



Membrane Fabrication And Application For Removal Of Pollutant From Wastewater

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Abstract: Dye contamination of wastewater has become one of the most critical environmental problems these days and can have adverse impacts on human health if discharged without any treatment. There are various techniques for the removal of dyes from wastewater such as adsorption, oxidation process, photocatalyst, biological decolorization, membrane separation technology, etc. In the present work, we have fabricated a polyvinylidene fluoride (PVDF) and membrane was modified by dispersing nano-sized titanium (IV) oxide (TiO_2) particles in a PVDF solution. PVDF flat-sheet composite membranes were synthesized using a phase inversion method. Polyester Nonwoven fabric was used as the support layer. Membranes fabricated with support had good mechanical, thermal strength than membrane fabricated without support. We have applied the synthesized PVDF flat sheet composite membrane for the removal of Acid Blue 113 dye of concentration 100 mg/L from wastewater. PVDF/ TiO_2 / non-woven polyester support membrane, PVDF/ polyester support membrane and pure PVDF membrane showed the 67.64%, 48.34% and 32.25% of Acid blue 113 dye removal, respectively. Experimental results indicated that the dye removal was found to increase with increasing the TiO_2 concentration in membrane matrix. PVDF/ TiO_2 /polyester non-woven support membrane showed the maximum Acid Blue 113 dye removal than pure PVDF membrane and it has a significant potential for the treatment of dye bearing wastewater.

Keywords: Acid Blue 113; Dye removal; Membrane technology; Wastewater treatment; PVDF

1. INTRODUCTION

Freshwater is an important resource for the survival of life on earth and also essential feed in many key industrial operations. The planet of earth is covered by 70% of water but fresh water constitutes only 3% of the global water and two third of that water is not available for use. Due to the limited access to freshwater, clean water is essential for life as well as economic and industrial development. The world's clean water demand has grown exponentially in recent years as a result of population rise and exponential industrialization in many countries (Mamah et al, 2021). Different techniques are applied to treat wastewater for maintaining standards of effluent treatment. Three strategies of wastewater treatment can be categorized as: (i) Primary treatment for settling inorganic and organic materials, (ii) secondary treatment for suspended particles, residual and dissolved organic and inorganic matter, and (iii) tertiary treatment to attain a final maximum allowed of discharge parameters. Ultrafiltration has aroused as an efficacious direction for utilization in the field of sewage disposal owing to its outstanding capability in the elimination of viruses, granules, and protein (Shinde et al, 2021).

Membrane technologies have received significant attention in recent years. Membrane performance has been improved by various studies. Commercial water and wastewater treatment membranes still suffer fouling of membranes, as caused by the deposition of dissolved or suspended particles on the surface of membrane. Many researchers have reported a variety of techniques to preventing membrane fouling, and as a result, membrane fouling control strategies have advanced significantly. However, conventional approaches to the control offouling of membrane still have limitations, including higher energy consumption, preventing wide application of membrane technology in water environments (Won et al, 2012). Membranes offer an important role in membrane-based water treatment processes, determining the technological and economic efficiency of the technologies described. Membrane improvement can have a significant impact on existing technology performance. The material and pore size of membranes are determined by the application for which membranes will be utilized (Lalia et al, 2013).

Popular polymeric materials are polysulfone (PSF), polyether sulfone (PES), polypropylene (PP), polyvinylidene fluoride (PVDF), polyimide (PI), and polytetrafluoroethylene (PTFE). The growth in the number of publications related to PVDF in wastewater treatment. PVDF is a desired choice in membrane development and its preference is derived from its availability, ease of modification, chemical stability, high mechanical strength, surface charge, and wide range operating temperature and pH. PVDF has been popularly used as a suitable material in wastewater treatment membrane. PVDF (polyvinylidene fluoride) is a popular organic polymer material used in ultrafiltration (UF), microfiltration (MF), and pervaporation (PV). Because it has great thermal stability and chemical resistance to strong reagents such as organic solvents, acids, and bases, it is used in membrane production procedures (Oh et al, 2009).

