

Synthetic reactive dye wastewater treatment by using nano-membrane filtration

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ABSTRACT

The batik industry is considered to be one of the largest textile cottage industries in the Southeast Asian region. Batik processing utilizes wax as a physical resistant and consumes a large amount of water during dyeing, fixing, and washing process; thus, generating harmful wastewater including dye, wax, and other auxiliaries. Respectively, an efficient wastewater treatment method is deemed necessary to meet legal emission standards. In this study, application of polyamide nano-membrane to remove dyes was evaluated for five different fiber reactive dyes' wastewater, namely reactive blue 15, reactive red 194, reactive yellow 145, reactive black 5, and reactive orange 16. The discussed dyes were tested in low concentration (16 mg/l) during a 60 min filtration process. The efficiency of filtration was calculated based on pre-process and post-process analytical experiments. The flux for all the samples ranged between 7.8 and 9.2 ml/cm²s. The permeate pH value of the samples was observed to slightly increase, within a range of 6.4–7.1. Conductivity measurements for the samples indicated dramatic reduction for each sample dye solution compared to the sample from the feed to permeate during the filtration runs. Chemical oxygen demand value in the permeate samples was reduced to zero, representing a dye removal efficiency of more than 90%, thus successfully meeting the environmental legal standard.

Keywords: Nano-membrane filtration; Batik industry; Wastewater treatment; Reactive dye

1. Introduction

It is a well-known fact that textile industries require significant amount of water [1]. The process generates large volume of wastewater containing harmful chemicals (dyes and auxiliaries) to the environment if discharged untreated [2,3]. Batik as the largest cottage industry plays an important role in the cultural value of the local families while being a major

source of their income. It is also directly ingrained into the livelihood of families who live in the Southeast Asian region specifically Malaysia and Indonesia [4]. Batik factories generate a large amount of wastewater that includes wax, resin, sodium silicate, and dyes similar to other textile processes. Unfortunately, many traditional textile industries, including the local batik factories, discharge their wastewater into the environment without appropriate treatments [4–6]. Presence of dyes is one of the main concerns of the wastewater from batik factories. The most commonly used dyes in

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all textile industries are fiber reactive dyes [2,6–8]. Generally, during this dyeing process, the amount of water and reactive dyes per kilogram of cloth ranges between 70 and 150 l, and 30 and 60 g, respectively [9,10]. Commonly 10–50% of the used reactive dyes exist as unfixed dyes in wastewater [11]. However, the amount of dye usage in the batik industries follows the range of 10–20% of conventional dyeing techniques, since brush dyeing is applied. Remazol and Procion MX reactive dyes are popular choices in this particular industry due to their specific physical and chemical properties [7,12].

Primary pre-treatment is capable of removing wax, resins, and other auxiliaries [13]; however, treating the reactive dyes' wastewater remains to be a significant issue in batik industry. Due to the aforementioned facts [14,15], early conventional wastewater treatment techniques, such as Fenton reagent [16,17], ozonation [18], photochemicals [19], electrochemicals destruction [20], activated carbon [21,22], oxidation [23], ion exchange [17,24], and membrane, were utilized for the treatment process [3,6]. Among all conventional treatment methods, the membrane process is considered to be the most appropriate water and wastewater treatment method [12,14]. Moreover, simplicity of usage for membrane plus ease of replacement and cartridge properties during the treatment cycle can play a significant role for membrane application in water and wastewater treatment industries [14,23,25].

Among all types of applicable membrane filters [14,26], the nano-filtration (NF) is widely applied and used in textile industry processing specifically for the treatment of wastewater from the dyeing process due to the pore sizes, high efficiency, low process cost, and user-friendliness [27–33]. Riera-Torres et al. [34] reported that the combination of membrane filtration with coagulation–flocculation treatments showed an efficiency of almost 100% dye removal in different studies of reactive dyes' solutions. Aouni et al. [35] investigated the application of NF and ultra filtration (UF) in textile wastewater treatment in terms of parameters retention such as conductivity, Chemical oxygen demand (COD), and color rejection. High COD and conductivity removal rate (>80% and >90%) was found by UF and NF treatment, respectively. The reactive dyes' color rejection was obtained at the rate of more than 90% by NF membrane filtration treatment. Sun et al. [36] applied a self-prepared thin-film composite NF membrane via interfacial polymerization on a dual-layer hollow fiber membrane surface during the dye removal of textile wastewater. Their findings indicate greater rejection rate (>99%) due to physical and chemical properties of membrane surface while encountering positive and negative groups of

