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Separation of Reactive Dyes using Natural Surfactant and Micellar-Enhanced Ultrafiltration Membrane

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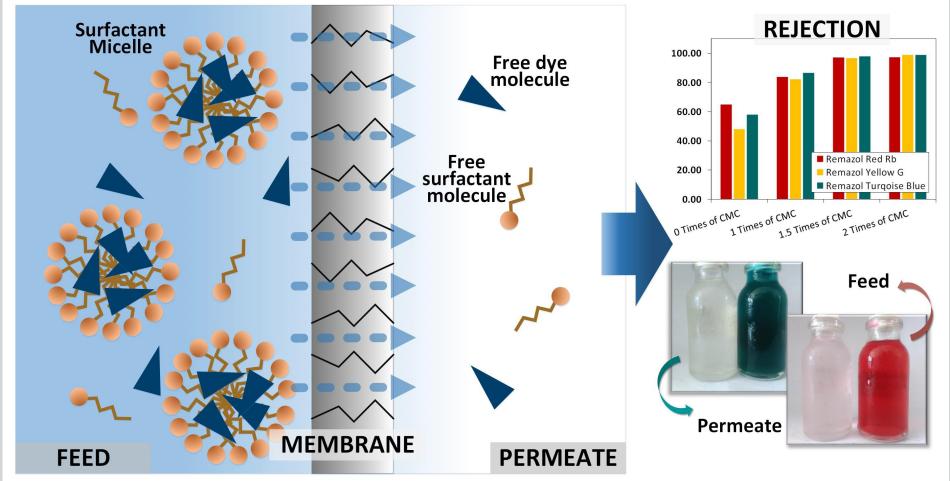
Highlights

- Saponin was used as the surfactant
- MEUF resulted on higher rejection compared to UF only
- MEUF with saponin surfactant successfully removed Naphtol and Remazol reactive dyes

Graphical abstract



Abstract

This study presented the membrane separation integrated with surfactant micellisation for the removal of dye molecules from aqueous media, commonly identified as micellar enhances ultrafiltration (MEUF). Three different naphthols or naphthalene dye (AS-LB, AS-OL, and AS-BR), three kinds of remazol dye (Red Rb, Yellow G, and Turquoise Blue) and a pure grade saponin were used in this study. This study investigated the MEUF performance to remove the reactive dye and to determine the effect of surfactant addition in the feed solution by determining the micelle loading profile. A significant decline of the initial normalized flux compared to the final flux was shown in all of the filtration processes for the removal of remazol dye. However, the flux profile of the naphthol feed showed a more stable trend. The addition of saponin as a surfactant in the feed solution improved the rejection of the dye pollutant, and this was because of the successful entrapment of the dye pollutant in the surfactant micelle structure. The highest rejections for remazol Red Rb, yellow G, and Turquoise Blue were 97.32%, 98.88%, and 98.88%, respectively. In addition, the highest rejection for naphthol AS-BR, AS-LB, and AS-OL were 99.08%, 94.16%, and 93.59%, respectively. Adding the surfactant decreased the value of micelle loading (amount of dye solubilized in surfactant micelle). It was confirmed that the MEUF successfully removed the dye pollutant from the wastewater and increased the rejection of the surfactant itself.

1. Introduction

The production of and demand for textiles in Indonesia have experienced rapid growth. In 2017, the domestic industry contributes to US$ 12,4 billion of export income, which is an increase of about 6% compared to the previous year [1]. The textile production consists of several steps and a significant amount of chemicals, i.e. dyes, is required. Dyes are used in the dyeing stage and are aimed to give the textile substrate an interesting color. Azo dyes, which account for approximately 50% of all commercial dyes (over one million tons annually), have been widely applied in the textile, paper printing, plastics, and cosmetics industries [2]. In addition, azo dyes are also classified as reactive and substantive dyes. Reactive dye is the most common textile dyes, including remazol and naphthol dyes. Remazol dye is a very common reactive dye used to provide color on cotton or wool [3]. In addition, remazol dyes are reactive azo dyes that create an additional reaction with the fibrous substrate and produce an ester bond that gives a bright color on the fabric. In addition, naphthol is widely used on the dyeing process of jeans and thick, dense fabric, giving a special deep strong color and possessing a fast reaction with the fabric. Naphthol dyes are water-insoluble ingrain dyes that create color inside the fabric [4].

