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Development of the ultra/nano filtration system for textile industry wastewater treatment

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Abstract. Advances in industrial development and waste management over several decades have reduced many of the impacts that previously affected ecosystems, however, there are still processes which discharge hazardous materials into environments. Among industries that produce industrial wastewaters, textile manufacturing processes play a noticeable role. This study was conducted to test a novel continuous combined commercial membrane treatment using polyvinylidene fluoride (PVDF), ultrafiltration (UF), and polyamide (PA) nanofiltration (NF) membranes for textile wastewater treatment. The synthetic textile wastewater used in this study contained sodium silicate, wax, and five various reactive dyes. The results indicate that the removal efficiency for physical particles (wax and resin) was 95% through the UF membrane under optimum conditions. Applying UF and NF hybrid treatment resulted in total effective removal of dye from all synthetic samples. The efficiency of sodium silicate removal was measured to be between 2.5 to 4.5% and 13 to 16% for UF and NF, respectively. The chemical oxygen demand in all samples was reduced by more than 85% after treatment by NF.

Keywords: textile; wastewater treatment; dye removal; nanofiltration; ultrafiltration

1. Introduction

In the last century, the increased global population partnered with growth in industrial development to support that population has caused a rise in demand for sustainable sources of clean water for drinking, hygiene, waste management and industrial processes (Luukkonen and Pehkonen 2017). Human activities, including industrial development, have become large water consumers and, subsequently wastewater producers. Treated and untreated wastewater has been discharged directly to the environment leading to destructively effects on fauna and other ecosystem components (Bagal and Gogate 2014, Liang, Sun *et al.* 2015, Zia, Watts *et al.* 2017). Rising awareness of the effects of wastewater discharge on ecosystem health has led to a push for better wastewater treatment across all industries.

The textile wet-processing industry produces large volumes of hazardous wastewater (Rashidi, Sulaiman *et al.* 2013, Liang, Sun *et al.* 2014, Holkar, Jadhav *et al.* 2016). Due to population distribution, economical parameters, and societies' eagerness (Stengg 2001), some textile wet-processing such as those involved in the batik industry, have become popular 'cottage industries' in South East Asian regions, specifically Indonesia and Malaysia (Legino, Sajar *et al.* 2016). A critical issue with having local small and medium enterprises (SMEs) involved in textiles in those regions is the discharge of untreated wastewater (Rashidi, Sulaiman *et al.* 2013, Birgani, Ranjbar *et al.* 2016). Among the variety of environmental effects caused by chemical components in textile wastewater, dyes and their chemical and physical effects in the effluents are the most concerning (Saha, Hossain *et al.* 2014, Raman and Kanmani 2016). The specific dyes in textile wet-processes have chemical and physical properties (pH, temperatures and others), that are fibre reactive but harmful to ecosystems (Amour, Merzouk *et al.* 2016, Ceretta, Vieira *et al.* 2020). The alkaline environment during fixation stages is necessary for reactive dye molecules to form covalent bonds with fibres. Generally, sodium silicate provide the alkaline environment during textile production processes (Tawfik, Zaki *et al.* 2014).

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Some textile manufacturing processes, such as that involved in the batik style, require the use of wax to create artistic elements (Kim 2013). While more than 80% of wax used in batik processes can be reclaimed from wastewater, the remaining amount cannot be removed by conventional methods or suspension phases of treatment (Rashidi, Sulaiman *et al.* 2015, Rashidi, Sulaiman *et al.* 2020). As a result, there is a need for effective pre-treatment staging to ensure that wax removal from wastewater occurs (Rashidi, Sulaiman *et al.* 2020). Although some studies have investigated new chemical, biological and physical wastewater treatments, these investigations were based on laboratory models or exemplars, and were conducted as pilot studies (Sathian, Radha *et al.* 2012, Köneçoğlu, Toygun *et al.* 2015, Asadollahfardi, Zangooei *et al.* 2018, Shoukat, Khan *et al.* 2019).

Pandian, Huu-Hao *et al.* (2011) investigated the use of bacterial granule methods for treatment of textile wastewater. They used bacterial granules on actual batik wastewater within constant operational conditions (anaerobic condition, room temperature, 14 days). The respective results showed that the method achieved good reactive dye removal results (> 96%) even though the chemical oxygen demand (COD) efficiency was in the moderate range (66.7%). The solar photocatalytic decolorization and detoxification wastewater treatment method for batik effluents was investigated by (Sridewi, Tan *et al.* 2011). The use of titanium dioxide (TiO_2) immobilized on poly-3-hydroxybutyrate (P_3HB) film had almost complete reactive dye removal, and more than 80% COD efficiency (Sridewi, Tan *et al.* 2011).

In addition to these chemical and biological treatment methods, other studies have focused on membrane-based treatment, as one of the most applicable treatment techniques, in textile wastewater treatment areas (Xia, Wang *et al.* 2017). Emulsion liquid membrane with support of polypropylene was used by (Harruddin, Othman *et al.* 2014) for batik dye wastewater in a laboratory scale. They found more than 99% removal of used reactive dye (reactive Black B) during the 3 hours' operational time (Harruddin, Othman *et al.* 2014). Some other types of membrane treatment techniques such as membrane bioreactors (MBR) are used to treat textile wastewater (Mousavirad and Akbari 2017). Due to operational issues, MBRs cannot perform industrial-scaled and economically-acceptable processes yet. The listed treatment techniques demonstrate operational advantages in textile wastewater treatment, however, processing difficulties, cost, and scaling issues prevent their widespread application in local factories. In addition, these methods are not efficient in actual wastewater treatment due to the inability to remove physical contaminants from the wastewater.

The lack of effective and easily implemented solutions highlights the necessity for continuing research to develop an effective wastewater treatment technique that will remove all harmful chemical and physical components in textile wastewaters. An emergent treatment is the use of nanomembrane technology for batik processing (Abid, Zablouk *et al.* 2012, Arslan, Eyvaz *et al.* 2016). Pre-treatment stage work on nano membranes in previous studies have demonstrated the potential to remove most physical particles, however, some wax particles remain (Rashidi, Sulaiman *et al.* 2020). These particles, along with other chemical components contribute to blockages, high fouling, and other negative operational parameters in nano membrane treatment process. Despite advances in treatment, the persistent presence of wax, resin and other fixing agents in wastewaters from batik processes suggests that efficient pre-treatments to remove physical components are needed. These treatments may contribute to reduced contaminants, but also may assist in improving the overall efficiency and economics of batik processes by avoiding blockages and reduction in the membrane flux value during nano filtration.

