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Research Article

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Surface Modification of TiO_2@Pvc Composite Membrane for Textiledye House (Brome Phenol Blue) Filtration

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Abstract

The continued increase in the costs of chemicals, energy and water makes their recovery more important today than it was years ago when separation techniques by membrane filtration were first introduced to the textile industry. The aim of introducing membrane filtration is not only to reduce water consumption and wastewater streams. The paper describes the results of research works and implementation project concerning cleaner technology and water reuse in textile dye house by TiO_2@PVC composite membrane. Fabricated membranes were characterized with various analytical and experimental techniques. Results showed that the TiO_2 blend TiO_2@PVC composite membrane were nano porous in nature with improved porosity and permeability. Addition of TiO_2 improved the mechanical stability and water permeability of the composite membranes.TiO_2 doped membrane showed better dye rejection behavior with a permeate flux. Size and charge based exclusions along with adsorption were identified as the separating principles. Fouling analysis clearly showed that TiO_2 incorporated membranes possessed better antifouling effect than membrane without TiO_2.Thus the TiO_2 blended TiO_2@PVC composite membrane are promising for the treatment of dye polluted wastewater.

Keywords: Filtration, Membrane, Composites, Nanoparticles, Wastewater, Pollution

Introduction

Membrane filtration as a means of purification or concentration relies on the principle that when a liquid is passed across or through a physical barrier, particles whose size is larger than the pores in the membrane are retained on one side of the barrier, while the remaining liquid is allowed to pass through [1]. This principle holds true for coarse filters, such as metal sieves, as well as much finer materials which are capable of selective filtration and concentration of molecules of different sizes [2].

Over the past 15 years membrane filtration, which uses a polymer or similar material with an extremely small pore size, has become increasingly popular in industrial processes where reliable and repeatable purification or concentration are required [3]. The technology is now being applied widely in dye manufacturing and textile coloring [4]. This article sets out to explain how membrane filtration works and where it can be used successfully in the dye industry.

Ultrafiltration (UF), a separation technique characteristically placed between microfiltration (MF) and nanofiltration (NF), has received growing attention in the field of dye effluent treatment. MF has restricted applications since MF membranes with large pore sizes in the 0.1–10 μm range fail to remove dye molecules with molecular weights ranging from a few hundred to over a thousand Daltons, whereas NF rejects effectively most dyes but faces a large energy requirement and serious membrane fouling issues [5,6]. UF can combine the advantages from both MF and NF to give satisfactory efficiency with much less energy consumption and is hence widely utilized for separating dyes [7].

Filters of any type serve two purposes. They retain some material and allow the remainder to flow through to the next stage in a process. When making a cup of tea using tea leaves, the strainer collects the leaves (known as the retentate or concentrate) and allows the liquid which has been flavored and colored by the leaves (the permeate or filtrate) to flow through [8]. Sometimes, as is the case when making tea, the retentate is an unwanted waste material and the permeate is the product of value. However, other applications rely on the efficient collection of the retentate. When panning for gold the prospector obviously wants to keep the small particles of metal but has no interest in the permeate water [9, 10].

The present work was aimed at fulfilling this gap in the literature by exploring the separation behaviors of dye mixtures across a TiO_2@PVC composite membrane. Herein, four representative dyes with different charges were used for various binary dye solutions, including brome phenol blue. The membrane filtration performance for the dye feed solutions was investigated. The dye separation

mechanisms were proposed. Multi-cycle operation was performed to validate the reusability of the membrane.

Experimental and Materials

Membrane Synthesis

Non-solvent induced phase separation (NIPS) method was used to make membranes. Polymer dope solution was prepared by dissolving PVC in DMAc. Concentration of PVC was kept at 12% (by wt.) The value of concentration of PVC are chosen in such a way (based on the literature survey) that the prepared membrane are porous and their application lies in the ultrafiltration range. The casting solution was kept at 70C, and magnetically stirred for 24 h to ensure homogeneity. Then, the solution was allowed to degas at room temperature overnight without stirring. Finally, the membrane was casted on the non-woven sheet using Automatic film applicator (Make: Sheen Instruments). The wet thickness was maintained up to 150 mm while casting. The casted membrane was immediately immersed into DI water bath (that act as non-solvent coagulation bath) for phase inversion, and kept under water for at least 24 h to ensure the removal of traces of solvent present in the membrane. Then, the membrane was dried at room temperature. All membranes were kept in DI water for few hours before use. TiO_2/PVC blend membrane were prepared by dispersing 0.5% ,1% , 1.5% and 2% TiO_2 nanoparticle composites in the solvent (DMAc), followed by addition of 12% PVC (all the percentages are on w/w basis). The optimized composition of the casting solution was selected based on the literature surveyed. The preparation of casting solution and membrane casting by phase inversion was done according to the aforementioned method.