During the dyeing process, approximately 15% of the total dyes product are lost and released in the water effluents [3, 4]. All depositions of these dyes

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on the water body cause a chromophore effluent with high chemical pollutants that are partly water soluble. The removal of color from this kind of waste is difficult because the dyes possess a high concentration of electrolytes that have characteristics of being resistant to light, resistant to oxidising agents and difficult to degrade once released into aquatic systems [5]. Some of the reactive dyes have a complex aromatic structure that resists degradation in conventional wastewater treatment [6]. Moreover, the undegradable chemical substances used in textile dyeing appear as mutagenic and carcinogenic materials [3].

Generally, to remove the dye pollutant from the effluent, the textile industry uses biological methods using aerobic-anaerobic microbe or physical methods such as adsorption and flocculation [4,7]. However, the methods are difficult to predict and still have many shortcomings, such as long operation time, and give unsatisfying results that poorly remove the reactive dye and show a low decolorizing effect [7]. One of the most sustainable and effective methods proposed to treat dye wastewater is low-pressure membrane applications. Membrane technology was applied to treat the dye wastewater because of the simpler process and a more predictable result. However, the regular ultrafiltration using membrane gives a low rejection percentage because of the low molecular size of the dyes. Nanofiltration (NF) and reverse osmosis (RO) membrane have been recognised as the superior techniques available for the separation of some commercial dyes. However, both the NF and RO membranes use a fairly dense membrane. The membrane permeabilities are low; thus, to obtain the desired throughput (permeate flux), a high operating pressure is required. Furthermore, previous studies show that a pressure of 8–12 bar is required to conduct the nanofiltration process [8].

Hence, an enhancement by taking advantage of surfactant micellisation was made to make the dye removal process easier, and the process is known as micellar-enhanced ultrafiltration (MEUF). The basic concept of MEUF is the performance of a membrane-based separation technique using the addition of surfactant to enhance the rejection of pollutant compounds [9]. Above the critical micelle concentration (CMC), the surfactant monomers form large amphiphilic aggregate micelles [10]. The small pollutant molecule that is usually excessively small to be rejected by ultrafiltration membranes can bind to the micelles because of ionic or hydrophobic interactions and subsequently separated together with them in the ultrafiltration step [9]. MEUF was reported to successfully remove various pollutants from the water body, such as heavy metals, phenolic compounds, hydrophobic organic chemicals, polycyclic aromatic hydrocarbons and also various dyes [11–14].

However, the commonly known MEUF process was mostly performed using a synthetic surfactant, such as hexavalent cetyltrimethyl ammonium bromide (CTAB), cetylpyridinium chloride (CPC), sodium dodecyl sulfate (SDS) [15,16] and others. Most synthetic surfactants are hardly degradable, nature persistently, and very toxic [17]; consequently, the remaining surfactant on the retentate and the permeating stream has the potential to create secondary pollution. As a result, the selection of surfactants that can be easily degraded is very important. The natural surfactant has a high potential to replace the synthetic surfactant on the MEUF process, such as saponin. Saponins as nonionic biosurfactants with a good surfactant property. Because of their special molecular structure and superiority with hydrophilic glycoside backbone and lipophilic triterpene derivative, saponins can solubilize hydrophobic compounds [18]. While saponins are toxic for cold-blooded animals and snails, they are not toxic to humans. A long term feeding of saponin to a mammalian animal also did not demonstrate any sign of toxic damage [19]. Saponin also is a biodegradable compound that can be naturally degraded by time, and the degraded product of saponin is about seven times less toxic than its parent compound [20]. Hence, the use of saponin as the substitute for synthetic surfactants could also be safe.

There was limited study of the MEUF process to remove dye removal using saponin. The previous research of the MEUF process using natural surfactant was conducted by Samal et al. [17] to remove methylene blue using the extract of reetha saponin as the surfactant. In this study, MEUF was conducted using saponin as a natural surfactant, saponin, to remove three types of reactive remazol dyes and three types of reactive naphthol dyes.