reactive dyes. Application of NF with micro-filtration (MF) pre-treatment stages showed the average values of 100, 60, and 35% for color rejection, COD, and salinity removal, respectively, for textile wastewater treatment [1]. Petrinic et al. [27] applied NF for treating textile printing wastewater containing reactive dyes. They observed high dye retention rates for all tested dyes' samples (>99.4%) plus the organic substances removal rate ranging between 20 and 50%. Application of hybrid membrane treatment techniques (MF/NF) in selected textile reactive dyeing bath effluent in different textile industries was reported by Tahri et al. [37]. The results indicated almost 99% removal percentage of colors plus 0.2 NTU of turbidity value. Avlonitis et al. [38] used NF membrane treatment techniques for simulated cotton wastewater treatment. Their results indicated complete de-colorization and feed effluent salt rejection.

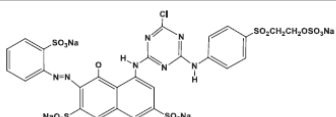
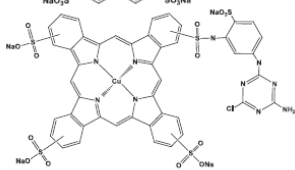
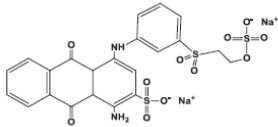
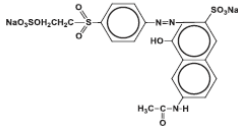
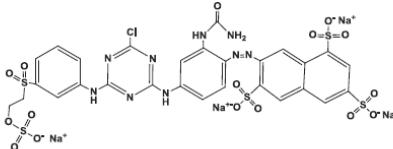
Correspondingly, fouling is the major common problem in all types of NF membranes. Generally, fouling decreases the membrane flux during the separation processes either on the surface of a membrane or within its pores [39]. Among these factors, colloidal fouling due to colloid formation on membrane surface by effluent contaminants, such as dyes and silica, is the main critical issue during NF membrane application for textile dyeing wastewater treatments [40]. However, polyamide components are mostly applied in nano-membrane fabrications due to their chemical and physical properties such as higher thermal stability and excellent mechanical properties [41]. Consequently, they attract reactive dye groups on the membrane surface. This property not only performs as the most efficient dye separation but also can increase fouling during the separation process. Accordingly, the NF membrane has been chosen in this study to investigate the application of accessible commercial nano-membrane in low concentration of batik dye wastewater treatment after brush dyeing process. Since the concentration of existing dyes in related wastewater is less than other textile dyeing methods, applying these types of nano-membrane wastewater treatment methods can be reasonable and effective.

2. Experimental section

2.1. Materials

The fiber reactive dyes that were used in this study were obtained from TMS ART Company (KL, Malaysia), and were used directly without any purification. The molecular weight (MW), structure, and the other properties of the dyes are shown in Table 1.

Table 1
The dyes properties and characterization

Commercial name	C-I	λ_{\max} (nm)	MW (g/mol)	Molecular formula	Structure formula
Reactive red 194	C.I. 18214	505	984.21	$C_{27}H_{18}ClN_7Na_4O_{16}S_5$	
Reactive blue 15	C.I. 74459	674	1282.96	$C_{41}H_{19}ClCuN_{14}Na_4O_{14}S_5$	
Reactive black 5	C.I. 20505	600	626.549	$C_{22}H_{16}N_2O_{11}S_3 \cdot 2Na$	
Reactive orange 16	C.I. 17757	492	617.54	$C_{20}H_{17}N_3Na_2O_{11}S_3$	
Reactive yellow 145	C.I. 93050	419	1026.2	$C_{28}H_{20}ClN_9O_{16}S_5 \cdot 4Na$	

2.2. Equipment

The membrane filtration device was used to study the capability of nano-membranes in removing reactive dyes from synthetic dye wastewater. The nano-membrane filtration device was locally designed and fabricated. The flat sheet membrane module that was used was made from stainless steel. The metering pump was used to provide the flow pressure. The schematic diagram of the membrane filtration device is shown in Fig. 1.