Membrane Module TiO_2@PVC Composite Membrane and Experimental Procedure

The schematic of TiO_2@PVC composite membrane was used in the experiments is shown in Figure 1. For all experiments, we operated at constant Cross Flow Velocity (CFV = 4 m/s). The permeate was not recycled in the feed tank [11].

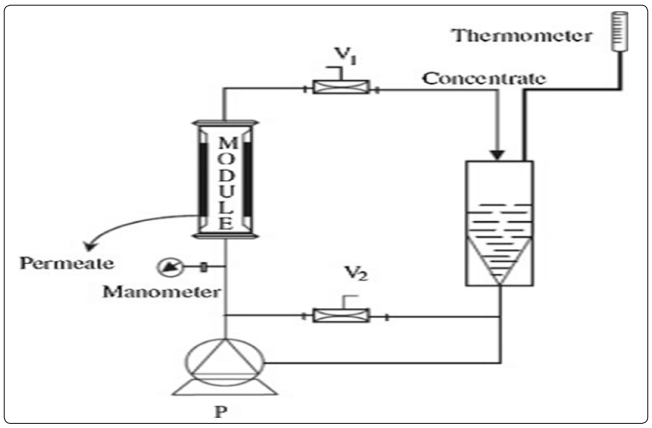

Figure 1: The schematic of TiO_2@PVC composite membrane

A membrane TiO_2@PVC composite membrane flat sheet was used to filter the colored solutions. The specifications of the membrane are given in Table 1.

Table 1: Ceramic membrane specifications

Membrane	**T170-50n TZ**
Type	Tubular
Active layer	TiO_2@PVC composite membrane
Nominal pore size	70 nm
Membrane	T170-50n TZ
Deionized water permeability	
Effective filtration area	50 cm^2
Maximum operating temperature	95 °C
Maximum operating pressure	10 bar
pH range	0–14

Experiments were carried out under three different temperatures (20, 30, and 40 °C) in order to observe membrane performances at each temperature. The process performances were studied in terms of both, permeate flux and permeate quality.

After each MF run, the membrane was subjected to a cleaning cycle which included in the first place a rinse with deionized water at 25 °C (15 min). Next, an alkaline cleaning with aqueous NaOH solution (pH 13) at 60 °C (1 h) took place.

Finally, the membrane was rinsed with deionized water until neutrality. The cleaning procedure after runs with the feed concentration included an additional step since alkaline cleaning was not enough to recover the initial permeability. It consisted of an acid cleaning step with the aqueous citric acid solution (pH 2) at 40 °C (1 h), followed by rinsing with deionized water until neutrality was reached.

All the cleaning steps, including rinses, were conducted at a CFV of 3 m/s and no pressure was applied. Once the membrane was cleaned, the water permeability was checked. The mentioned cleaning process allowed initial flux recoveries higher than 90%.

The permeate flux is calculated according to Eq. (1)

(1)Jp=VAt[12]

Where Jp is the permeate flux (L/m2h), V is the permeate volume (L), A is the effective membrane area (m2) and t is the sampling time (h). At the same time, permeate samples were collected for water quality analysis. The rejection coefficient (R) is calculated as a percentage according to Eq. (2)

(2)R%=1-CpCf×100

where Cf is the concentration in the feed stream and Cp is the concentration in the permeate stream[13].

The volume reduction factor (VRF) is equal to the initial feed volume divided by the retentate volume:

(3)VRF=VfVr[14]

Darcy's law is commonly used to determine filtration resistance in permeate transport through porous membranes according to Eq. (3)

(4)Jp=ΔPμRt

where Jp is the permeate flux (L h−1 m−2), ΔP is the transmembrane pressure (Pa); μ is the dynamic viscosity of the feed (Pa s) and Rt is the total filtration resistance (m−1)[15].

Resistances in series models of fouling often subdivide the total membrane resistance Rt into three components, namely intrinsic membrane resistance Rm, external (concentration polarization) resistance Rcp; and internal resistance Rf, due to fouling.