This study is focused on the investigation of the MEUF performance using saponin as the natural surfactant to remove six different dyes. Specifically, the performance investigation was based on the normalized flux of permeate, flux profile, concentration of pollutant on permeate, and rejection of dye pollutants. The effect of saponin concentration added to the feed solution was also investigated. The effect of saponin micellar solubilisation was examined by calculating the loading capacity of the micelle and the coefficient of equilibrium distribution.

2. Experimental

2.1. Materials

The model wastewater was prepared using remazol dyes (Red Rb, Yellow G, and Turquoise Blue) and naphthols or naphthalene-based azo dyes (AS-LB, AS-OL, and AS-BR). All of the dyes were supplied by Nat Collection, Indonesia, in dry powder form. The dye powder was kept on vacuum storage, half-filled with silica gel to maintain the water content. The dye was diluted in distilled water, supplied by Mer-C, Diponegoro University, Indonesia, prior to its use as the dye pollutant. The properties and the molecular structure of the dyes are listed in Table 1. The micellar-enhanced ultrafiltration was conducted by adding saponin as the surfactant in the feed and a pure saponin in solid powder form procured from Sigma-Aldrich (Singapore) in a 99% pure standard with a critical micellar concentration in the range of 0.001–0.1wt.% and molecular weight of 634.8 g/mol. All of the chemicals were used without any further purification. A flat sheet polyethersulfone (PES) membrane with molecular weight cut-off of 10 kDa (Sterlitech, USA) was selected as the ultrafiltration membrane, and the membrane was cut into a circle shape with an outside diameter of 3.9 cm and an effective area of 34.195 cm^2.

Table 1
The physical and chemical properties of the synthetic dyes.

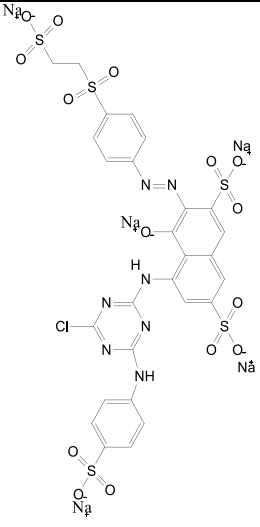
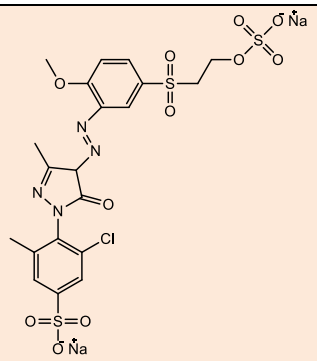
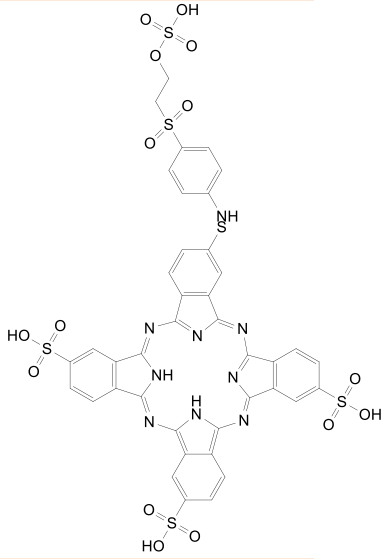
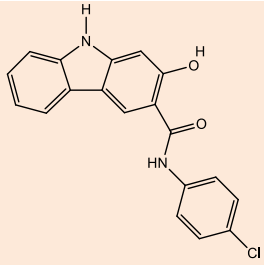
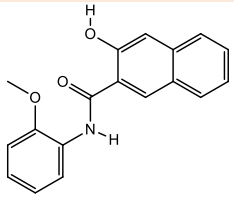
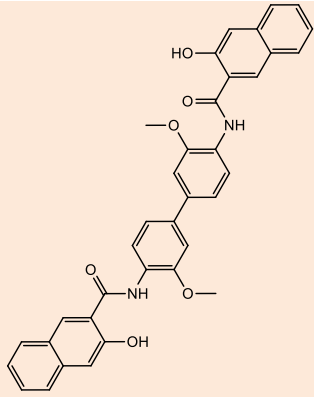
Code	Dyes	Molecular Formula	Molecular weight (g/mol)	Maximum wavelength (nm)	Molecular Structure
a)	Remazol dye Red Rb	$C_{27}H_{18}ClN_7Na_4O_{15}S_5$	984.2	521	

