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Performance of tight ultrafiltration membrane in textile wastewater treatment via MPR system: effect of pressure on membrane fouling

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Abstract. Industrial textile wastewater can be considered as main water polluting source in which constitutes a threat to human health and ecosystems; due to high water consumption and generated a large volume of color liquid waste. In the present study, the effect of various applied pressure in membrane photocatalytic reactor (MPR) system using ZnO-PEG nanoparticles and polypiperazine amide tight ultrafiltration (UF-PPA) for textile wastewater treatment was systematically investigated mainly through membrane fouling phenomenon. Results showed that the final permeate flux after 180 min was found to increase with the increase of applied pressure which obtained 0.4133 at 6 bar. Under 6 bar of pressure, the dye rejection of permeate was successfully reduced by approximately 100%. The Field Scanning Electron Microscopy (FESEM) analysis was also revealed that 6 bar of applied pressure did not affect or changed the structure of membrane cross-sectional pattern of UF-PPA membrane. In summary, the integrated usage of ZnO-PEG nanoparticles in photocatalysis combined with UF-PPA process improved the membrane fouling phenomenon and able to completely remove the colour from the feed of industrial dye wastewater.

1. Introduction

The increasing demand in the textile industry has significantly contributed to the economic growth in Malaysia. It was estimated that 5000 tons of dyeing materials produced worldwide are released into the environment every year [1]. This has raised much public consideration as it has significant risks to

human health and ecological safety. In fact, the presence of dye in receiving water; even in a small amount; can cause aesthetic pollution, eutrophication, and perturbations problems due to the complexity and recalcitrant compounds [2]. There are several conventional treatments have been carried out in treating dye wastewater based on physical, biological or chemical processes. Although these treatments have been widely applied in the real industry, there are few drawbacks have been evaluated such as complex processes, time-consuming and not environmentally safe due to the addition of chemical substances during the coagulation process. These approaches usually are costly and treatment efficiency is inadequate and only offered for partial degradation of water pollutants [3,4]. Therefore, it is important to develop advanced treatment technology to fully degrade and overcome the water pollution that specified in industrial effluents that have the major sources of dye pollutants.

The membrane photocatalytic reactor (MPR) have been extensively proposed as an alternative treatment for dye wastewater in recent years. MPR is a hybrid system that configured by two techniques which are photocatalysis process and membrane separation technology. Specifically, photocatalysis is used for the decomposition of organic pollutants, while the membrane separates the photocatalyst and products or by-products from the photocatalytic decomposition [5]. MPR has some significant advantages which are a simple process, continuous process, keeping the photocatalyst confined in the reaction environment and a shorter retention time [6]. The typical photocatalysis process started when the energy of a photon is equal to or higher than the band gap of the semiconductor photocatalyst [7]. The valence band electron is then excited to the conduction band whereas the positively charged hole in the valence band and vice versa condition for conduction band. The conduction band electron reduces oxygen into O_{2-} adsorbed to photocatalyst surface while the positively charged hole oxidizes the organic pollutants directly or indirectly by water to produce hydroxyl free radicals (HO•). These generated species played an important role in the disintegration of harmful organic pollutants in wastewater and convert them into CO_2 and H_2O. On the other hands, photocatalyst played a critical role in the performance of the photocatalysis process in order to produce a better quality of treated wastewater. The previous study reported that ZnO-PEG nanoparticles obtained the highest colour removal efficiency, 73% compared to the commercial ZnO (56%) due to the smaller average size of nanoparticles and lesser agglomerate particles [8]. For this reason, ZnO-PEG nanoparticles via precipitation method was used in the present study.

It was noticeable from the literature that reverse osmosis (RO) and nanofiltration (NF) membrane can be considered as well-known techniques for the several commercial dye membrane separation technology [9]. Low permeate flux and required high operating pressure are the important drawbacks for these membranes. The application of ultrafiltration (UF) membrane has not been widely utilized in the textile industry since it makes direct reuse impossible and requires further filtration by either NF or RO [9]. Lin *et al.*, has demonstrated that tight UF membranes can be a stand-alone alternative to NF membranes for the effective fractionation of dye and Na_2SO_4 in the direct treatment of high-salinity textile wastewater [10]. Therefore, the performance of MPR in presence of ZnO-PEG nanoparticles and tight UF membrane for industrial textile wastewater has been adopted in the present study. The detailed research on the effect of operating pressure on membrane fouling was studied. Hence, the present study attempted to achieve lesser fouling and excellent dye degradation efficiency via MPR system in the presence of ZnO-PEG nanoparticles by studying the effect of pressure.