Therefore, this study was conducted to test a hybrid membrane wastewater treatment consisting of commercial UF/NF membranes to treat physical and chemical components from synthetic wastewater samples to meet local and international discharge standard (Standard B) of the environmental quality regulation on industrial effluents (Tüfekci, Sivri *et al.* 2007).

2. Materials and methods

This study uses an experimental method to test whether UF and NF are more effective than conventional methods for removal of physical components in batik processing wastewaters. Experiments used the UF and NF characteristics against a variety of temperature, pH, chemical oxygen demand, dye, wax and resin, and sodium silicate measurements with simulated samples provided based on actual samples from batik processing company. The experiments were exploratory in nature, and act as a pilot study to encourage further work, however, whenever possible, we simulated the conditions of a real processing plant.

2.1 Chemicals

The wastewater samples used in this study were synthesized using wax, sodium silicate, and five different types of fiber-reactive dyes which were provided by TMS ART Company (KL, Malaysia), and used without pre-purifications in order to more realistically simulate the process of treatment according to the actual parameters of batik wastewater. The dyes included: Reactive Red 194 (R), λmax: 505 nm; Reactive Blue 15 (TB), λmax: 674 nm; Reactive Black 5 (NB), λmax: 600 nm; Reactive Orange 16 (O), λmax: 492 nm; Reactive Yellow 145 (Y), λmax: 419 nm; in mixtures of sodium silicate (Na_2O_3Si); and paraffin wax ($C_{20}H_{42}$–$C_{40}H_{82}$).

2.2 Sample preparation

Each wastewater sample was derived from pre-treated synthetic effluents taken after baffle tank pre-treatment stages as described in our previous studies (Rashidi, Sulaiman *et al.* 2020). Two litres of synthetic pre-treated wastewater samples were prepared for each separation run. All samples consisted of fibre-reactive dyes, sodium silicate and wax particles (a combination of paraffin wax and resin

Table 1 Ultra and nanofiltration membrane specification

Membrane Specification	UF	NF
Membrane type	FP200	TS80
Material	PVDF	Aromatic PA
max. pH range	1.5-12	2-11
max. pressure (bar)	10	14
max. temperature (°C)	80	45
apparent retention character/mwco	200,000 MW	200 Da
hydrophilicity	1	-
solvent resistance	+++	-

Table 2 Pre-treated textile wastewater characterization

Parameter	Unit	Actual value
temperature	°C	45-55
pH	-	9.2-9.5
COD	$mg.L^{-1}$	1290-1420
dye	$mg.L^{-1}$	15.3-15.6
wax and resin	$g.L^{-1}$	0.35-0.65
sodium silicate	$g.L^{-1}$	0.67-0.71

mixtures). It should be noted that the dye, sodium silicate and wax concentrations before pre-treatment stage by baffle separation tank were 16 $mg.L^{-1}$, 1 $g.L^{-1}$ and 7.7 $g.L^{-1}$, respectively. Each experiment consisted of continuous treatment runs of 120 and 60 minute duration for ultra- and nanomembranes (UF and NF, respectively). The timespan was selected to represent conditions during actual processing of batik textiles. The UF and NF membrane characteristics are detailed in Table 1.

2.3 Ultra and nano filtration membranes

The UF and NF membranes chosen for the treatment stages were polyvinylidene fluoride (PVDF) FP200 tubular ultrafiltration membrane, manufactured by PCI Membrane, USA; and 4040-TS80-TSF-sheet membrane (TRISEP Corporation, CA, USA). The membrane properties and the pre-treated samples chemical and environmental parameters characteristics are shown in Tables 1 and 2, respectively.

Due to heterogeneity of the pore distribution on the UF membrane surface, the initial pure water fluxes (PWFs) of each run were not constant. Therefore, the normalized value between the fluxes of synthetic textile wastewater permeates and pure water was considered as the reference indicators.

2.4 Ultrafiltration membrane module set-up

The ultrafiltration device used in this study was designed in-house, consisting of a stainless steel tubular membrane module with peristaltic pump (HV-07522-20, Cole-Parmer, USA), fixed pressure gauges, two tanks and a magnetic stirrer. This set-up mimicked the actual industrial process and was designed and built locally for this process. Every test was repeated three times for reducing the uncertainty and every time with the new membranes.

2.5 Nanofiltration membrane module set-up

In order to analyse the effectiveness of nanofiltration membrane for removal of reactive dyes from the wastewater samples, the NF setup was locally designed and fabricated. The material of the membrane module was stainless steel. The metering pump (C921, LMI Milton Roy, USA), was used to induce the flow and the necessary pressure.

2.6 Analytical methods

A spectrophotometer (Genesis 20, Thermo Scientific, USA) at a visible wavelength (325-750 nm) was used to measure the effectiveness of removal of dye, sodium silicate and wax. Sodium-silicate removal efficiency was tested within each experiment using established silicate (silicic acid) test reagents (MERCK, Germany); measured against the related absorption curve analysed by a UV spectrophotometer (Perkin Elmer Lambda 25 UV/VIS Instrument L6020060, USA).

In order to measure pH and COD range of each synthetic sample a Metrohm pH meter analyzer, model 827 (Switzerland) and HACH spectrophotometer, model DR/890 were used. Furthermore, in the graphs and tables which indicate the data of each treatment run, BU, AU, BN and AN are used as the abbreviations of before and after ultra- and nanofiltration, respectively. The operating parameters for ultra- and nanofiltration test runs were set at: 5 bar, 120 minutes and 1 bar and 60 minutes for pressure and time, respectively. All test runs were conducted at 25°C and 1 $L.h^{-1}$ for temperature and flow rate. Remarkably, each experiment was repeated three times in order to ensure its accuracy and reproducibility in both UF and NF stages.