The membrane chosen for this study was 4040-TS80-TSF-sheet membrane manufactured by TRISEP Corporation, CA, USA. The membrane was made from aromatic polyamide with non-woven fiberglass wounded fibers support. According to the manufacturer, the MW cut off for the membrane was 200 Da. The rejection capabilities of the membrane specified by the manufacturer are shown in Table 2.

2.3. Sample preparation

Each dye sample was prepared based on the characteristic of the actual batik dye wastewater (0.5–30 mg/l). From that, synthetic dyes solution was prepared with a concentration of 16 mg/l in Milli-Q ultrapure water. Working volumes of 21 were prepared for each dye liquor bath. The operating parameters for each test run were set at 25°C, 5 bar, and 60 min for temperature (T), pressure (P), and time, respectively. The permeability of membrane used in each filtration of dye solution was tested by ultra-pure water in a 30 min filtration run.

2.4. Sample coding

To simplify the presentation of the data, the dye samples used in this study were coded in the order as shown in Table 3.

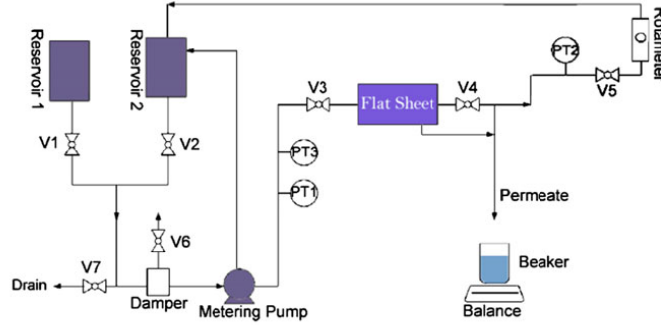


Fig. 1. NF apparatus setup.

Table 2
Nano-membrane characterization (based on specification given by manufacturer)

Model	Average salt rejection (%)	Minimum salt rejection (%)	Permeate flow GPD (m ³ /d)*
4040-TS80-TSF	99.00	97.00	2,000 (7.0)

*Performance is based on the following test condition: 2,000.0 ppm MgSO₄, 110.0 psi, 25°C, 15% recovery, pH 8.0, 30 operation.

Table 3
Dye samples coding

Solution No	type	Dye	Code
1	Single	Reactive yellow 145	Y
2	Single	Reactive blue 15	TB
3	Single	Reactive orange 16	O
4	Single	Reactive red 194	R
5	Single	Reactive black 5	NB
6	Mixture	Reactive yellow 145 + Reactive blue 15	M2
7	Mixture	Reactive yellow 145 + Reactive blue 15 + Reactive orange 16	M3
8	Mixture	Reactive yellow 145 + Reactive blue 15 + Reactive orange 16 + Reactive red 194	M4
9	Mixture	Reactive yellow 145 + Reactive blue 15 + Reactive orange 16 + Reactive red 194+ Reactive black 5	M5

2.5. Analytical methods

In this study, low-range concentrations of synthetic dye wastewater treatment in the shortest possible time were tested for individual dye samples filtration process. The effects of the treatment parameters, such as flux, rejection, filtration efficiency, pressure difference (ΔP), pH, COD, and conductivity, on the nano-membrane filtration process in fixed filtration flow pressure were tested for 60 min. It is duly noted that in every filtration run of the same dye sample, the same membrane was used.