2. Methodology

2.1. Textile wastewater and membrane characterization

The dye wastewater sample that fed was collected from the textile factory located at Batu Pahat, Johor namely as SDWW for research purpose. Each experiment in the present study were performed by polypiperazine-amide (PPA) UF membrane, UA60. It has been considered both a tight UF membrane as well as an open or loose NF membrane. Table 1 gives the main characteristics of these membranes provided by the manufacturer, Osmonics.

Table 1. Main characteristics of UF-PPA membrane.

Characteristics	UF-PPA
pH tolerance (at 25ºC)	2.0-11.0
Pore size/MWCO	1,000 Da
Maximum operating temperature	45ºC
Polymer	Polypiperazine-amide
Contact angle	30.13 11.24

2.2 Synthesis of ZnO nanoparticles

In the present study, ZnO-PEG nanoparticles were self-synthesized via precipitation method in accordance with the previous study of Hairom and co-workers [11]. A 0.15 M solution of oxalic acid dehydrates (obtained from R&M Marketing, Essex, U.K.) was added slowly into 0.1 M solution of zinc acetate dehydrated (obtained from R&M Marketing, Essex, U.K.) under room temperature (25°C). After 5 min, 0.015 g/L of PEG (obtained from R&M Marketing, Essex, U.K.) were then added in the mixture [12]. To yield high production of ZnO, the mixture was stirred for about 12 hours. ZnO nanoparticles are settled at the bottom and the excess liquid was removed; then the precipitate was filtered and dried in oven less than 100°C for about 1 hour to remove any excess water. Afterward, the obtained precipitate was calcined in the furnace (Nabertherm model, Germany) under 550 °C for 3 h to remove all the impurities. The white powder of ZnO-PEG nanoparticle was formed and ready to use as a photocatalyst.

2.3 Experimental and set-up operation

The experiments were carried out using the combination of photocatalysis and cross-flow membrane filtration unit, namely as MPR which consists of a membrane sample with an effective area of 20.6cm^2. The membrane sample was wetted out by circulating reverse osmosis water (RO) under 6 bar for about 30 min to avoid any compaction during permeation or separation experiments. A schematic representation of MPR illustrated in Figure 1 that mainly composed of 2L photocatalytic reactor and a membrane separation unit. A laboratory pilot plant could operate either in batch or continuous mode. After a feed of SDWW wastewater at pH 11 introduced into the photocatalytic tank, 0.10g/L of ZnO-PEG photocatalyst was then added to allow the photocatalysis process took placed in the system [13]. The mixtures were stirred by using overhead stirrer (HS-30D, 83W, Daihan Scientific, Korea) at 300rpm for 30 min in the dark to reach adsorption-desorption equilibrium. The operation temperature must be kept constant at 25ºC by the recirculating cooling water using the water chiller (CW-5300A, 1800W, S&A Industrial Chiller, China). Following that, the ultraviolet (UV) lamp (11 W, TUV 11W T5 4P-SE, Philips, Poland) was switched on and the reaction mixture in photocatalysis process was irradiated by UV light for 20 min. The degraded dye then flowed into stainless steel flat sheet membrane module, 9.8cm × 9.8cm × 5.1cm using a master flex peristaltic pump at different trans-membrane pressure (4.0-6.0 bar). The flux was collected for about 3 hours and its volume was measured in every 5 min by using a measuring cylinder. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) obtained from R&M Chemicals, UK were used in this research for solution pH adjustment. For treated water quality analysis, color intensity of the samples was determined from its absorbance at 333 nm using UV-Vis Spectrophotometer (LABOMED, INC., Spectro UV-2650, U.S.). The dye rejection was then determined using the following equation:

$$Dye\ rejection\ percentage, R\ (\%) = \frac{C_f - C_p}{Cp} \times 100\% \quad (1)$$

C_f and C_p, are the colour in feed and permeate, respectively.

