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PERFORMANCE EVALUATION OF NANOFILTRATION MEMBRANES FOR DYE REMOVAL OF SYNTHETIC HAND-DRAWN BATIK INDUSTRY WASTEWATER

This study evaluated the performance of nanofiltration (NF) membrane for the treatment of hand-drawn batik wastewater containing synthetic dyes as well as real batik wastewater. Three commercial NF membranes (NF270, TS40 and XN45) were used. The effect of transmembrane pressure, NF membrane types, synthetic dyes concentration, and solution types on flux and rejection were investigated. The results showed that the use of all NF membranes could reach dye removal of ca. 99%. NF270 membrane exhibited the highest flux, 2–3 times higher than that of TS40 and XN45 membranes. NF270 membrane was further used for treating real batik wastewater. The results showed high rejections in terms of total suspended solids (TSS), chemical oxygen demand (COD), and total dissolved solids (TDS) were obtained. The practical applicability of NF270 membrane for real hand-drawn batik wastewater treatment fulfilled the quality standards in terms of TSS, COD, and BOD parameters. Overall, the NF270 membrane showed favorable performance for batik effluent treatment.

1. INTRODUCTION

The homemade hand-drawn batik industry is the oldest among traditional textile industries in Central Java, Indonesia. For the past centuries, many local communities have depended on the hand-drawn batik industry for their livelihoods. The hand-drawn batik industry has improved the country's economic growth because of the high batik demand, both local and global [1]. Unfortunately, high batik demand requires a large amount of water. The process used by the hand-drawn batik industry commonly pro-

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duces a large volume of wastewater containing a high amount of organic matter such as dyes. Generally, the ratio of water and dyes during the dying process is 50 dm^3 and 25 g per 1 kg of cloth. Commonly, 10–50% of dyes are wasted as batik effluent. The majority of the traditional batik industry does not have an efficient wastewater treatment process [2], thereby discharging wastewater into the environment without any treatment. The presence of dyes in water bodies may have a fatal effect on the environment and human health [3]. Figure 1 shows an illustration of hand-drawn batik textile and batik wastewater.

Fig. 1. An illustration of batik textile (top panel) and batik wastewater (bottom panel) taken directly from one of small/medium hand-drawn batik industries in Semarang, Indonesia)

In general, dye compounds commonly are characterized by a high COD, BOD, and salinity. The presence of dye substances in te water bodies will block sunlight, which can inhibit the photosynthesis activity of aquatic organisms. Some dyes also cause allergies to human skin and severely damage the kidney, respiratory, liver, and reproductive systems in human beings [4]. Therefore, treatment of wastewater containing dyes is required before discharging directly to the environment.

Numerous technologies have been proposed for dye wastewater treatment, such as adsorption [5], coagulation/flocculation [6], ozonation [7], precipitation [8], and membrane filtration [9, 10]. Among these technologies, the NF process is the most appropriate technology to separate dyes from batik wastewater and produce freshwater reusable for the batik washing process. NF membranes have a molecular weight cut-off (MWCO) of 200–1000 Da while dyes usually used in the batik industry (e.g., remazol, indigo) have a molecular weight of 262–1300 Da. This indicates that NF should have the ability to retain dyes from dye wastewater [11]. Furthermore, NF has been widely used for wastewater treatment from dyeing processes because it has high efficiency of pollutant removal and is user-friendly [12]. A previous study reported that NF and ultrafiltration (UF) membranes can be used for the COD, TDS, and dye colour diminishing in textile wastewater treatment [11]. High COD rejections of 80% and 100% were obtained by UF and NF filtration, respectively. A total decolourization and more than 90% of dye colour removal have been achieved by the UF and NF membrane [13]. These suggest that the NF process could be suitable for reducing such pollutant indicators as COD and dye colour of textile wastewater. Nevertheless, a previous study reported that the NF membrane failed to satisfy the water reuse requirements in terms of COD removal, as evidence the COD removal efficiency of NF6 membrane is approximately 60% and the COD value in the permeate solution is more than 90 mg/dm^3; thus the combination of two NF membranes is required [14]. However, the application of two NF membranes certainly increased the investment costs [14]. Furthermore, various dyes used by hand-drawn batik industries have consequences on the selection of NF membranes and different operating conditions. These recommend that NF membranes should be systematically investigated to enhance membrane performance without increasing the cost of operations. Therefore, further investigation of NF membrane performance for batik wastewater is still required.

In this work, various NF membranes (NF270, TS40, and XN45) were studied to treat solutions containing the batik synthetic dye component. The dye rejection and permeate flux were observed at various trans-membrane pressures and dye concentrations. Appropriate conditions were used for treating local hand-drawn batik wastewater, a mixture solution of dyes, and dye/NaCl solutions. The evaluation of the fouling phenomenon will provide potential support for investigating the performance of NF membranes in dye wastewater treatment. TDS, COD, and TSS were also determined to evaluate membrane separation efficiency.