3. Results and discussion

3.1 Ultrafiltration flux performance

The comparison between the flux values for each synthetic wastewater samples filtration runs are shown in Figure 1. The related fluxes in all the samples follow the same trend within the range of 20–100 $L.m^{-2}$ h^{-1}. The minimum and maximum values of dye samples flux belonged to reactive red 194 (R) and reactive yellow 145 (Y), respectively (Figure 1). The reduction value in all dye samples illustrated the same trend over the filtration time which may be related to the trapping phenomenon in the membrane processes (Karin and Hanamura 2010). Previous researchers have found similar results, for example, (An, Guo *et al.* 2017) reported that permeates were mainly due to physical particles like wax and resin trapped in the pores of the membrane during the filtration process. These particles form a filtration cake that additionally contains silica, and that filtration cake supports the creation of a gel layer from dye groups on the surface of the membrane (An *et al.*, 2017). The reduction of flux rates could also be partially

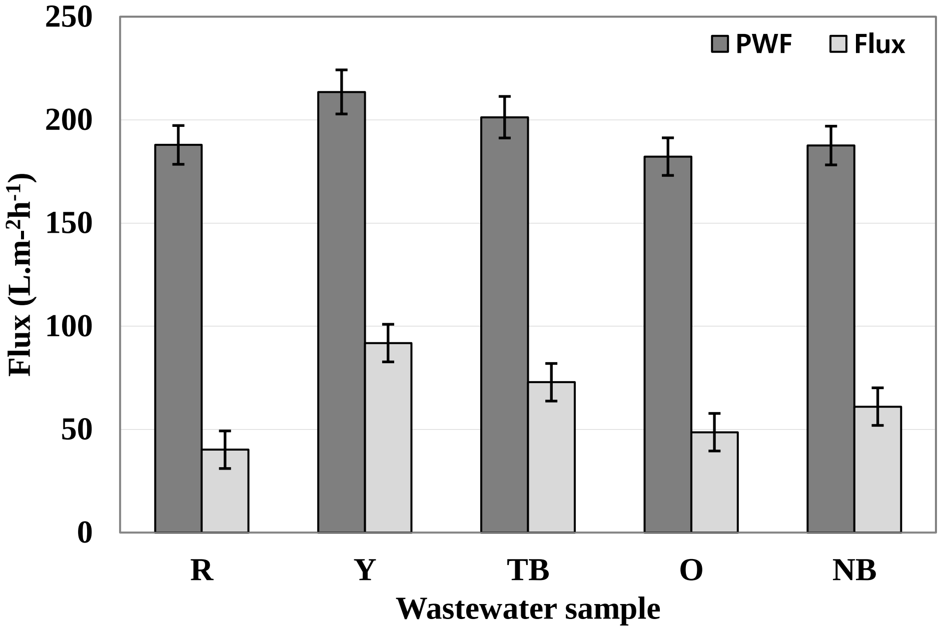

Fig. 1 Dye samples flux ratio by PVDF membrane ultrafiltration
*NB: Reactive black 5, O: Reactive orange 16, R: Reactive red 194, Y: Reactive yellow 145, TB: Reactive blue 15

a result of descending fractional pore size and blockages from existing compounds in the samples as reported by (Porcelli and Judd 2010). A third contribution to flux reduction rates and membrane operational performance may be fouling ratios (Le-Clech, Chen *et al.* 2006, Sabouhi, Torabian *et al.* 2020). The observed range of flux rates, however, was similar for all tests, which suggests that beyond the make-up of the physical particles and chemical components in the wastewater, the PVDF tubular membrane physical properties plays a role. According to figure 2, PVDF membranes show the complete rejection for all dye samples which is a reason for wax particles having bigger sizes than the membrane pores. The achieved data of wax removal is in agreement with this phenomenon.

3.2 Wax removal efficiency

The wax removal efficiency of each pre-and post-treated samples with UF membrane are shown in Figure 2. Data indicated that the wax removal efficiency values in all synthetic samples were in the same range and the total difference between the highest and lowest value was immaterial (< 2%). Moreover, the highest wax removal efficiency in single dye wastewater samples are related to TB and R dyes with 96.1% and 95.7%, respectively. The results presented similar physical interaction within the wax particles and UF tubular membrane surface. This was due to the same ranges of wax particle size and concentrations in feed synthesized wastewaters in all samples. Additionally, chemical and physical properties of the PVDF membrane such as pore size, and hydrophilic and electrical charge (piezoelectric) behaviours showed good physical particles removal efficiency when dealing with wastewater samples (Lai, Groth *et al.* 2014). The wax removal efficiency when using the UF membrane application was more than 94% for all dye samples. This supported a recommendation for the wider uptake of PVDF tubular membrane filtration in textile wastewater treatments. The results also indicated that the remaining wax particles concentration in all treated samples were inconsequential for critical operational issues in further treatment (nanofiltration). The nanofiltration operational flux confirmed this phenomenon. The related results were in agreement with correlated scientific outcomes for the same pre-treatment technique via similar membrane used in other industrial wastewater treatments (Karakulski and Morawski 2011).

3.3 Sodium silicate removal efficiency

UF membrane application produced high wax removal efficiency, and also had an effect on the other existing chemical components in textile wastewaters. The sodium silicate removal efficiencies were enhanced through UF membrane treatment as indicated in Figure 3. The efficiency of removal of sodium silicate in all dye samples ranged between 95.4% (in the case of O) to 97.7% (in the case of NB) effective. The differences in related efficiency values were negligible (i.e., 2.3% and 4.6% for O and NB, respectively); that is, the variance can be explained by operational condition changes. The role of reactive dye properties such as constituent halogen elements like Cl and vinyl sulfone formation groups (OSO_3Na, SO_3Na, and CH_3CONH) still needs to be considered in future work.

Table 3 Dye rejection efficiency by PVDF ultrafiltration membrane

Type	*DP (%)	R	Y	TB	O	NB
Dye rejection efficiency (%)	±1.5	13	12	15.5	15.1	14

*Deviation percentage
** Detection limit (0.003A)