The feed dye solutions and permeate color intensity were measured by Thermo Scientific Genesis 20 visible spectrophotometer at a visible wavelength (325–750 nm), and analyzed by integration with absorbance curve. Rejection efficiencies (R %) were calculated using Eq. (1):

$$R\% = 1 - \frac{C_p}{C_f} \times 100 \quad (1)$$

where C_f and C_p are feed and permeate dye concentrations, respectively.

The pH and conductivity range of each dye solution and permeate were measured using a Metrohm pH meter analyzer model 827(Swiss) and Cheetah multi parameter meters model DZS-708(China), respectively. The pure water flux (PWF) of each membrane, together with the dye solution, was observed and recorded using flux equation software.

The COD of each sample was tested for both before and after filtration using the HACH portable COD spectrophotometer, model DR/890(USA). Each experiment was repeated at least three times in order to ensure its accuracy and reproducibility.

3. Results and discussion

3.1. The effect of dyes on flux performance

The comparison between the PWFs and the dyes permeate fluxes for each filtration runs are shown in Fig. 2(a) and (b). From the Figures, the permeate fluxes for all of the single dye samples were within the range of 8.1–9 ml/cm²s. The lowest and highest flux values for single dyes goes to reactive black 5 (navy blue) and reactive blue 15 (turquoise blue), respectively. For dye mixture samples of nano-filtration, the highest flux value was observed for the mixture of five dyes. However, the other mixtures of dye samples have also showed the same pattern in the flux values.

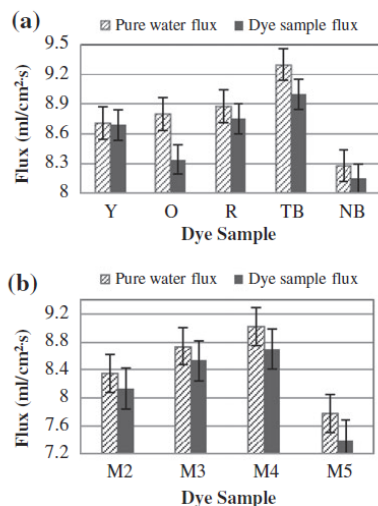


Fig. 2. Dye samples flux (a) single dye and (b) mixture dye.

These reductions in permeate fluxes for every filtration were due to the effect of capturing and trapping of the dye molecule groups into the membrane pores during the filtration processes. This occurs due to the formation of a partial filtration cake and gel layer on the membrane surface area, as well as a reduction in the fractional pore size and blockage by compounds absorbed via the membrane pores during the filtration cycle, thus decreasing the fluxes. The result is also consistent with the previous studies [42].

Previous studies have shown that the fouling during the treatment cycle will result in the reduction of flux permeation, thus decreasing the membranes' performance [43,44]. However, the changes of flux recorded for this experiment were unnoticeable, which can be concluded that the fouling phenomenon in this study was negligible.

Since the pore distribution on the nano-membrane surface area base was not homogenous, the initial PWFs of each filtration run recorded diverged between each membrane. Due to this reason, the normalized values between the fluxes of dye permeate and pure water were used as a basis of comparison.

Fig. 3 represents the relative fluxes for nano-filtration experiment carried out to all of the dye samples. The highest relative flux decline was observed for the orange dye followed by the mixture of five dyes (M5). The reactive orange dye sample showed a higher electrostatic charge behavior compared to the other single dye samples, since it contains higher value of OSO₃Na, SO₃Na, and CH₃CONH groups. Moreover, SO₂CH₂CH₂ and also β-sulfato derivative groups are the most important vinyl sulfone-masking group, with higher reactivity performance, existing in reactive orange dye. Based on these aspects, the reaction rate of reactive orange dye in constant concentration value (16 mg/l) was rather higher than other single dye samples [45].

Furthermore, a total number of charged groups in M5 were higher than the other mixtures since it contains all single dyes with same ratio. Accordingly, the

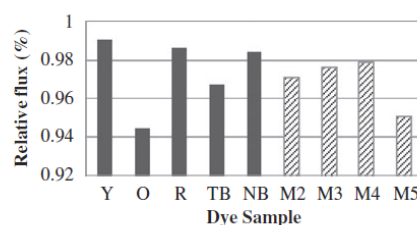


Fig. 3. Relative flux of dye samples.

trapping value of both orange and M5 dyes in membrane pores resulted significant decline in the fluxes due to the Donnan effect and rejection transpired phenomena [46].