The development of new membrane materials has gained remarkable the interest of both academics and industry, with the goal of improving membrane performance and/or increasing membrane resistance to various foulants. Different methods, and modifications have been investigated over the years to produce antifouling membranes with enhanced flux and rejection properties. The introduced nanoparticles to polymer membranes might be silica, Al_2O_3 , Fe_3O_4 , ZnO , ZrO_2 , TiO_2 , CdS , carbon nanotubes (CNTs), metal organic frame works (MOFs), nano- silica (SiO_2) and zeolites. Among different metal oxide nanoparticles, TiO_2 had received the most attention because of its stability, availability. TiO_2 are mostly used as a photocatalyst in water and wastewater treatment. When TiO_2 mixed to PVDF membrane, TiO_2 nanoparticles not only enhance the hydrophilicity of PVDF membranes to increasing the flux but kill bacteria the fouling problem of PVDF membrane (Alkhouzaam and Qiblawey, 2021, Cao et al, 2006). There are several ways to prepare porous polymeric films, such as sintering, stretching, track etching and phase separation process the method of fabrication of membrane dependent on the type of polymer used and the solvent used to dissolve the polymer. The majority of membranes are prepared by phase inversion method (Witte et al, 1996).

One of the greatest difficulties as faced by Environmental Engineers today is the pollution of the dye in the industrial effluents. A large amount of colored wastewater is discharged into the river through factories such as textiles, paper and cosmetics. Dyes present in the water can cause very serious health problems, which can burn the eyes, stimulate the stomach and cause symptoms of allergy (Mahmoudian and Kochameshki, 2021, Xu et al, 2014). Dye pollutants have aroused widespread concern due to their serious toxicity to aquatic organisms and human beings. The cationic dye methylene blue (MB), Crystal violet (CV) or methyl violet 10B is a basic dye its consider as carcinogenic, causes severe eye irritation while commonly used in industrial applications such as textiles, pharmaceutical products, and aquaculture, has adverse environmental effects. It is due to this imperative to treat wastewater containing MB dye intermediates before discharging it into the environment (Mansora et al, 2020, Zhang et al, 2020, Zeng et al, 2017). Several studies have presented methods to remove dyes from wastewater, including catalysis, biological processes, ozonation, adsorption, and membrane technology. Membrane-based technology for removing dyes from wastewater has received considerable attention nowadays because of its less processing cost, high effectiveness, and less environmental impact (Pervez et al, 2020, Seyed et al, 2020).

2. MATERIALS AND METHODOLOGY

2.1. Materials

Polyvinylidene fluoride (PVDF) a polymer raw material, Dimethylformamide (DMF) a solvent and Polyethylene glycol (PEG-200), binding and dispersing agent were purchased from Modern Science Apparatus Pvt. Ltd; Nashik. Polyester non-woven support (NWPET) was purchased from SVNIT Surat 395007 (Gujarat) which is used as a support to the membrane to enhance the mechanical and thermal strength of PVDF membrane.

2.2. Membrane Preparation

2.2.1. Membrane Preparation Without support

PVDF and TiO_2 were dried at $100^\circ C$ for 24 h to eliminate the absorbed water molecules. The dope solution was prepared by dissolving different wt% of dried PVDF, TiO_2 , PEG dispersed in solvent DMF. The dope solution compositions used in membrane preparation are listed in Table 1. The polymer dope mixture was subjected to continuous stirring in orbital shaker at $60^\circ C$ until it was homogeneous after that it was kept for 24 h to release air bubbles. The degassed dope solution was cast on a clean glass plate. After 24 h of immersion, the membranes were removed from the water. The membrane was dried in the air

at room temperature until a dry flat-sheet composite membrane was obtained. Overall process of membrane fabrication is depicted in Figure 1.

Table 1: Compositions of Dope Solution for Composite Membrane Preparation

MEMBRANE CODE	PVDF	DMF	TiO ₂	PEG
M1	1.5 gm	8.5 gm	–	–
M2	1.5 gm	8.5 gm	0.1 gm	–
M3	1.9 gm	7.6 gm	–	0.5 gm
M4	1.9 gm	7.5 gm	0.1 gm	0.5 gm

2.2.2. Membrane Preparation With polyester non-woven support

The dope solution compositions used in membrane preparation are listed in Table 2. The casting solution was casted on a polyester non-woven fabric used as support. Glass plate containing film with support dipped into the coagulation bath for precipitation. After 24 h of immersion, the membranes were removed from the water. The membrane was dried in the air at room temperature until a dry flat-sheet composite membrane was obtained.