2. EXPERIMENTAL

Materials. Indigo violet-14R (product code AMB-0016-07) and remazol yellow-FG (product code: AMB-0017-02) were purchased from a traditional market in Bantul, Yogyakarta, Indonesia. The molecular weight of indigo dye ($C_{16}H_{10}N_2O_2$) and remazol dye ($C_{22}H_{16}N_2Na_2O_{11}S_3$) were 262 and 627 Da, respectively. The chemical structures of indigo dye and remazol dye are shown in Fig. 2.

5 dm^3 of a batik effluent sample was collected from a rinsing bath which is located at the local hand-drawn batik industry in Semarang, Indonesia. It was prefiltered using a paper filter (Macherey-Nagel^{TM} MN 640, diameter 110 mm) prior be used, as presented in Table 1. Then, the batik effluent sample was kept in a cold room after prefilter. The characteristics of batik effluent samples were then analyzed. Solutions of dyes

of various concentrations (100, 200, and 300 mg/dm^3) were prepared by dissolving dyes in 1 dm^3 deionized water under stirring. NaCl was acquired from Sigma-Aldrich (Belgium). NF270 membranes were provided by Dow/Filmtec (USA), while TS40 and XN45 membranes were purchased by Trisep Corporation (USA). Deionized water was used for preparing all solutions.

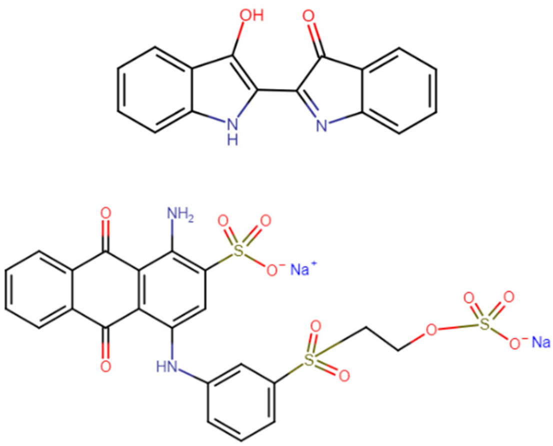

Fig. 2. The chemical structure of indigo dye (top) [15] and remazol dye (bottom) [16]

Table 1

The characteristics of raw and pre-filtered hand-drawn batik wastewater[a]

Sample	Raw hand-drawn batik wastewater	Pre-filtered hand-drawn batik wastewater
pH	7.91	8.05
TSS, mg/dm^3	68.0	57
BOD, mg O_2/dm^3	182	106
COD, mg O_2/dm^3	362.5	291
Colour	black	black
NH_3-N, mg/dm^3	0.3624	≤0.015
Cr, mg/dm^3	0.2239	≤0.008

[a]The analysis at the Environmental Laboratory. Environmental Service, Semarang, Indonesia.

Experimental set-up. NF process was performed through lab-scale crossflow filtration (Fig. 3). This device consisted of a feed tank, a pump, a pressure gauge connected to the feed side of the membrane, a flat–sheet membrane module, and a permeate collection.

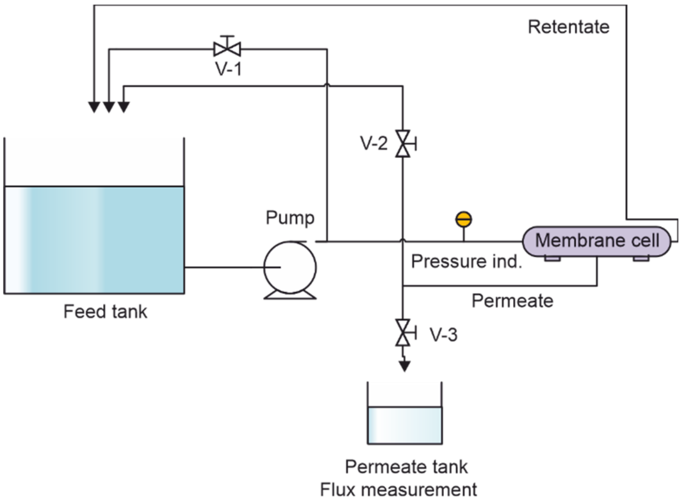

Fig. 3. The schematic of a simplified nanofiltration experimental set-up [17]

The experiments of crossflow filtration involved four tests: the filtration of single dye, mixture of dyes, dye/salt, and real hand-drawn batik wastewater. Before the cross-flow filtration, all NF membranes with a surface area of 7.065 cm^2 were soaked in deionized water overnight at room temperature. At the beginning of each experiment, all NF membranes were pre-compacted using deionized water at varied trans-membrane pressures from 0.5 up to 0.7 MPa for 60 min without stirring. After compaction, the pure water flux test was conducted and the flux was measured. The pure water permeability was determined by measuring the slope of a linear plot of pure water flux against applied trans-membrane pressures.