Characterization of TiO_2@Pvc Composite Membrane

The characterization methods of chemical composition, crystalline phase composition (XRD) and Thermo-gravimetric analysis (TGA/DTG) were already explained in a previous work. The surface morphology, the presence of possible defects and the pore structure of the sintered MF membranes were analyzed by Scanning Electron Microscopy (SEM) (Hitachi, S-4500). The apparent porosity, water adsorption and apparent density were measured in accordance with ASTM C373-88 method using distilled water as an immersion medium.

Results and Discussion

Microstructure

The micrographs of MF membranes prepared with (0-20 wt.%) of corn starch are shown in Fig. 4a–e, the micrographs indicate that the effect of corn starch content on the microstructure of MF membranes is very remarkable. The addition of starch by more than 10 wt.% produced MF membranes with more and bigger pores which lead to more porous structure. An increasing of the connectivity between pores can be seen as dark areas in the image (Fig. 4).

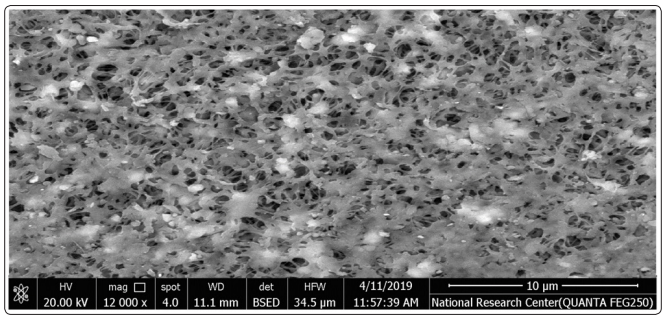

Figure 2

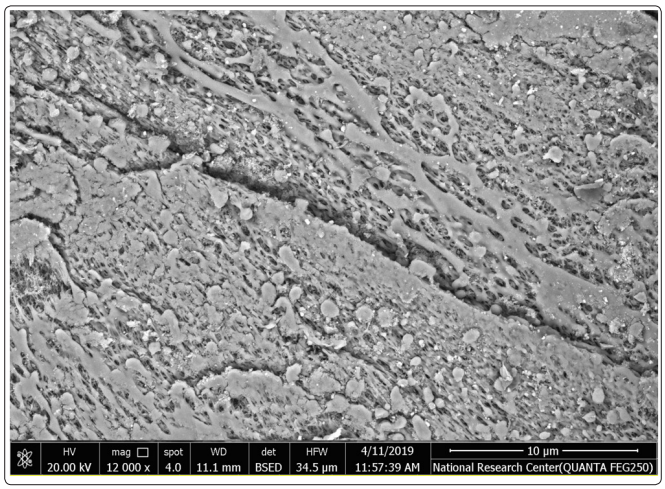

Figure 3

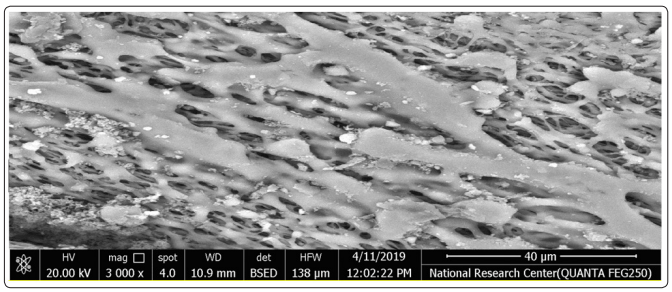

Figure 4: SEM images of MF membranes elaborated with: (a) PVC; (b) 15 wt. %/TiO_2/PVC; (c) composite membrane with dye

Scanning electron microscopy (SEM) was applied to investigate the surface and cross sectional morphology of the prepared membranes using VEGA\\TESCAN SEM, Czech Republic. For cross-sectional images. The membranes were fractured in liquid nitrogen. The samples were coated with gold before SEM analysis. In addition since SEM device was equipped with dispersive X-ray analysis (EDAX) detector, this analysis was used to inspect dispersion ofnano-TiO_2 particles inthecrosssectionofthefabricated membranes.