Table 2: Compositions of Dope Solution for Composite Membrane Preparation With Support

MEMBRANE CODE	PVDF	DMF	TiO ₂	PEG
M5	1.9 gm	7.6 gm	–	0.5 gm
M6	1.9 gm	7.59 gm	0.01 gm	0.5 gm
M7	1.9 gm	7.5 gm	0.1 gm	0.5 gm
M8	1.9 gm	7.45 gm	0.15 gm	0.5 gm

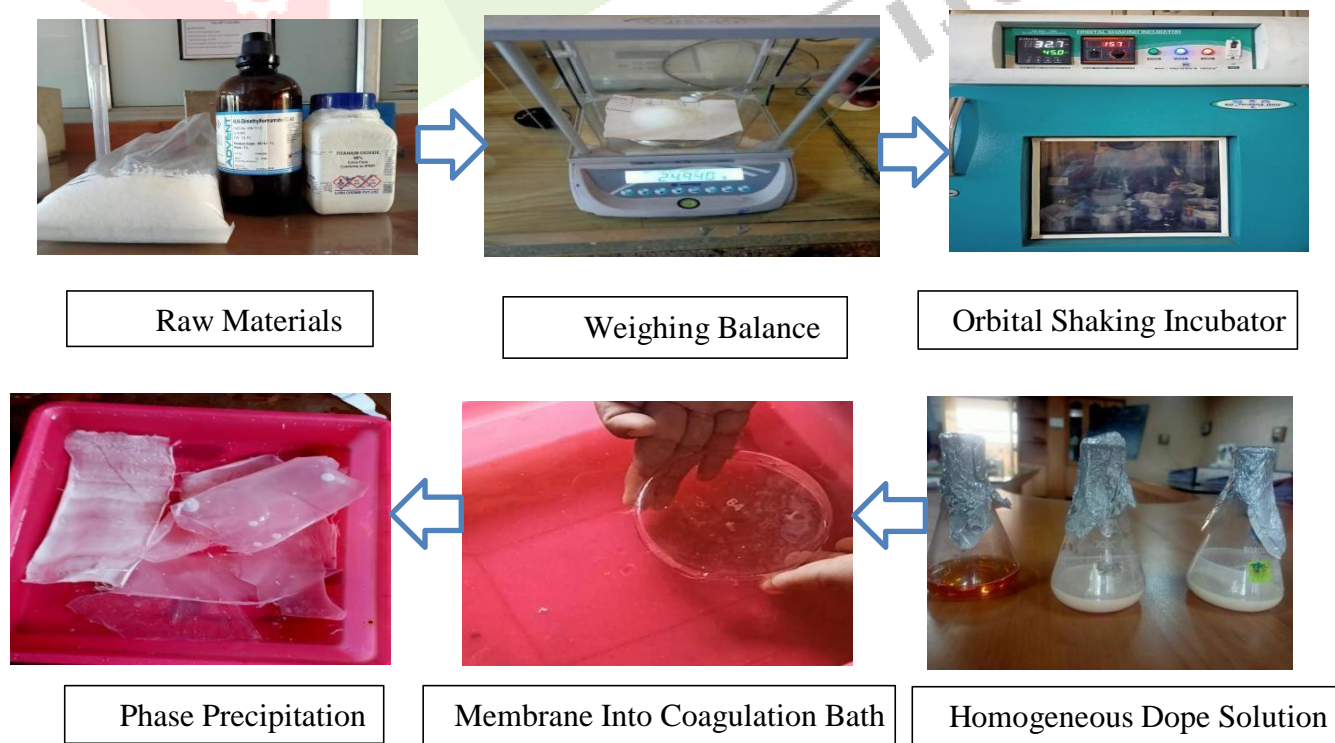


Figure 1: Overall Process of Membrane Fabrication

2.3. Acid Blue 113 dye removal experiment

Membrane performance was tested using Acid Blue 113 dye as a pollutant. Dead end filtration process was applied for tested membrane performance. Firstly, dye wastewater was prepared with a feed concentration of 100 mg/L by dissolving Acid Blue 113 dye into DI water in a 1000 mL volumetric flask. The membrane samples were cut with effective membrane area was 20 cm² (5cm×4 cm). Then Membrane was fixed into booster funnel such that membrane should cover all the holes of the booster funnel after that the booster funnel was inserted into the mouth of the booster flask then turned on the vacuum pump which create pressure gradient between booster flask and booster funnel. Immediately the dye feed solution of 100 mg/L concentration was poured into booster funnel and constant flow rate of dye Acid blue 113 was maintained, which has allowed the sample to draw completely through the membrane and collect into vacuum flask. Spectrum of Acid Blue 113 dye was established using UV-visible spectrophotometer (UV1800, Shimadzu Japan). Maximum wavelength of UV absorption, λ_{max} of dye was found as 566 nm. Initially calibration chart was prepared based on the analysis of dye solutions of unknown concentrations. The quantification of dye in the residual solutions was performed using UV- visible spectrophotometer.