The first set of experiments was conducted to determine the single dye rejection performance of NF270, TS40, and XN45 membranes. After pure water flux measurement, the feed tank was filled up with 1 dm^3 of indigo dye solution and was placed into the stirred cell with a fixed stirring rate at 200 rpm for all experiments. Indigo dye was selected as a dye marker in this study since it is commonly found in hand-drawn batik wastewater from the batik textile industry and is necessary to be removed before discharging to the environment due to its carcinogenic properties. The filtration test was conducted for 160 min under a batch mode where the only concentrate was returned to the feed tank and the permeate was collected for further analysis. The trans-membrane pressure (TMP) was varied from 0.4 up to 0.6 MPa.

The second set of crossflow filtration was conducted to determine the removal of dyes from the dye mixture using the NF270 membrane. The dye mixture solution consisted of 100 mg/dm^3 remazol dye and 100 mg/dm^3 indigo dye. The filtration was performed at an applied TMP of 0.4 MPa for 160 min under a stirring rate at 200 rpm. Meanwhile, the indigo dye/salt rejection performance of applicability NF270 membrane was-evaluated using 100 mg/dm^3 indigo dye and NaCl 1000 mg/dm^3 at applied TMP of 0.4 MPa for 160 min under stirring rate at 200 rpm.

To explore the applicability of the NF process for real wastewater treatment, we studied the short-term filtration of NF270 membrane for separation pre-filter local hand-drawn batik wastewater at applied TMP 0.4 MPa with a constant stirring rate of 200 rpm. During the filtration experiments, the permeate volume was periodically collected to measure the permeate flux (J). To analyze NF membrane fouling, the measurement of pure water flux before (J_0) and after (J_a) filtration was performed by flushing the NF membrane with deionized water after use for the adsorption fouling. Samples of 0.005 dm^3 were periodically taken from the feed and permeate for analysis.

Analytical methods and calculations. The permeate flux is the volume of permeate produced per unit area of the membrane surface and per unit time determined using the following equation

$$J = \frac{V}{At} \tag{1}$$

where V is the permeate volume, dm^3, A is the active membrane surface area, m^2, and t is the permeation time, h.

To evaluate the fouling phenomenon, the following equations were used

$$DRt = \left(1 - \frac{J}{J_0}\right) \times 100\% \tag{2}$$

$$DRr = \left(\frac{J_a - J}{J_0}\right) \times 100\% \tag{3}$$

$$DRir = \left(\frac{J_0 - J_a}{J_0}\right) \times 100\% \tag{4}$$

where DRt is the total fouling ratio, DRr is the reversible fouling ratio caused by dye particles deposition on the membrane surface, and $DRir$ is the irreversible fouling ratio caused by dye particles entrapment in membrane pores.

The salt concentration was measured with a conductivity meter (Hanna Instrument, HI98303) and pH with a pH meter (Hanna Instrument, HI98107). COD and TSS were measured according to Standard Methods [18]. The dye concentration was measured with a UV-Vis spectrophotometer (Thermo Fisher Scientific, Genesys 20) at a wavelength of 552 and 480 nm for indigo dye and remazol dye solution, respectively. The rejection of dye was calculated using the following equation

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{5}$$

where C_f and C_p are dye concentrations, mg/dm^3, in the feed and permeate solutions at a sampling time during the filtration process, respectively.

Membranes characterizations. SEM (JEOL JSM-6510 LA) was used to observe the morphology of the pristine and fouled membrane's top surface. Before the analysis, the entire membrane was coated with gold-sputtered for 1 minute.

3. RESULTS AND DISCUSSION

3.1. PURE WATER PERMEABILITY

Pure water permeability is an important characteristic of a membrane for evaluation of its permeate flux production. The pure water flux of NF270 membrane increased linearly with increasing TMP as presented in Fig. 4. A line correlation was with $R^2 = 0.97679$.

