = \frac{(Jw - Jr)}{Iw} \times 100\%$$

The level of total flow loss due to obstruction (RTtotal) can be computed using the following equation:

$$R_t = \frac{(Jw - Jp)}{Jw} \times 100\%$$

3. Result and Discussion

3.1. FTIR analysis

Analysis of chemical properties and identification of functional groups was carried out by the FTIR test shown in Figure 1. The composite membrane showed several additional peaks compared to the PVDF membrane. In the range of 2000-3000 cm⁻¹, asymmetric C=O and CH₂ functional groups were formed, indicating the presence of Zeolite attached to the surface of the membrane. The range of 1100-1200 cm⁻¹ indicates the presence of sulfonate groups in the composite membrane, while the peak of 1280 cm⁻¹ indicates the presence of PVDF material. The IR spectrum of the composite membrane showed that zeolites were successfully coated on the surface of the PVDF membrane. In addition, the results also show that through the dipcoating method, a composite UF membrane can be produced [8].

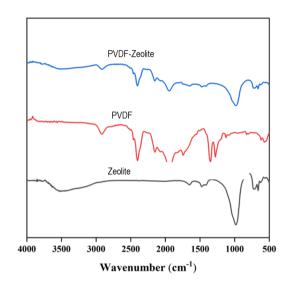


Figure 1. FTIR spectrum of composite PVDF membrane

3.2. Membrane performance

Composite membranes are applied in industrial wastewater filtration to assess separation characteristics and the presence of organic impurities. Figure 3 shows that the decrease in humic compound amounts is associated with reduced absorbance value. Composite membranes can achieve a lower absorbance of up to \sim 75%. Based on this, it can be stated that the composite membrane can remove around \sim 75% of humic compounds contained in wastewater. The ability of the composite membrane to purify wastewater can also be seen in. The removal of humic compounds increased dramatically in composite membranes with a ratio of GA and H_2SO_4 (1:2) compared to membranes without modification. Likewise, the composite

membrane with a GA and H₂SO₄ (2:1) ratio can remove almost the same humic compounds as in Figure 3. These findings indicate that the combination of Zeolite can produce better permeability and selectivity.

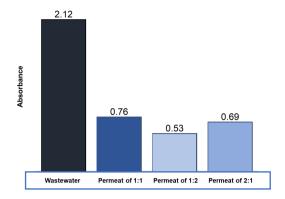


Figure 3. Performance of Composite Membranes for Wastewater Filtration at a Wavelength of 254 nm,
Wastewater Absorption, and Permeate Ultrafiltration

Figure 4 shows the blocking parameters of the PVDF membrane that has been coated with Zeolite with crosslinker ratios in the form of GA and H₂SO₄ of 1:1, 1:2, and 2:1. PVDF membrane that has been coated with Zeolite with a ratio of 1:2 has a higher FRR value compared to 1:1 and 2:1. However, membranes with a 1:2 ratio have lower clogging parameters (RFR, Rir, Rr, and Rt) than 1:1 and 2:1. Foulant on the surface of the PVDF membrane with 1:2 ratio of GA and H₂SO₄ is easier to remove because the adhesion of organic matter is lower than that of 1:1 and 2:1 ratios. The hydrophilic membrane surface allows interaction between the membrane surface and less foulant. Therefore, adding hydrophilic Zeolite can increase the anti-organic fouling on PVDF membranes that have been modified using the dip-coating method with a 1:2 ratio of GA and H₂SO₄.

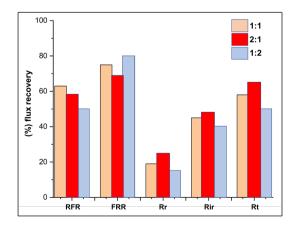


Figure 4. Blockage Parameters

4. Conclusions

Based on the research that has been done, the tendency of clogging by organic substances on the surface of the composite PVDF membrane is reduced. FTIR analysis results prove that the dip-coating method was successfully used to coat the surface of the PVDF membrane with Zeolite. In addition, the modified membrane using the Zeolite dip-coating method with a 1:2 ratio of GA and H₂SO₄ was able to remove humic compounds in wastewater by about 75%.

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