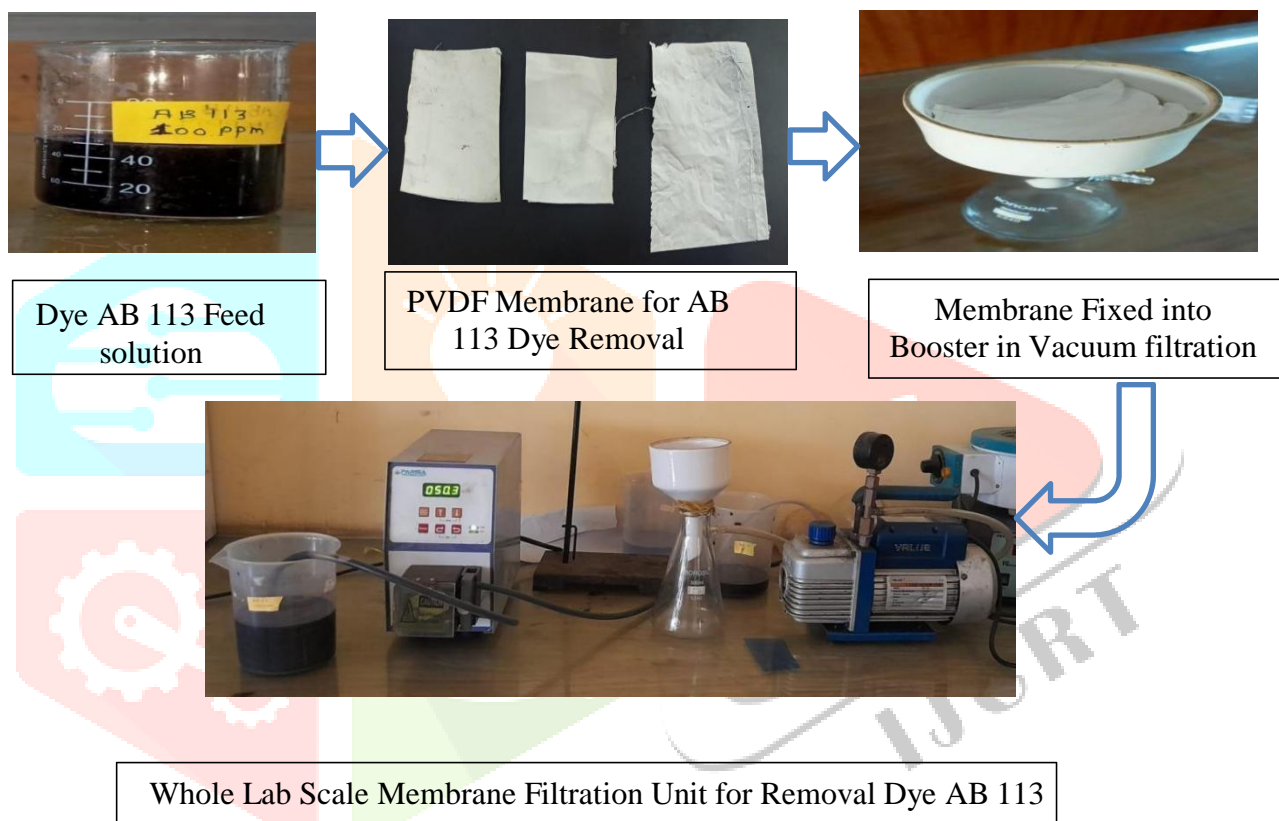


Figure 2: Overall Membrane Filtration Unit for Dye Acid Blue (AB)113

3. RESULT AND DISCUSSION

3.1. The Effect of additional TiO₂ nanomaterial into membrane matrix

PVDF/TiO₂ composite flat sheet membranes were prepared via phase inversion method by mixing different amounts of the TiO₂ nanoparticles in PVDF casting solution. The hydrophilicity of composite PVDF/TiO₂ membranes were diverse by addition of different quantities of TiO₂. The addition of TiO₂ also improves the permeability of membrane. Membranes (M5, M6, M7, M8) had good mechanical strength. The rate of AB 113 removal was higher for TiO₂ entrapped membrane as compared to neat PVDF membrane. The experimental result indicated that the membrane surface can be modified by adding TiO₂ nanoparticles, PVDF membrane surface was changed from hydrophobic to hydrophilic after TiO₂ addition.

3.2. Membrane Failure

Membranes (M1, M2, M3, M4) that we had fabricated without polyester non-woven support by the process of phase inversion as shown in Fig 3., these membranes did not have good mechanical, thermal strength and antifouling

property also did not have pressure sustainability capacity so that these are not applicable to apply directly for application purpose of wastewater treatment.



Figure 3: Membranes After Drying

3.3. Effect of polyester non woven support on membrane strength

Membranes (M1, M2, M3, M4) that we had fabricated without polyester non woven support by the process of phase inversion the membranes did not have good mechanical, thermal strength. also did not have pressure sustainability capacity so that its did not applicable to apply directly for application purpose after getting this failure then we have fabricated membranes (M5, M6, M7, M8) on polyester non woven support. Experimental result indicated that membranes (M5, M6, M7, M8) fabricated with support had high mechanical, thermal strength and showed good AB 113 dye removal than membrane fabricated without non woven Polyester support.

3.4. Acid Blue 113 dye removal results