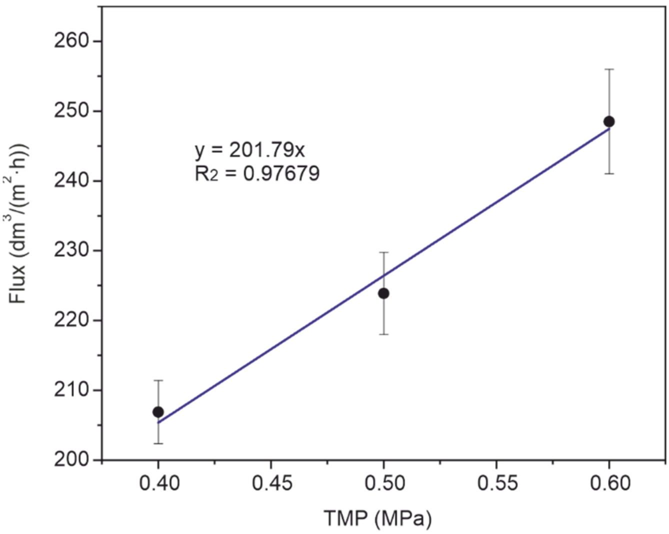

Fig. 4. Pure water flux of NF270 membrane in function of TMP

3.2. EFFECT OF TRANS-MEMBRANE PRESSURE, INDIGO DYE CONCENTRATION, AND MEMBRANE TYPE ON NF PERFORMANCE

The effect of trans-membrane pressure (TMP) on flux and indigo dye rejection by NF270 membranes is presented in Fig. 5.

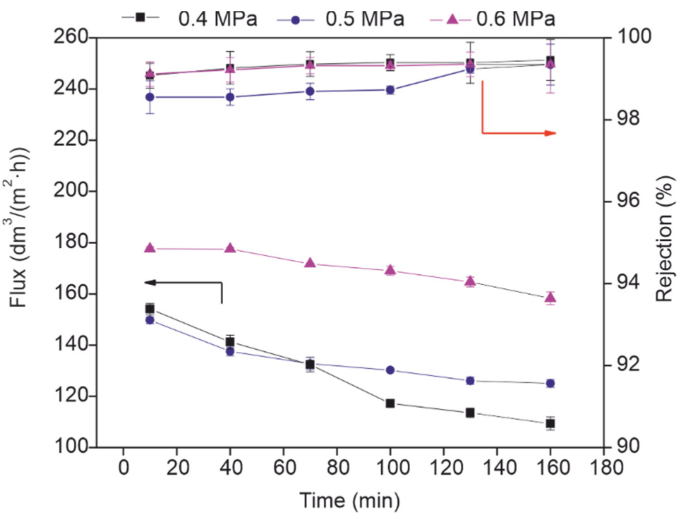

Fig. 5. The effect of TMP on flux and indigo dye rejection
(initial dye concentration: 100 mg/dm^3, NF 270 membrane)

The highest fluxes and dye rejection were obtained at the highest TMP, i.e., 0.6 MPa. The higher TMP resulted in the higher permeate flux as indicated by the steady flux values of about 127.95±6.76, 133.54±9.22, and 169.79±7.4 dm^3/(m^2·h) for TMP 0.4, 0.5, and 0.6 MPa, respectively. Notably, TMP is the driving force of the NF process; thus, as the TMP increases, the more water penetrates the permeate side. Although the highest flux was obtained at the highest TMP, the flux decrease during the nanofiltration process was observed for all applied TMP. It is due to both concentration polarization and fouling. Considering the rejection data as presented in Fig. 5, it is reasonable to state that most of the dye is rejected by the membrane resulting in fouling via gel or cake layer formation on top of the membrane surface. A longer filtration process leads to thicker cake layer fouling resulting in a further decrease in membrane flux. Rejection measurements showed that the increase in applied TMP from 0.4 to 0.6 MPa did not increase in dye rejection. All experiments at different TMP showed rejection higher than 98%.

Figure 6 presents the effect of indigo dye concentration on flux and rejection during the nanofiltration process. It can be seen that the membrane flux gradually decreased over the filtration time, indicating concentration polarization and fouling phenomena occurred during the filtration process. The decrease occurs because first concentration polarization and then due to the solute-membrane interaction as well as the effect of pressure used causing the indigo dye molecules to transform into gel and cake layers on the membrane surface area, thus blocking the water permeation across the membrane. This observation is also similar to that of a previous study [19]. It is important to inform that, investigating the effect of concentration of a dye on flux could not be conducted directly from the flux behaviour data. One should consider the initial water flux of the membrane used. The same membrane can have different initial flux when it is cut and used in the laboratory. For example, the initial water flux of NF membranes used for the experiments at the study of the dye concentration with TMP of 0.4 MPa were 154.05, 165.77, dan 157.14 $dm^3/(m^2 \cdot h)$ for the initial dye concentration of 100, 200 and 300 mg/dm^3, respectively.