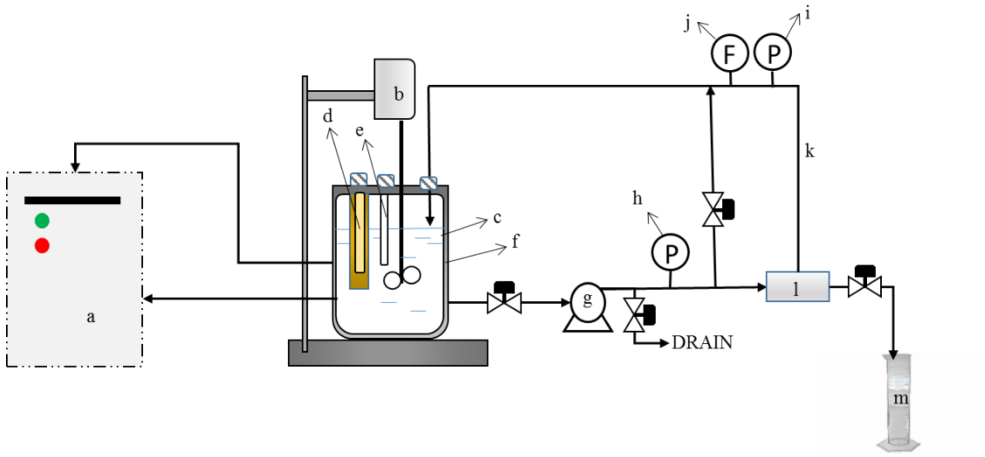

Figure 1. Schematic diagram of membrane photocatalytic reactor (MPR). a) water chiller, b) overhead stirrer with stand, c) photocatalytic reactor, d) UV lamp, e) feed, f) cooling jacket , g) pump, h & i) pressure gauge, j) flow meter, k) recycle flow, l) membrane filtration system and m) measuring cylinder.

2.4 Flux Decline Analysis

The flux decline was calculated based on permeability solution in order to investigate the behavior of membranes. The initial flux of the membranes was calculated as the volume of permeate (V) divided by unit area (A) per unit time (t) according to the following equation:

$$J_0 = \frac{V}{A/t} \tag{2}$$

Then, the instantaneous permeate flux (J) at each run was calculated in the time intervals t_1 and t_2 in accordance to the Equation 3. Subsequently, the flux was normalized as Equation 4 for investigated membrane fouling between different parameters. The graph was plotted as normalized flux against operation time for comparison purpose and analysis of permeate flux decline.

$$J = \frac{V_2 - V_1}{A(t_2 - t_1)} \tag{3}$$

$$Normalised\ flux = \frac{Solution\ flux, J}{Pure\ water\ flux, J_0} \tag{4}$$

2.5 Membrane Characterisation

The surface and cross-sectional morphology of UF-PPA membrane sample during optimum pressure, 6 bar and fresh UF-PPA membrane were determined using Field Emission Scanning Electron Microscopy (FESEM) (Gemini, SUPRA 55VP-ZEISS, Japan) at 10.0 and 2.0 kV. The small pieces of membrane samples were dried before the observation conducted. The samples were coated in gold before placed on the specimen holder for membrane surface observation while the membrane samples for cross-sectional analysis were immersed in the liquid nitrogen for about 6 until 7 hours. The samples were then fractured and coated in gold in order to generate electrical conductivity.