We had fabricated PVDF flat sheet composite Membranes and performance was tested using Acid Blue 113. In order to investigate the effect of dye concentration of feed solution on separation performance of membrane. Membrane were tested by lab scale filtration setup. Dead end filtration process applied for Acid Blue 113 dye removal in this process flow of feed dye solution is perpendicular to the membrane surface. We had applied the synthesized PVDF flat sheet composite membrane for the removal of Acid Blue 113 dye of concentration of 100 ppm. PVDF / TiO₂ / non woven polyester support membrane, PVDF / polyester support membrane and Pure PVDF membrane showed the 67.64%, 48.34% and 32.25% of Acid blue 113 dye removal respectively. Experimental result that indicated the dye removal increased with increasing the TiO₂ concentration in membrane matrix. Membrane PVDF/TiO₂/polyester non woven support membrane that showed the maximum Acid Blue 113 dye removal than pure PVDF membrane as shown in Figure 4.



Figure 4: Experimental Image of Dye AB 113 After Removal

4. CONCLUSIONS

In the present work, we have fabricated flat sheet membrane from polyvinylidene fluoride (PVDF) polymeric material which has high chemical stability and high mechanical strength. Membrane was modified by dissolving nano-sized titanium (IV) oxide (TiO₂) particles in a PVDF solution. PVDF flat-sheet composite membranes were fabricated by a phase inversion method. Membranes (M5, M6, M7, M8) fabricated with support had good mechanical and thermal strength than

membrane fabricated without support. We have applied the synthesized PVDF flat sheet composite membrane for the removal of Acid Blue 113 dye of concentration of 100 mg/L. PVDF / TiO₂ / non-woven polyester support membrane, PVDF /polyester support membrane and Pure PVDF membrane showed the 67.64%, 48.34% and 32.25% of Acid blue113 dye removal respectively. The experimental results indicates that the membrane surface can be modified by adding TiO₂ nanoparticles into membrane matrix by changing the membrane surface from hydrophobic to hydrophilic after TiO₂ addition and this flat sheet composite membrane could have great potential for Acid blue 113 dye removal from the waste water.

5. ACKNOWLEDGEMENT

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