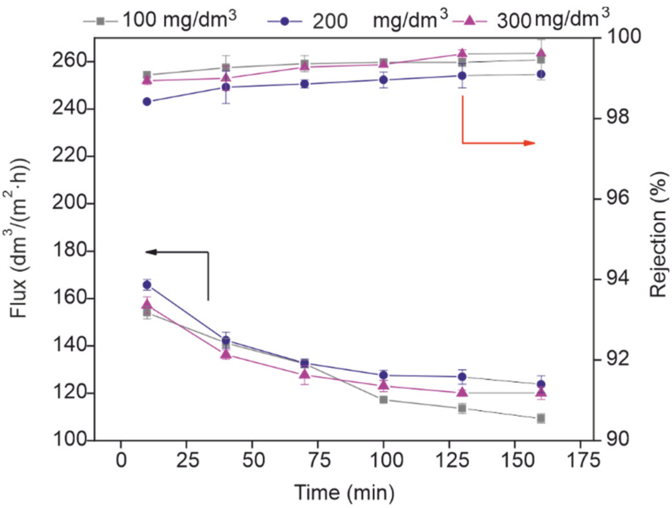

Fig. 6. The effect of dye concentration on membrane flux and indigo dye rejection (TMP 0.4 MPa, NF270 membrane)

The increase in feed concentration did not change the dye rejection by NF membranes (99.9, 98.8, and 99.9% for the feed concentration of 100, 200, and 300 mg/dm^3, respectively). All changes in rejection data were within the range of deviation standard. This suggests that separation by sieving mechanism seems to be a more dominant mechanism than solution diffusion as well as charge exclusion [20].

The membrane surface morphologies of pristine and fouled NF membranes were observed by SEM. The visualization of indigo dye deposition on the NF membrane surface was confirmed by the SEM image results (Fig. 7). The surface of all pristine NF membranes was smooth and clear, meaning no visible deposited particles on pristine NF membranes surfaces. By contrast, all fouled NF membranes showed deposited particles on their surface. The accumulation of dye particles on the TS40 membrane surface is more apparent than the deposition of the dye particle on both NF270 and XN45 membrane surfaces. This observation indicates that the TS40 membrane was easier to be fouled by a dye solution. The occurrence of fouling in a membrane certainly affects membrane performance, resulting in flux decline. These results are confirmed by Fig. 8, which presents the flux behaviour and indigo dye rejection for different NF membranes.

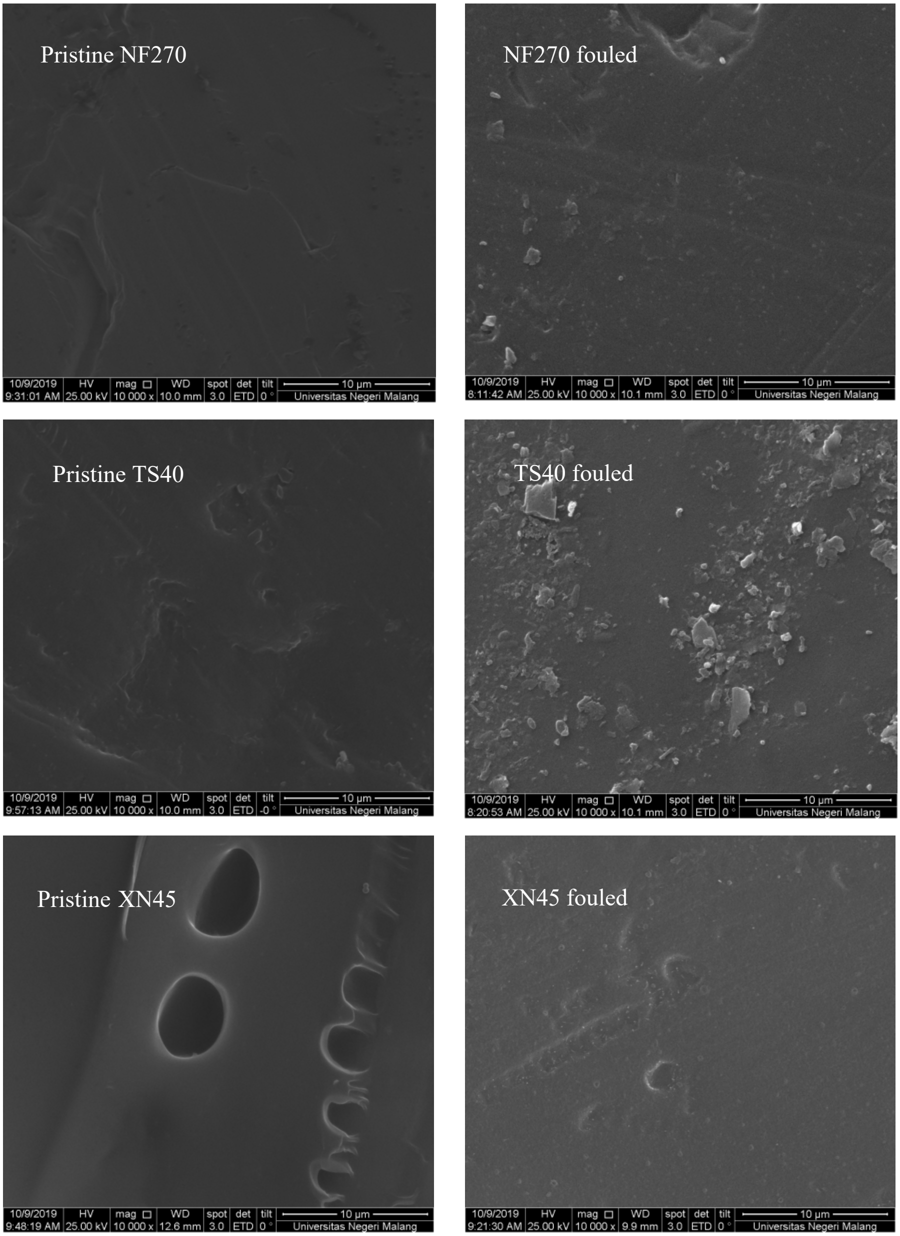

Fig. 7. SEM images of top surface morphologies of pristine and fouled NF membranes