3. Result and discussion

3.1. Effect of operating pressure on normalized flux

The effect of pressure on the normalized flux by varying the pressure from 4.0 to 6.0 bar was investigated as depicts in Figure 2. With the decrease operating pressure in MPR, UF-PPA membrane flux decline

had a tendency to alleviate. The trend of flux that function of time is initially found to decline rapidly and afterward, remains nearly constant. As seen in Figure 2, the normalized flux exhibits the highest flux by increasing operating pressure from 4.0 until 6.0 bar for constant reaction time, 3 hours. Moreover, the highest flux was obtained at 6 bar for applied SDWW wastewater in the MPR system. It revealed the facts that the higher the pressure, the greater rate of flux that can be obtained. This is due to the increase in driving force through the membrane which is in accordance with the Poiseuille's law [14,15]. Consequently, the enhancement of the convective flow of solutes toward the membrane surface can be achieved. In addition, these solutes may be transported back into the bulk solution mainly due to shear-induced particle diffusion when the applied pressure is below the value needed to reach a non-linear behaviour [15]. It is clear that the applied pressure of UF-PPA membrane at 6 bar was sufficient for the high production of permeate.

It should be noted that flux may not increase proportionally with pressure at high pressures in certain conditions. It was related to the mass transfer-controlled region that has mentioned in the study of Cheryan in which the higher pressure resulted in the build-up of a solute layer on the membrane surface [16]. Furthermore, it will slow-up the transportation of components through the membrane. The extremely high pressure was not necessary for the production of permeate in the application of MPR. Additionally, these higher driving forces entail that a higher proportion of solutes are able to penetrate through the pores causing inner pore adsorption or clogging [15]. It also might increase the cost of operation and thus, bring effect to the economic and technical viability of tight ultrafiltration processes.

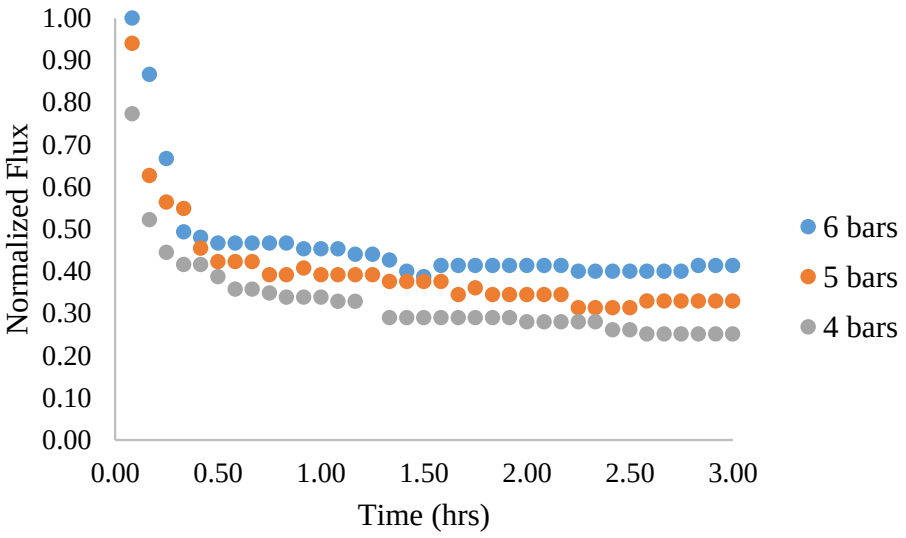

Figure 2. Normalized flux against time for different operating pressure.

3.2. Rejection of dye in different operating pressure

The dye rejection percentage at various operating pressure was demonstrated in Figure 3. It clearly indicated that the dye rejection linearly increases with the increase of operating pressure in the MPR process. As shown in Figure 3, 6 bar are found to be more favorable for decolorisation of SDWW wastewater with 100% of dye removal efficiency. This observation can be explained by the increase in mechanical compaction that leads to an increase in membrane density. In facts, this phenomenon tends to decrease the pore size and consequently, the rate of diffusion of dissolved solute through the membrane is reduced [17]. Furthermore, these findings may be related to the convection or diffusion theory based on Spiegler–Kedem model in which assumed that solute rejection by a partially retentive membrane should increase with trans-membrane solvent flux [18]. The similar result was observed in the study of He *et al.*, and Lin *et al.*, when varying the operating pressure, producing a maximum rejection at higher pressure which obtained up to 99.0% and 95.0%, respectively [19, 10]. However, it

should be noted that extreme pressure may result lower dye rejection due to the increase of concentration polarization [21]. It could be deduced that the findings in the present study proved that the influence of pressure on dye rejection was positive but not very significant because the rejections of dye are all over 97.0%. Hence, the results revealed that ZnO-PEG nanoparticles and UF-PPA membrane have the potential to remove dyestuff effectively from SDWW wastewater.