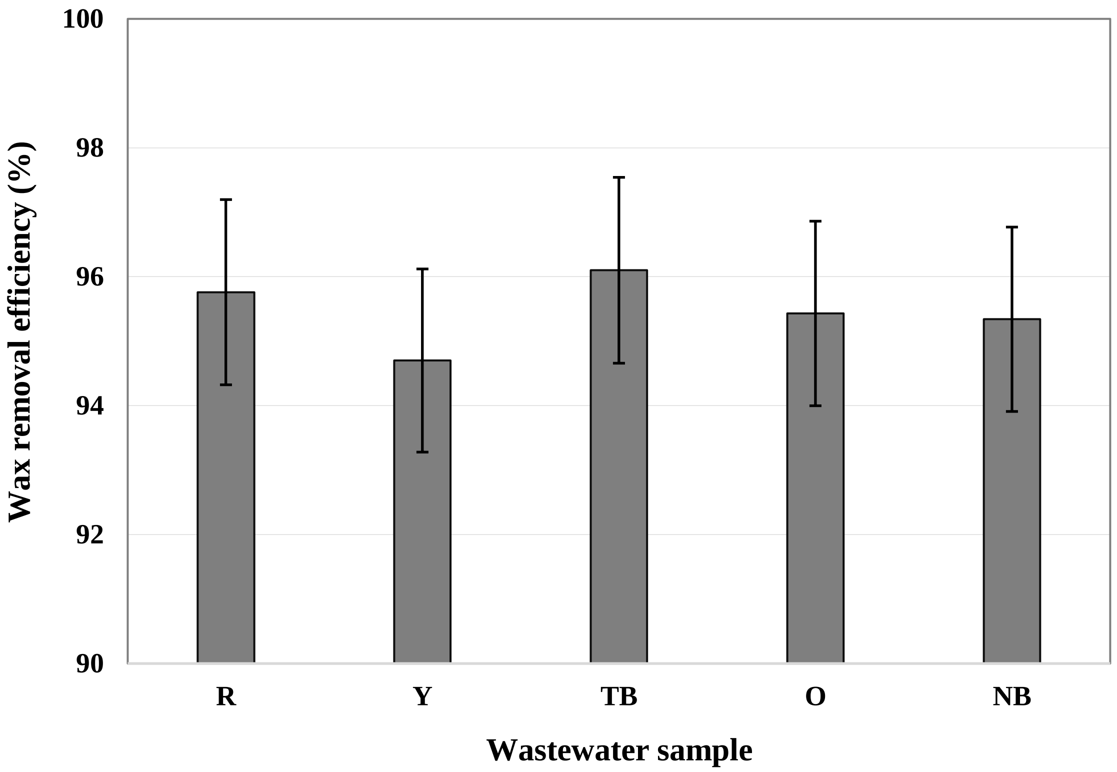

Fig. 2 Overall wax removal efficiency by UF application
*NB: Reactive black 5, O: Reactive orange 16, R: Reactive red 194, Y: Reactive yellow 145, TB: Reactive blue 15

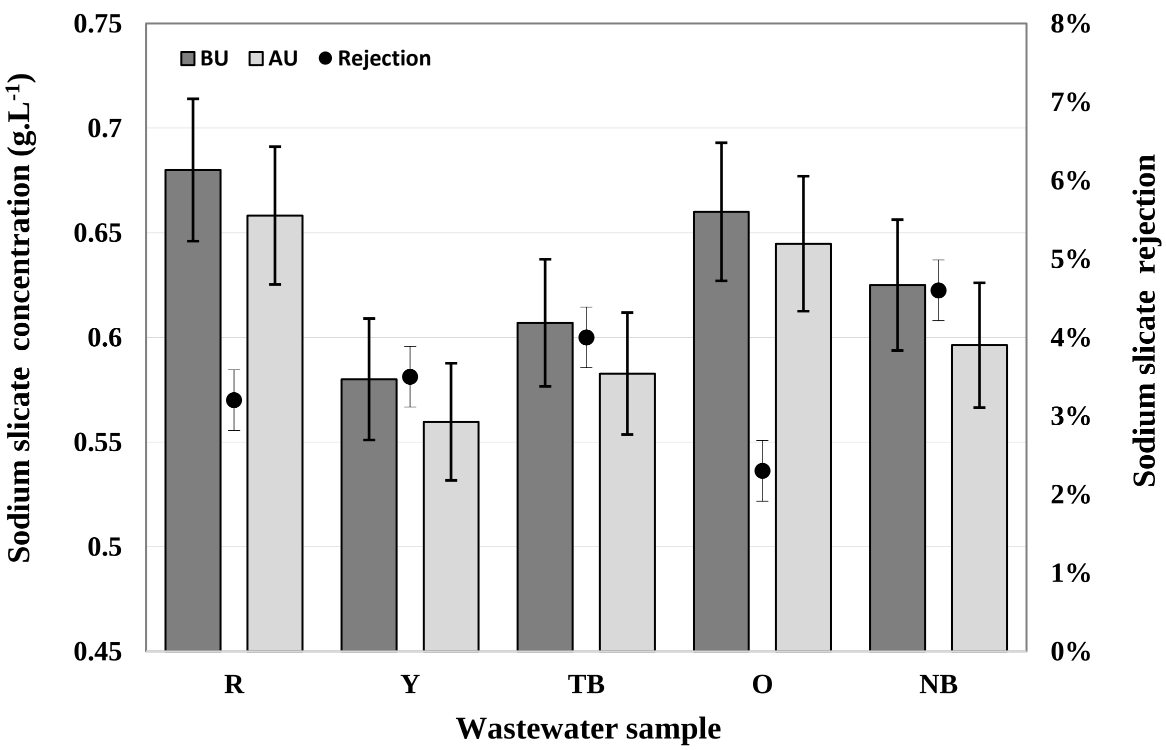

Fig. 3 Sodium silicate concentration and rejection efficiency in dye samples
*NB: Reactive black 5, O: Reactive orange 16, R: Reactive red 194, Y: Reactive yellow 145, TB: Reactive blue 15

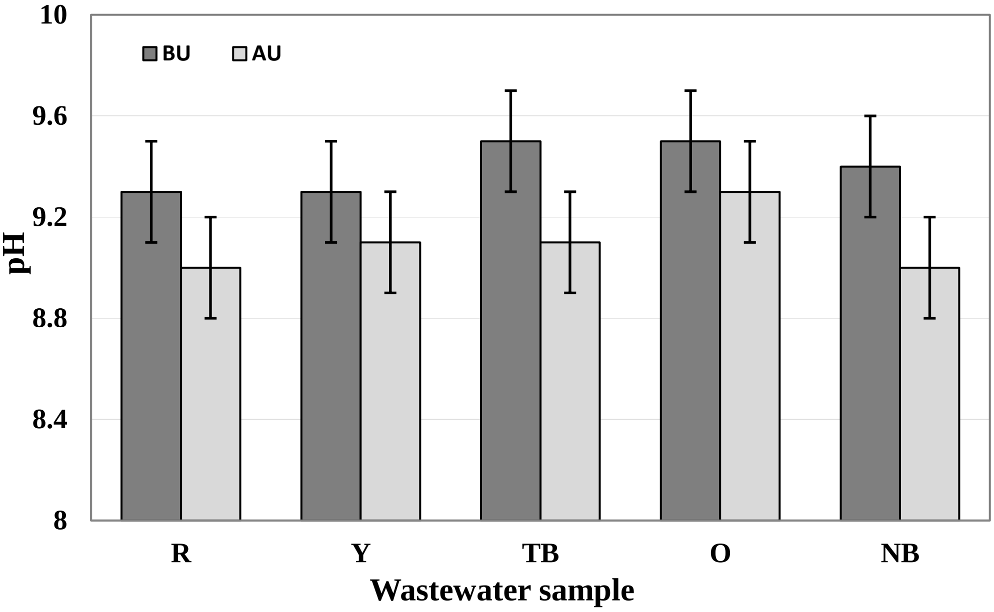

Fig. 4 pH changes in dye samples before and after UF
*NB: Reactive black 5, O: Reactive orange 16, R: Reactive red 194, Y: Reactive yellow 145, TB: Reactive blue 15