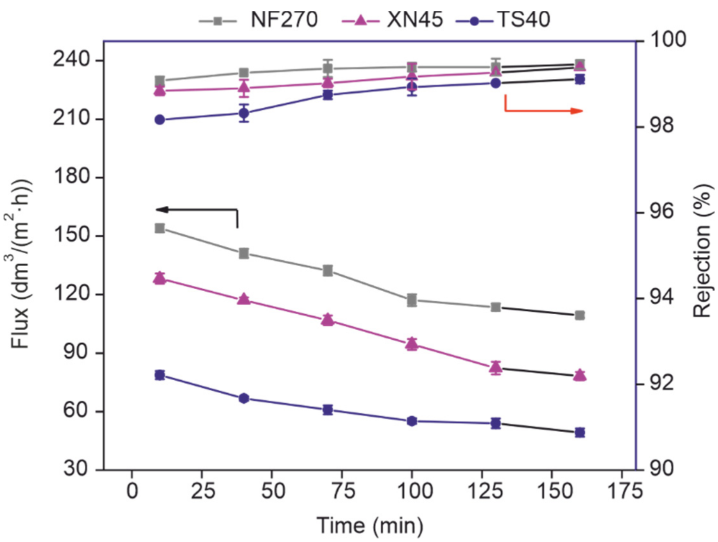

Fig. 8. The effect of membrane type on flux behaviour and indigo dye rejection (TMP 0.4 MPa, dye concentration 100 mg/dm^3)

It can be seen from Fig. 8 that the highest flux was demonstrated by the NF270 membrane. The flux of the NF270 membrane was 2–3 times higher than those of the other two membranes. The rational reason is that the NF270 was the most hydrophilic NF membrane as indicated by its lowest contact angle (CA) (CA for NF270 = 21.4° [21] compared to CA for TS40 = 28° [22] and CA for XN45 = 39.8° [22]). The hydrophilic character helps the membrane to improve the water flux as water molecules are entrapped on the membrane surface to form a water layer by hydrophilic groups through hydrogen bonds [23]. Moreover, the highest steady water flux was obtained by NF270 membrane, as listed in Table 2. This result agrees well with previous publication reporting that the flux of NF270 membrane was significantly higher than those of the other NF (NF90 and NF99) membranes during filtration of rinsing wastewater from indigo dyeing process of a denim manufacturing plant [24].

Table 2

The steady water flux of NF membranes

Steady water flux at TMP = 0.4 MPa, dm^3/(m^2·h)	NF270	XN45	TS40
	206.87±11.52	173.98±5	112.01±5.4

All NF membranes demonstrated high indigo dye rejection and no significant difference from each other was observed. At the end of the filtration process, indigo dye rejections of NF270, TS40, and XN45 membrane of 100 mg/dm^3 indigo dye at TMP 0.4 MPa were 99.4, 99.1, and 99.3%, respectively.

The results of pH measurements showed a minor increase in the pH from feed dye solution to all permeate dye solutions of NF270 membranes (Table 3). This phenomenon can be explained by the interaction between NF membrane polymer and indigo dye particles. The polymer of the NF270 membrane is polyamide. In general, dye structures have chlorodiamino reactive groups that encourage the production of strong reaction affinity when adsorbed by a polyamide surface. This allows a dye solution with acidic properties in the permeate to be neutral [25]. The same result was demonstrated by the TS40 and XN45 NF membranes.

Table 3

The effect of NF membranes and TMP on pH change from feed (indigo dye, 100 mg/dm^3) to permeate solution

Membrane, TMP	Feed	Permeate
NF270, 0.4 MPa	6.62±0.01	7.02±0.01
NF270, 0.5 MPa	6.83±0.01	7.13±0.02
NF270, 0.6 MPa	6.83±0.02	7.11±0.02
TS40, 0.4 MPa	6.72±0.01	7.27±0.01
XN45, 0.4 MPa	6.81±0.02	7.24±0.04

3.3. NF MEMBRANE FOULING ANALYSIS

To analyze the membrane fouling mechanism, some parameters of membrane fouling, such as total fouling, reversible fouling, and irreversible fouling, were calculated, as shown in Fig. 9.