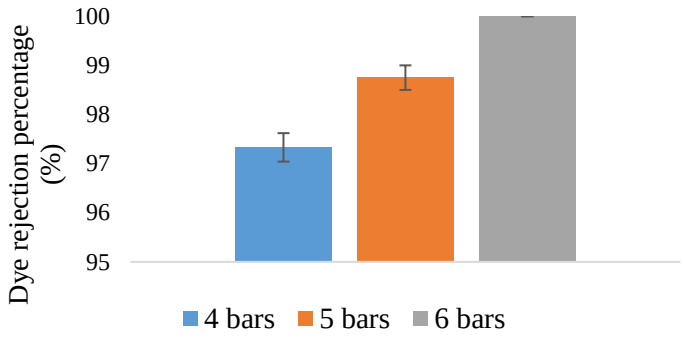

Figure 3. Dye rejection percentage (%) with the respect to different pressure

3.3. FESEM Analysis

Comparative FESEM analysis in terms of membrane surface at 10.0kV (magnification: X10, 000) and cross-sectional at 2.0kV (magnification: X800) for fresh and fouled UF-PPA membrane at 6 bar are shown in Figure 4. As revealed in Figure 4(b), the fouled of UF-PPA membrane has contaminants and pollutions entrapped on the membrane surface which is mainly from photocatalyst and chemical elements in SDWW wastewater. It could be clearly observed that UF-PPA membrane is porous and asymmetric. Moreover, the cross-sectional of fouled UF-PPA membrane at 6 bar did not become different from the fresh UF-PPA membrane. In addition, no cracks were detected on the cross-sectional observation in which signified that the membrane did not become brittle by the applied pressure and no negative effect on the membranes stability. It can be concluded that 6 bar of applied pressure in the MPR system has a significant influence on UF-PPA membrane fouling behavior and permeate quality.

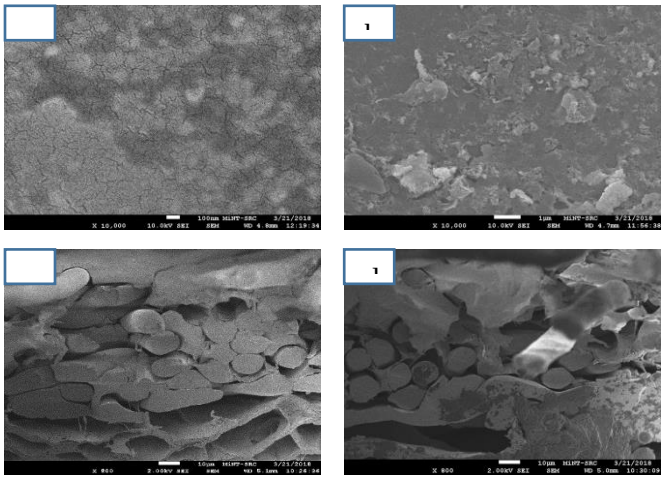

Figure 4. Membrane surface FESEM image a) fresh UF-PPA membrane and b) Fouled UF-PPA membrane at 6 bar. Cross sectional FESEM image of c) fresh UF-PPA membrane and d) Fouled UF-PPA membrane at 6 bar.

Conclusion

The influence of applied pressure on the UF-PPA separation process via the MPR system was systematically investigated in the present study. The rapid development of the fouling layer can be observed during the first 1 hour and 30 min. Afterwards, the permeate flux reached a pseudo-steady state after the fouling layer was fully established. Increasing pressure led to the increase in final normalised flux. Furthermore, the maximum final normalised flux and dye rejections was achieved at 6 bar with ~60% of flux decline and 100% removal, respectively. FESEM observation confirmed that 6 bar is the appropriate pressure to be applied in the MPR system since there is no significant difference of structure between the fresh and fouled UF-PPA process. In conclusion, the presence of ZnO-PEG and UF-PPA process in the MPR system become an advanced treatment method for treating dye wastewater.

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