3.4 Dye removal efficiency

The relative dye rejection efficiency through the application of PVDF membrane for all dye samples is represented in Table 3. The change in dye concentration value in the feed and permeate synthetic wastewaters in each filtration run was insignificant for all dye samples. The highest dye removal within all single dye samples was that of TB dye with 15.5% efficiency. This occurred due to the dyes' molecular size and weight in contrast with tubular membrane pore size and chemical and physical characterization (Ciabattia, Cesaro *et al.* 2009). The dyes' small size compared with the membrane pore size, made the dye rejection by the application of ultrafiltration membrane negligible. The rejections results can be explained by wax particles physically trapped in membrane surface pores forming filtration cakes and decreasing membrane pore ratios.

In addition, PVDF membrane's piezoelectric behaviour played an important role in dye attraction during ultrafiltration membrane treatment. This factor can be explained by the different electrical charge behaviour which can accelerate the entrapment process. The reactive dyes' usage was based on reactive and leaving groups showing different absorption efficiencies through the UF treatment. The highest electrical charge belonged to O and NB dyes, which were due to the existence of strong leaving groups (Rashidi, Sulaiman *et al.* 2015). These samples demonstrated more dye rejection which is in agreement with the other related efficiency results such as sodium silicate and heavy metal rejection via UF treatment.

3.5 pH changes

Figure 4 displays the pH change for pre- and post-treatment of ultrafiltration membrane in synthetic wastewater samples which were in the range of 8.9 to 9.5. In spite of low chemical component rejection, specifically dye and sodium silicate through the usage of ultrafiltration membranes, the pH reduction is insignificant. pH reduction phenomenon can be explained based on piezoelectric behaviour and chemical and physical properties of PVDF membranes such as surface tension and pore size. The largest pH value decline belonged to TB, NB dyes with 0.4 units. This can be explained by higher sodium silicate component removal by the UF membrane in the related samples. Moreover, the other UF treatments achieved acceptable chemical and environmental parameters in all samples hence supporting the pH results.

3.6 COD changes

The COD values in each pre- and post-treatment by ultrafiltration membrane runs are displayed in Figure 5. Based on the results, COD reduction rate in all synthetic wastewater samples after the UF membrane treatment were in the range of 218 $mg.L^{-1}$ to 342 $mg.L^{-1}$. Higher rejection efficiency for chemicals including dyes, sodium silicate and wax could be contributing throughout the treatment. COD value increased considerably based on existing chemical auxiliaries in synthetic wastewater samples but the remaining wax particles can also affect COD parameters (Rashidi, Sulaiman *et al.* 2013). Hence, higher rejection of dye reactive groups and sodium silicate derivatives are in part explained by the active surface behaviour properties of the PVDF membrane. Previous work has demonstrated that reactive dyes have the highest effect on COD among other existing components, increasing it by forming active groups (Rashidi, Sulaiman *et al.* 2015). In addition, the dye groups reacted with water based on hydrolysis, which also increases COD. The largest decrease in COD value for

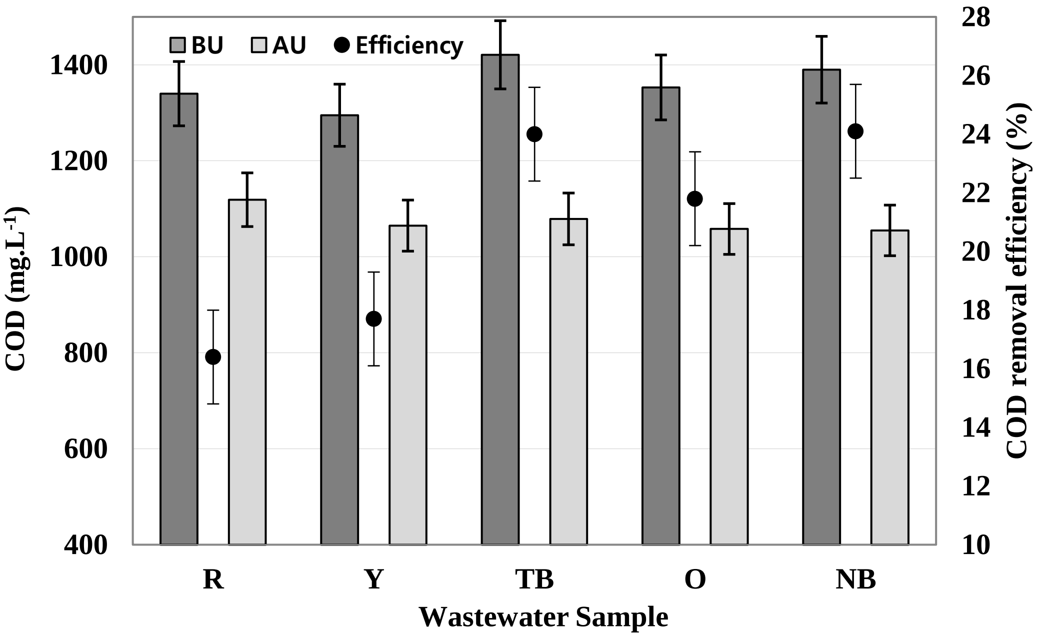

Fig. 5 COD changes and removal efficiency in dye samples before and after UF
*NB: Reactive black 5, O: Reactive orange 16, R: Reactive red 194, Y: Reactive yellow 145, TB: Reactive blue 15

single dye synthetic wastewaters after UF membrane treatment runs was for TB dye with 342 mg.L^{-1}.

The samples that resulted in more leaving groups. Higher COD reductions occurred with the NB and TB dyes samples. These results were due to more reactivity with other materials such as wax and sodium silicate as reported elsewhere (Denyer, Shu *et al.* 2007).

3.7 The NF membrane flux performance

Figure 6 compares the PWFs and the dye permeate fluxes in each run at the operational pressure of 5 bar. It showed that the permeate fluxes of all the dye samples were between 3.1 and 5.1 L.m^{-2} h^{-1}. The minimum and maximum flux values for dye samples belonged to O and NB dyes, respectively. Entrapment of dye molecule groups by membrane pore networks are a potential reason for permeate flux reduction in every filtration run. The flux reduction might occur for to two major reasons: (1) formation of a filter cake and gel layer (2) decrease in membrane fractional pore size because of obstruction by the molecules absorbed in the pores which is in accordance with the previous studies (Schäfer, Fane *et al.* 2000). Literature from others reports that membrane fouling during the treatment process is the main reason for reduction of permeate flux and membrane performance (Vrouwenvelder, Kappelhof *et al.* 2003). Since the flux variation in this experiment was insignificant, it is reasonable to claim that fouling was negligible.