NF process with NF270 membrane at TMP of 0.6 MPa demonstrated the lowest total fouling and irreversible fouling. Moreover, as confirmed in Fig. 5, the applied higher TMP increases more solute to penetrate and get entrapped on the membrane surface or into the membrane pores, resulting in permeate decline across the membrane, thus lowering membrane permeability. However, the value of reversible fouling was very low (<5%) in all variations of dye concentrations and TMP. This result indicates that the effect of irreversible fouling was more predominant than the effect of reversible fouling. This may be due to dye particles having adsorbed and entrapped into membrane surface and pores during filtration process. Thus, the restoration of membrane flux becomes slightly complicated.

At TMP of 0.4 MPa, nanofiltration of indigo dye solution using NF270 membrane showed that the total fouling and irreversible fouling were lower for 100 mg/dm^3 than for 200 mg/dm^3 and 300 mg/dm^3. The higher feed concentration caused the higher concentration polarization (reversible fouling). Furthermore, this reversible fouling can alter to irreversible fouling by the interaction of dye particles and membrane.

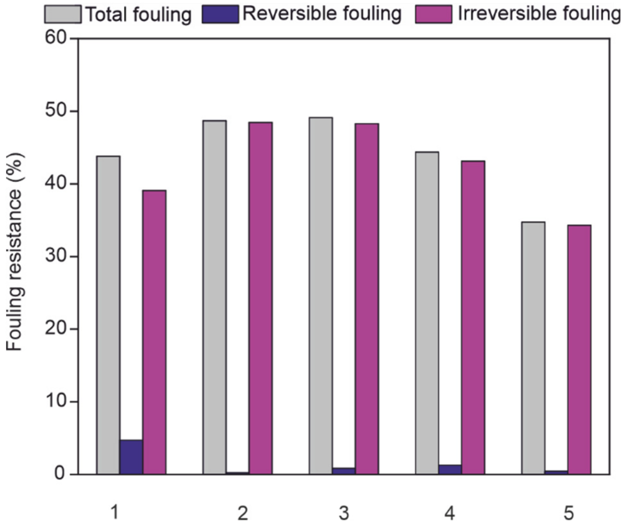

Fig. 9. The effect of TMP and indigo dye concentration on NF270 membrane fouling resistance: 1 – 100 mg/dm^3, 0.4 MPa, 2 – 200 mg/dm^3, 0.4 MPa, 3 – 300 mg/dm^3, 0.4 MPa, 4 – 100 mg/dm^3, 0.5 MPa, 5 – 100 mg/dm^3, 0.6 MPa

Fig. 10. Visualization images of feed solution, permeate from NF270 and pure water

Despite the high rejections of indigo dye, removal of dye colour has not yet been complete. This point was consistent with the results of the visualization images of permeate of NF270 membrane, as it is shown in Fig. 10. The permeate of NF270 membrane is slightly coloured compared to water. This implies that NF270 membrane had visually reduced dye colour from feed to permeate solution.

3.4. PERFORMANCE OF NF270 MEMBRANE IN TREATMENT OF INDIGO/REMAZOL DYE MIXTURE AND INDIGO/NaCl SOLUTION

In this work, a dye mixture was used as the feed solution of NF process. The effect of NaCl was also investigated. The NF270 was used because this membrane showed a better performance than the others. Figure 11 demonstrates the effect of dye mixture on the separation performance of NF270.

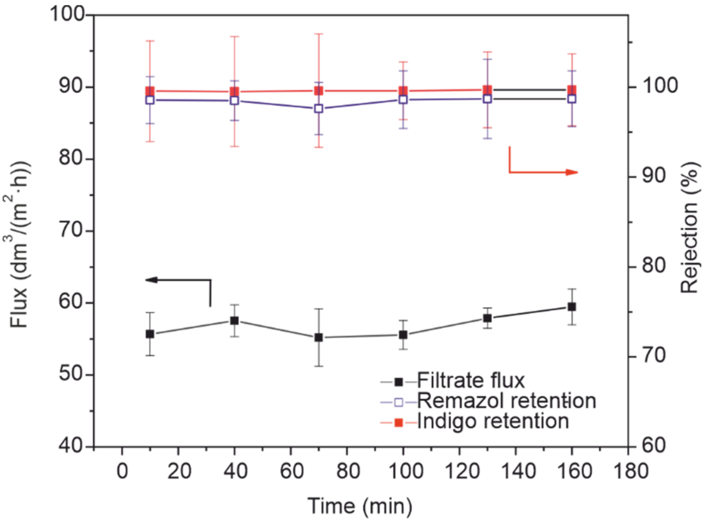

Fig. 11. Nanofiltration of dye mixture solution
(initial each dye concentration 100 mg/dm^3, TMP 0.4 MPa, NF270 membrane)

The NF270 membrane showed high rejection for both indigo and remazol dyes (higher than 96%). The flux resulted by the filtration of dye mixture solution was smaller than the flux of single dye (Fig. 6). This indicates that there was interaction between indigo and remazol dyes. Figure 12 shows the effect of NaCl on the separation performance of NF270 membrane. The presence of salt in the aqueous solution of indigo dye could affect stability and performance of the NF membrane. It is seen that the rejection ability of NF270 membrane of the dye is relatively high (higher than 96%), while the rejection ability to NaCl is lower than 38%. Moreover, the flux was 67.17 dm^3/(m^2·h) at the beginning of the filtration, and after 160 min of separation process, the flux was reduced to 62.93 dm^3/(m^2·h), which was caused by membrane fouling.