FTIR of Prepared Compounds

Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is a vibrational spectroscopy that records absorptions of IR light by chemical bonds in all molecules including polymers. Since different bonds absorb IR light at different wavelengths, FTIR spectroscopy is often referred to as fingerprint spectroscopy. As a consequence pure compounds have characteristic and unique FTIR spectra. Scanning was carried out from 4000 cm^{-1} (2.5 pm) to 500 cm^{-1} (20 pm) to confirm the formation of the graft copolymerization with FTIR-spectrophotometer (Shimadzu-IRTracer-100, Japan) at the Chemistry Department, Al-Mustansiryah University, Iraq.

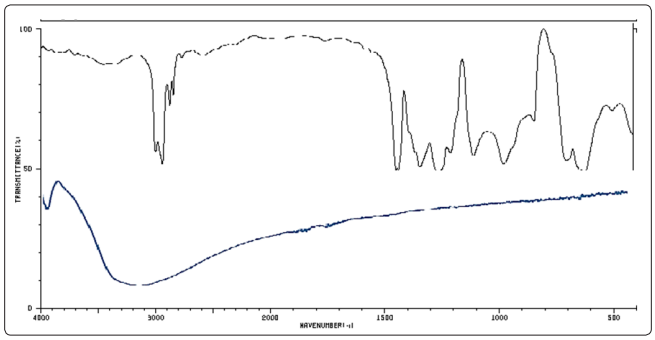

Figure 5: FTIR of TiO_2 and composite membrane

Membrane Performance Test

Analysis of Resistances

Fig 6 Illustrates the membrane fouling of ultrafiltration in treating textile wastewater at CFV = 6 m/s and TMP = 2.05 bar with different temperatures 20, 30 and 40 °C. R_m decreases with increasing temperature, due to lower values of the viscosity of the liquid, and because of the increase of the mass-transfer coefficient according to the film model, both effects providing higher pure water permeate flux at higher temperature. On the contrary, R_a increases with temperature, indicating more severe fouling phenomena at the higher temperature [16]. As consequence, a temperature increase results first in a greater external fouling on the membrane surface probably due in an increment of the internal fouling due to adsorption and

pore blocking. As filtration times progress, the adsorption resistance (R_a) increased. This increase due to high turbulence (CFV = 6 m/s) can cause the relatively smaller or finer particles. The finer particles present in textile wastewater are then deposited either in the membrane pore opening or into membrane pores channels [17].

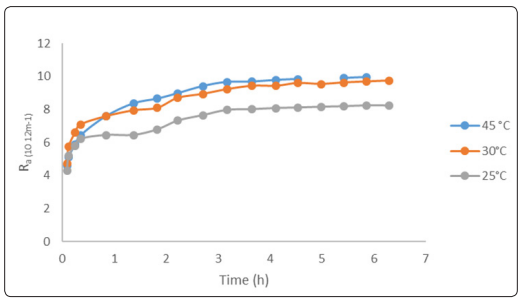

Figure 6: Evolution of the intrinsic resistance and adsorption resistance with time at different temperatures (CFV = 6 m/s, TMP = 2.05 bar)

Effect of Temperature

From the relation between VRF and filtration time, it is easy to deduce the influence of VRF for the experiments. Fig. 7 shows the effect of temperature on permeate flux decline, the flux increases with VRF increases, due to increasing fouling [18]. Moreover, these curves could be divided into three periods: an initial stage with a rapid decrease of the permeate flux; a second stage with a smaller decrease of the permeate flux that takes place around VRF = 1.25 and a final stage with observed a constant flux after VRF = 1.25.

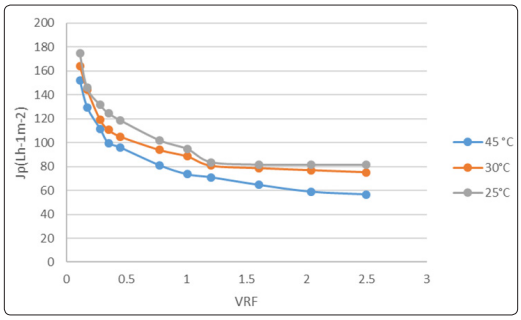

Figure 7: Evolution of the permeate flux with the volume retention factor (CFV = 6 m/s, TMP = 2.05 bar)

The results obtained during experiments with textile wastewater showed that permeate flux decline from the beginning of the run to the steady-state condition was lower at the higher temperature (Fig 4). In fact, as an example, for a fixed TMP of 4 bar, permeate flux decreased by 80.5% from its initial value when the operating temperature was set at 20 °C. Lower permeate flux decline as temperature increases is a consequence of the reduction of membrane fouling and concentration polarization under higher temperature [19].