Due to the heterogeneity of the pore distribution on the NF membrane surface, the initial pure water flux (PWFs) of each run showed deviations between each membrane. The basis of comparison was set to be the normalized values of PWF and dye permeate flux. Figure 6 displays the relative fluxes of treated dye samples via nanofiltration. The largest relative flux reduction was detected for the O dye. The O dye sample resulted in higher electrostatic charge behaviour comparing to other dyes, because of higher contents of [OSO_3Na], [SO_3Na] and [CHCONH]. The [$SO_2CH_2CH_{23}$] and ß-sulfato derivative groups are significant vinyl sulfone masking groups which are the most reactive among all reactive orange dyes (Armagan, Ozdemir *et al.* 2003, Órfão, Silva *et al.* 2006). Hence, the orange dye reaction, while in constant concentration of 16 mg.L^{-1} was faster than the other samples (Vrouwenvelder, Kappelhof *et al.* 2003). According to the Donnan effect and rejection transpired phenomena, the entrapment of O in the pores leads to decrease in flux (Denyer, Shu *et al.* 2007).

3.8 The sodium silicate rejection efficiency

The effects of NF treatment application on remaining sodium silicate removal in all samples are shown in Table 4. The sodium silicate removal efficiency in all dye samples is in the range of 13% to 16.3% for NB and TB dyes, respectively.

The related efficiency value differences are negligible, however, minor changes can be explained based on the changes in operational conditions. The role of reactive dyes together with their chemical properties such as constituent halogen elements like Cl and vinyl sulfone formation group (OSO3Na, SO_3Na, and CH_3CONH groups) was considerable given the experimental conditions (Rashidi, Nik Sulaiman *et al.* 2016).

Consequently, higher reactive and leaving groups (R and D) such as [Cl], [OSO_3Na], [SSO_3Na], [OPO_3Na_2], and [SO_3Na] components in dyes samples can affect the removal efficiency of sodium silicate. Therefore, reactions between dye groups and other chemical components such as paraffin groups (wax) in synthetic wastewaters will increase

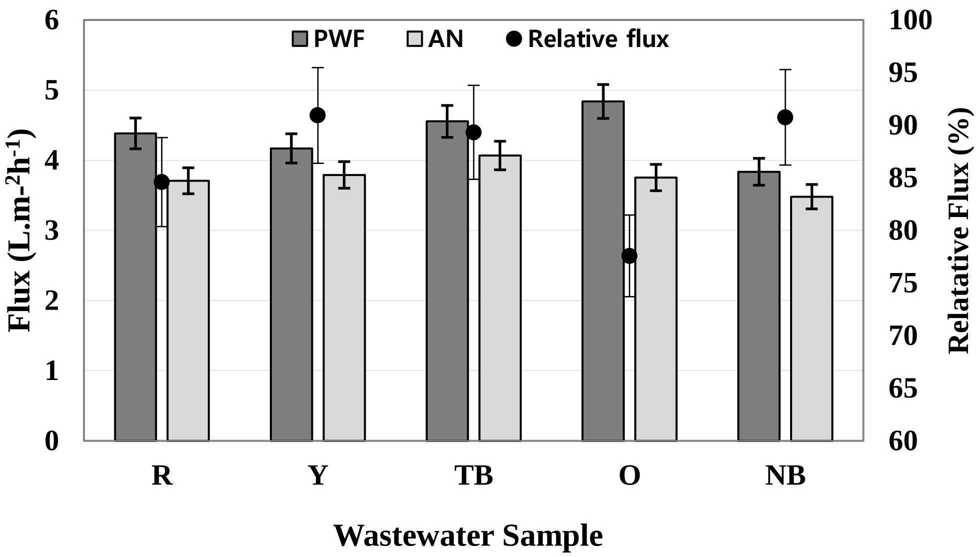

Fig. 6 Dye samples flux ratio by PA membrane nanofiltration
*NB: Reactive black 5, O: Reactive orange 16, R: Reactive red 194, Y: Reactive yellow 145, TB: Reactive blue 15

rejection efficiency. The equations below explain the related phenomenon in detail and are in agreement with previous studies (Tang, Fu *et al.* 2007).

$$D\text{–}R\text{–}Cl+H\text{–}OH \rightarrow D\text{–}R\text{–}OH+H\text{–}Cl \quad (1)$$

$$D\text{–}F\text{–}CH_2\text{–}\ CH_2\text{–}\ OSO_3H+H\text{–}OH \rightarrow D\text{–}F\text{–}CH_2\text{–}\ CH_2\text{–}\ OH+H_2SO_4 \quad (2)$$

$$\underset{aq}{Na_2SiO_3}+\underset{aq}{HCl}\rightarrow \underset{s}{SiO_2}+2\underset{aq}{NaCl}+H_2O \quad (3)$$

$$C_2H_{2n+2}+Cl+Cl_2 \rightarrow C_2H_{2n+2}Cl_2+HCl \quad (4)$$

Table 4 Sodium silicate rejection efficiency by PA nanofiltration membranes

Type	*DP (%)	R	Y	TB	O	NB
Sodium silicate removal efficiency (%)	±1.5	15.3	15.8	16.3	15	13

*Deviation percentage

3.9 The dye rejection efficiency and characteristic

Table 5 displays the NF efficiencies for the dye rejection process. NF illustrated complete rejection efficiencies in dye removal from the samples so that the concentration of reactive dye after nano membrane filtration was too low to be detected by spectrophotometry. All samples demonstrated thorough rejection in the filtration process and total discolouring performance in comparison to the other dyes. It is suggested that this result is due partially to greater molecular weight, higher electrostatically charged active groups and various reactive sectors (mostly multi-valent charged ions) for reaction with the active polyamide layer of nanofiltration membranes.

The presence of active groups such as chlorodiamino s-triazine ($C_3H_4ClN_5$ chemical structure please) in dye samples significantly enhances the affinity of dyes towards polyamide NF membranes and is a parameter in dye rejection efficiencies by nanofiltration membrane. This is because of the strength of ionic groups and molecule size in dye samples (>600 g.mol^{-1}) (Akbari, Remigy *et al.* 2002, Van der Bruggen, Curcio *et al.* 2004) and is desirable in accordance with previous studies (Dhale and Mahajani 1999).