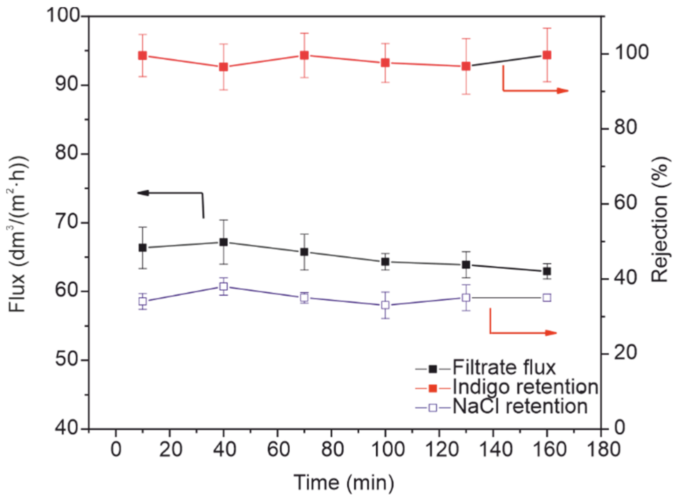

Fig. 12. The effect of NaCl on flux behavior and dye rejection during nanofiltration (indigo dye initial concentration 100 mg/dm^3, TMP 0.4 MPa, NaCl concentration 1000 mg/dm^3)

3.5. PERFORMANCE OF NF270 MEMBRANE IN BATIK WASTEWATER TREATMENT

A hand-drawn batik effluent sample after pretreatment using filter paper was ready to use to further evaluate separation performance of NF270 membrane. The average permeate flux of batik wastewater was 48.55 dm^3/(m^2·h), which was lower than that of indigo/salt dye mixture solution (64.78 dm^3/(m^2·h)). It could be caused by complex composition of batik wastewater – dye components, inorganic salts, and macro pollutants led high fouling effect, as presented in Table 1. However, as shown in Table 4, NF270 demonstrated appropriate performance with quality standards in terms of TSS, COD, and BOD removal efficiency. This implies that NF270 membrane can be considered as a promising technology in batik wastewater treatment.

Table 4

Quality of batik wastewater before and after treatment with NF270 membrane at TMP of 0.4 MPa

Parameter	Feed (after pre-filtered)	Permeate	Quality standards of wastewater[a]
pH	8.05	7.81	6.0–9.0
Colour	Black	Slight coloured	–
COD, mg O_2/dm^3	362.5	83.8	<150
BOD, mg O_2/dm^3	182	35.2	<60
TSS, mg/dm^3	68	29	<50

[a]Regulation of Central Java Province, Indonesia, No. 5, 2012 (concerning wastewater quality standards).

4. CONCLUSIONS

Three commercial NF membranes were evaluated based on their performance during treatment of model dye solutions as well as hand-drawn batik wastewater containing indigo dye. The obtained results showed that the high TMP and the increased indigo dye concentration significantly affect the permeate flux of NF270 membranes. The effectiveness of the NF270 membrane was also confirmed by the result of the visualization images of NF270 membrane permeate, which was slightly coloured compare to water. Meanwhile, the accumulation of dye particles on the TS40 membrane surface is more apparent than the deposition of dye particles on the NF270 and XN45 membrane surfaces (determined from the SEM results). However, all the NF membranes showed high dye rejection (98–99%) but different permeate flux. The NF270 membrane exhibited the highest flux, which is ca. 2–3 times higher than that of TS40 and XN45 membranes. This study also reported that the solution pH did not significantly change from the feed to the permeate solution, with the pH value of the permeate of all the NF membranes being within a range of 7.02–7.27. At 0.4 MPa, the NF270 membrane showed high rejection of dyes when indigo/remazol dye mixtures and indigo dye/NaCl solutions were treated. The NaCl removal was obtained in the range of 34–38% by NF270 membrane during indigo/NaCl filtration process. The practical applicability of NF270 membrane for real wastewater treatment entered into quality standards in terms of TSS, COD, and BOD removal efficiency. Based on the result obtained, the NF270 membrane showed favorable performance for treating batik effluent.

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