The temperature of textile wastewater was controlled from 20 to 40 °C using a water bath. Fig.5 Shows the variation of the permeate flux after 6 h of filtration at different feed temperatures. The permeate flux increases by 18% with increases of feed temperature from 20 to 40 °C. As seen, at a higher temperature cake layer formation is limited and permeate flux is almost constant. It must be mentioned that by increasing temperature, permeate flux increases. Temperature has double effects on permeation flux; increasing temperature decreases viscosity, and as a result increases permeation flux. From another point of view, increasing temperature increases osmotic pressure and this decreases permeation flux [20]. Therefore, because of the bilateral effects of temperature must be specified. Higher feed temperature leads to lower viscosity of feed and also higher solubility of some feed constituents. The same reduces concentration polarization and transport of solvent through the membrane intensifies, yielding a higher permeates flux. It should be noted that the elevation of feed temperature normally increases the energy cost and the potential of scaling, and reduces the durability of the membrane system in spite of superior thermal stability of ceramic membrane compared to the polymeric membrane [17].

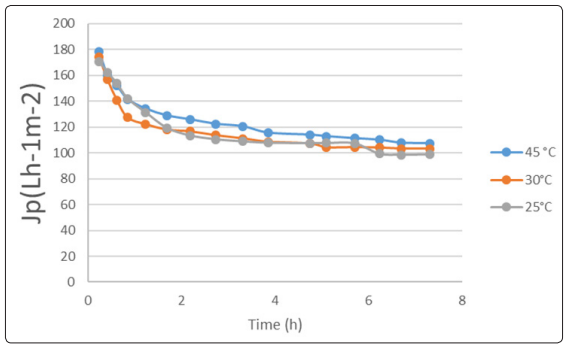

Figure 8: Effect of temperature on permeate flux (CFV = 6 m/s, TMP = 2.05 bar)

The collected permeate under a TMP of 2.05 bar was used as feed for all the ED system. This pre-treatment step was obtained a clear permeate by removing organic matters.

The cumulative permeate volume Vp obtained as a function of time for the ceramic membrane at different temperature and with constant CFV = 6 m/s, is represented in Fig. 9. As it can be observed, these volumes increased with processing time, but simultaneously, a decrease occurred in the permeate rate. Additionally, for a given time, the volumes decreased with increased temperature. Fig. 9 also includes the cumulative permeate volume obtained in the previous experiments for the filtration of pure water with the ceramic membrane [21]. The lower values of Vp obtained of textile wastewater in comparison to those of pure water were due to the fouling of the membrane. It is also seen that there is a linear relationship between the permeate volume of pure water and time, which implies that Jp is constant. This is in accordance to the resistance in the series model, given by Darcy's law.

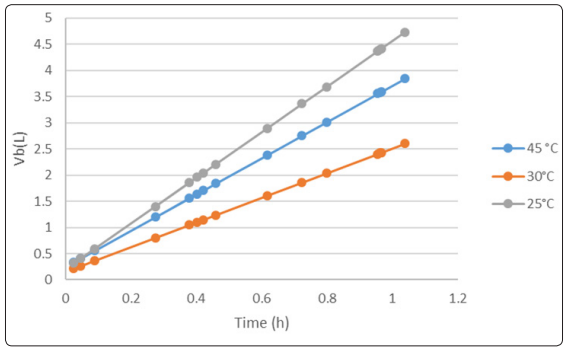

Figure 9: Evolution of the cumulative permeate volume with processing time for the wastewater filtration with the ceramic membrane at a tangential velocity CFV = 6 m/s

Conclusion

Due to the special properties of TiO_2 nanoparticles and PVC polymer, TiO_2 embedded PVC membranes were prepared via non solvent induced phase separation method. The results from this study showed that TiO_2 nanoparticles could be dis-persed uniformly within the PVC membranes at 0.5, 1.0, 1.5,2 wt.% TiO_2 embedded PVC membranes. Even though hydrophilicity, pure water flux and antifouling properties of TiO_2 embedded membranes were higher than those of neat PVC membrane, the rejection of composite membranes reduced due to the increase in mean pore radius. However, flux decline of PVC/TiO_2 membranes were significantly lower than that of neat PVC membrane. It was concluded that incorporation of TiO_2 nanoparticles improved fouling resistance of PVC/TiO_2 membranes

There is no conflict of interest for that paper.

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