The high rejection efficiency value rates in nanofiltration membrane found in the synthetic samples can be explained partly by the Donnan effect and the sieving mechanism (Denyer, Shu *et al.* 2007). The removal efficiency and mechanism in NF membranes are dependent on the physical trapping and electrostatic charge of detached foulants. For purification of neutral components, the sieving mechanism contributed to the removal process which occurs due to neutral solutes; size exclusion and also the molecular weight which is transferred through the NF membrane by different flow rates and pressures (Van der Bruggen and Vandecasteele 2003, Elkady, Ibrahim *et al.* 2011).

The results were similar to those of others focusing on reactive dyes and sodium silicate rejection by NF membranes (Marcucci and Tognotti 2002). Thus, we propose that the Donnan and other electrostatic attraction mechanisms contributed (Hu, Liu *et al.* 2018).

Due to the presence of free amino groups, we add that the active surface containing polyamide nanofiltration enhances the speed of reaction with groups of dyes in alkaline environment (Kwak, Jung *et al.* 1999, Xu, Feng *et al.* 2011). Nevertheless, some amide groups may also be contributing as detailed below (equation 5 and 6).

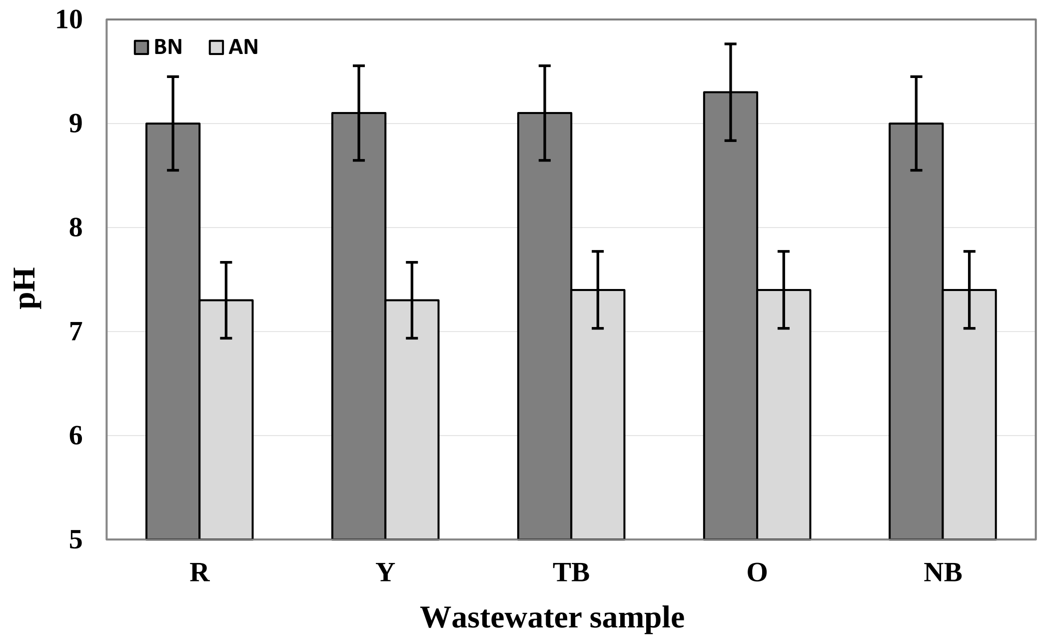

Fig. 7 pH reduction efficiency in dye samples before and after NF
*NB: Reactive black 5, O: Reactive orange 16, R: Reactive red 194, Y: Reactive yellow 145, TB: Reactive blue 15

Table 5 Dye rejection efficiency by PA nanofiltration membranes

Type	R	Y	TB	O	NB
Dye rejection Efficiency (%)	ND*	ND	ND	ND	ND

* Not detected

$$H_2N\text{–}Polyamide\text{–}COOH\text{+}Dye\text{–}Cl \rightarrow \text{Dye} - HN - Polyamide - COOH \tag{5}$$

$$H_2N\text{–}Polyamide\text{–}COOH\text{+}Dye\text{–}x\text{–}CH_2CH_2\text{–}y \rightarrow \text{Dye} - x\text{–}\ CH_2CH_2\text{–}HN - Polyamide - COOH \tag{6}$$

$$(x\text{=}O,\ SO_2,\ldots,y\text{=}Cl,So_3H,\ldots)$$

3.10 pH changes

The pH was measured for inlet and outlet synthetic wastewater (Figure 7). According to Figure 7, the maximum pH occurred in feed dye solutions which then continuously decreased to the minimum value in permeates of all samples. Since the amount of sodium silicate and reactive dyes are noticeably reduced, the pH reduction trends are justifiable. The removal of sodium silicate with strong alkaline behaviour contributed to the permeate pH being lower in comparison to the feed in all dyes samples (around 1.5 unit). The observed pH reduction in this study is in agreement with previous studies (Birgani, Ranjbar *et al.* 2016).

The reduction rate in pH in all dye samples for NB and O respectively was 1.6 to 1.9 (range, error). Incomplete removal of sodium silicate by NF membrane (due to the small size of sodium silicate molecules and their inactivity when in polyamide nanofiltration membranes) was caused by the permeate pH in all samples being slightly alkaline.

Although the polyamide nanomembrane has a slightly negative zeta potential charge in neutral pH (Verliefde and Dirk 2008), it is observed that the membrane has very desirable effectiveness in anionic reactive dye removal. This is due to the presence of free amine groups (-NH^{3+}) in polyamide structure which provides a positive surface charge to the membrane. The positive surface charge will increase the affinity between anionic reactive groups and the membrane and will increase dye rejection efficiency (Bruni and Bandini 2008). This behaviour, in addition with counter-ion site-binding and Donnan effect can play the main role in attracting chemical components by the NF membrane.

On the contrary, we observed accelerated attraction and trapping processes by the NF surface and propose it is due to bonds between reactive dyes and polyamide surfaces releasing leaving groups. The leaving groups present in related reactive dyes consisted of [Cl], [OSO_3Na], [SSO_3Na], [OPO_3Na_2] and [SO_3Na] components.

Since the reactive groups of dye molecules are positively charged, they are capable of reacting with the membrane surface and ionic groups. This justifies the Donnan exclusion effect (Denyer, Shu *et al.* 2007), leading to rejection (Elkady, Ibrahim *et al.* 2011). Therefore, ethyl sulphones and aliphatic amines in the β-position were converted into leaving groups, which facilitated the transport of lower reactive groups through the nanomembrane.