On the other hand, the percentage of relative fluxes in M3 and M4 are slightly higher than M2 (Fig. 3). This phenomenon occurred due to the molecular size and weight in M2, which is rather higher. Moreover, in comparison with other mixtures, higher concentration ratio of reactive groups in Turquoise Blue and Yellow reactive dyes in M2 supports the mentioned reason, although hydrolyze occurs in separation process by leaver groups (especially SO_3Na groups) [45]. Accordingly, a higher level of fouling can be faced in M3 and M4.

3.2. The effect of nano-membrane filtration on the final pH of permeate

The pH value was measured for both feed dye solution and permeates of all tested dyes (Table 4). The result demonstrates a minor increase in the pH from the feed dye solution to permeate in all singles and mixtures of the dye samples. This can be explained by the reduced amount of reactive dyes found in the permeate, as a result from the filtration process. The removal of tested reactive dyes with acidic properties has caused the permeate samples' pH behaviors to enter the neutral region during the filtration process.

Additionally, this particular polyamide nano-membrane demonstrated negative charges when it reacts with the reactive dye solution, with less acidic characterization [47]. Then, the reactive dyes bond with polyamide surface by setting leaving groups free in acidic environment. The existing leaving groups in this reactive dyes contained Cl, OSO_3Na , SSO_3Na , OPO_3Na_2 , and SO_3Na components [45].

Consequently, the positive charges of reactive groups in dye molecule reacted with the membrane surface and ionic groups. It can be justified by Donnan exclusion effect [46], and rejection transpired [10,12,48]. Based on these phenomena, ethyl sulfones and aliphatic amines in the β -position were also transformed into leaving groups, which allow the lower

reactive groups to pass through the nano-membrane [45].

However, major differences of pH between feed and permeate samples were observed in reactive red 194 dye, and a mixture of reactive blue 15 and reactive yellow 145 for single dye solution samples and dyes mixture, respectively. This can be explained by the existence of chlorodiamino s-triazine reactive groups in dye samples structures, which exhibited strong reaction affinity behavior, and absorption to the nano-membranes' polyamide effective surface layer, rendering the reactive groups with acidic behavior in the permeate samples to be reduced [49].

On the other hand, the final pH of the samples taken from retentate was lower compared to the initial pH feed solution in each of the dyes samples. This was caused by the increased concentration of dye groups in reduced amount of water media in retentate compared to the feed dye solution.

3.3. The rejection and efficiency characteristic of filtered dye samples

Fig. 4 represents the high efficiencies of the nano-membrane in the dye molecule rejection process. The data were derived from the spectrophotometer curve in the visible range for each reactive dye solution samples, both pre- and post-filtration processes.

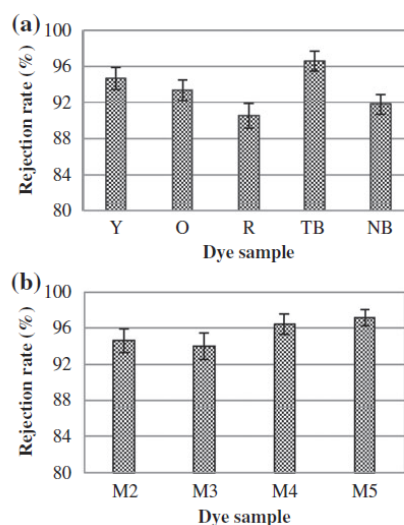


Fig. 4. (a) and (b) Single dye and mixture dyes samples rejection rate.

Table 4
Dye samples pH

Dye	NB	R	O	Y	TB	M2	M3	M4	M5
Feed pH	6.5	6.5	6.7	6.6	6.5	6.7	6.4	6.3	6.5
Permeate pH	6.9	6.8	6.9	6.8	6.8	7	6.6	6.5	6.8

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