The R dye results, however, show the most significant differences between the pH of feed and permeate samples. The observed presence of chlorodiamino s-triazine reactive groups in dye samples structures explains this phenomenon; the reactive group has high affinity behaviour, and is absorbed into a membrane's active surface layer. Thus, the acidic reactive groups of permeate samples can be decreased (Venkataraman 2012).

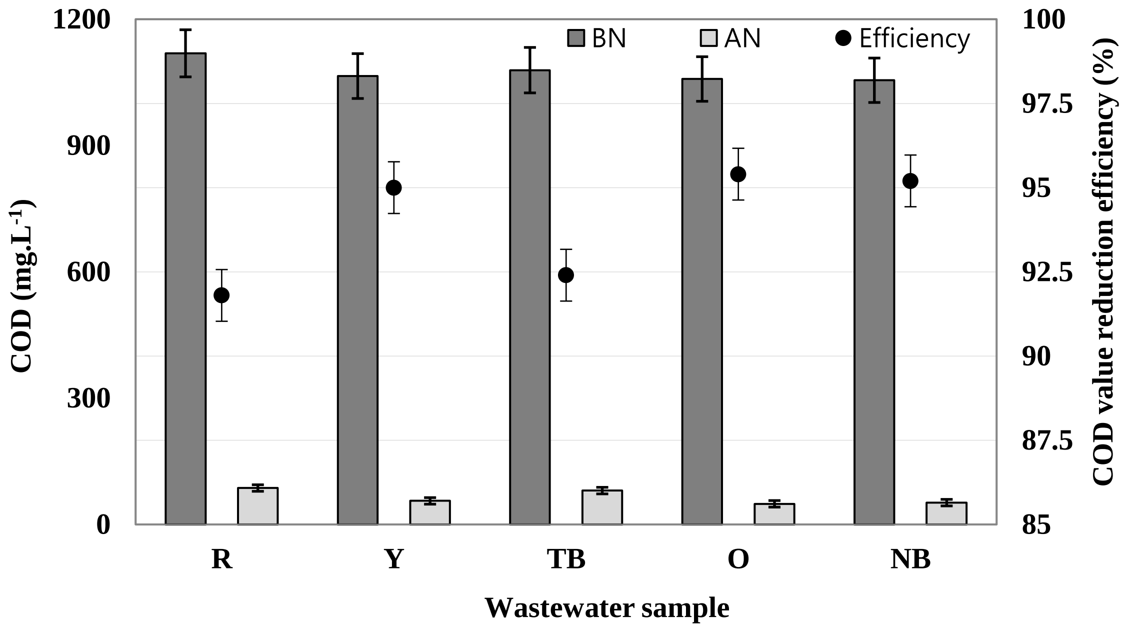

Fig. 8 COD changes and removal efficiency in dye samples before and after NF
*NB: Reactive black 5, O: Reactive orange 16, R: Reactive red 194, Y: Reactive yellow 145, TB: Reactive blue 15

3.11 COD changes

Figure 8 shows the variation of COD of each sample before and after the hybrid treatment process. The post-filtration process enhanced the dye samples' COD up to 86.5 mg.L^{-1}, which results in complete removal by NF. Sodium silicate, reactive dye groups and dye colour molecules removal are the main reasons to COD change throughout the filtration in the polyamide active layer. Factors to consider include the separation mechanisms such as Donnan, Steric exclusion, counter-ion site-binding effect, which play key roles in the mechanism of COD removal and separation (Marcucci and Tognotti 2002, Allegre, Moulin *et al.* 2006, Yadav, Mukherji *et al.* 2013).

Additionally, the formation of strong covalent and hydrogen bonding between the nanomembrane and the reactive dyes results in most of the dye molecules being captured by the membrane.

4. Conclusion

This research was conducted to study the effect of hybrid membrane technology for textile industries wastewater treatment, a growing area of concern for sustainable water and environmental management in developed and developing countries. The main challenges in ameliorating textile wastewater are caused by wax, dyes, and chemical components. The membrane filtration techniques used in this study illustrated reasonable efficiency in removal of these contaminants. To summarize, we found that:

- Although the dye rejection rate in UF was in the range of 12 to 15.5%, the NF membrane resulted in near-complete dye rejection for all dye samples.
- The sodium silicate rejection for UF and NF membrane in all samples was in the range of 2.5 to 4.5% and 13 to 16.3 %, respectively.
- The permeate pH in the dye samples decreased in comparison with feed samples by both UF and NF. While these amounts were immaterial via using UF, the NF application demonstrated high efficiency in pH reduction due to rejection efficiency.
- The COD in all dye samples treatment by UF and NF reduced. The UF and NF reduced more than 1000 mg.L^{-1} resulting in a range of 218 mg.L^{-1} to 342 mg.L^{-1}. This phenomenon occurred due to effective chemical and physical component rejection by treatment through membranes during each filtration run.

The results of this study lead to a conclusion that hybrid ultra/nano membrane treatment illustrates not only decreases the operational time, but also increases the efficiency of COD and dye removal. Although low concentration of some textile waste product components still remained, the resulting treated effluent from this hybrid system surpasses local and international discharge standard (Standard B) of the environmental quality regulation on industrial effluents and wastewater. The hybrid membrane system has the capability of being applied in combination with the baffle-tank, which was designed and proposed in our previous work, to make a physical pre-treatment package for textile wastewater with high efficiency of wax, dyes, and sodium silicate and other components removal.

We have reflected on the methods used and found that due to wax presence in the textile wastewater, it is not feasible to apply membrane technique without pre-treatment. Therefore, a pre-treatment baffled tank system is proposed in the first phase of our project for wax removal and in the second phase, the hybrid membrane treatment system is applied for removing dyes and remaining suspended solid components. Nonetheless, this study has demonstrated that future work on the challenges should entertain these methodological advancements:

- Integration of the two-separation process of baffled tank and hybrid filtration for decreasing the retention time and simultaneous removal of wax, dyes and COD.
- Studying the effect of different membrane material characterisations and activity for meeting optimum operational parameters, especially membrane flux and fouling which make it feasible to apply baffled tank treatment and membrane filtration simultaneously in a submerged system.
- Studying the impacts of other parameters on the efficiency of membrane system (e.g. temperature, pore size, and initial dosage of contaminants) and other reactive dyes.
- Comparative study on other methods of textile-wastewater pre-treatment with the baffled-membrane system proposed in this project regarding removal efficiency, time and energy requirement.

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