Table 1 (Continued)

b)	Remazol Yellow G	$C_{20}H_{19}ClN_4Na_2O_{11}S_3$	669	426	
c)	Remazol Turquoise Blue	$C_{40}H_{25}CuN_9O_{14}S_5$	1079.6	663	
d)	Naphthol azo AS-LB	$C_{19}H_{13}ClN_2O_2$	336.8	455	
e)	Naphthol azo AS-OL	$C_{18}H_{15}NO_3$	293.3	621	
f)	Naphthol azo AS-BR	$C_{36}H_{28}N_2O_6$	584.6	368	

2.2. Model of dye wastewater

To prepare the model solution of dye wastewater, a specific amount of powder dye was added into the distilled water to achieve 300 ppm concentration for both remazol and naphthol dyes. The preparation of naphthol solution was performed by a heat-assisted homogenisation and followed with regular homogenization. Three parts of naphthol dye and a part of Turkey Red Oil (TRO) were added into hot water (80 °C). The mixture was stirred on low speed (500 rpm) and the temperature was maintained for the first 5 minutes. After 5 minutes, the solution was stirred at high speed (1000 rpm) without any additional heating until the temperature drops to room temperature (about 15 to 20 minutes). The solution was adjusted to the base condition at a pH of 8 using NaOH. The diazonium salt was separately dissolved in the distilled water at ambient temperature and then the naphthol dye solution was carefully added to achieve 0.8% concentration. The solution was then stirred at high speed (1000 rpm) for the next 10 minutes. The homogeneous solution was ready to use as the dye wastewater solution. Regarding the remazol dye solution, the homogenization was conducted without any heating by using a triangle prism magnetic stirrer bar to avoid any sedimentation. Further, all of the wastewater model solutions were directly used for the ultrafiltration process not more than 30 minutes after the homogenisation process to avoid deposition of the dye.

2.3. Micellar-enhanced ultrafiltration process

Saponin was used to substitute the synthetic surfactant on the micellar-enhanced ultrafiltration process. The saponin concentrations were varied at 1, 1.5 and 2 times of its CMC. The ultrafiltration process with no saponin addition was also conducted as the standard comparison. The CMC of the Sigma saponin was in the range of 0.001–0.1wt.%. A self-conduct analysis of the pure commercialized saponin showed that the pure saponin reached a CMC at the concentration of 0.07wt.%s using a water solvent.

The ultrafiltration experiments were performed using a self-fabricated laboratory-scale cross-flow system filtration module, as illustrated in Figure 1. The filtration apparatus was equipped by a single closed feed tank with a maximum capacity of 1 L, an open tank for permeate, a gauge pressure indicator, a control valve (1/4 inch needle valve, SS 316 Compact Steel) to adjust the pressure along the equipment, and a gear pump to fed the solution into the membrane module. For each experiment, a new membrane was used. The membrane was rinsed with distilled water and then was soaked on the distilled water overnight to remove the preservative products. The clean membrane was compacted for two hours by filtering a pure distilled water before the filtration process.

The ultrafiltration and micellar-enhanced ultrafiltration processes were conducted at room temperature (±25 °C), 150 kPa of transmembrane pressure and natural pH of wastewater feed in the tangential cross-flow system. The partially recycled operating method means that all the retentate was returned to the feed tank. The permeate stream was partially sent back to the feed tank, and some of the permeate was taken as the analysis sample. The volume of feed solution was 500 mL for all the filtration conditions, and the flow rate was dependent on the tangential velocity of the pump, which was maintained for all operations. The experimental conditions (temperature, tangential velocity, filtration time, and transmembrane pressure) for all filtrations were remained constant.

Before each filtration process, the hydraulic permeability of the membrane was determined by measuring the flux of pure water (F_w) under the same operating conditions used in the filtration of model wastewater [6]. The flux was measured every 20 minutes for an hour, and the average flux was determined as the pure water flux (F_w). The feed tank was then filled with the solution of the wastewater model to conduct the experiment of dye waste removal. The filtration was conducted for 120 minutes, and the permeate flux (F) was calculated for every 5 minutes. The data was then presented as the value of normalized flux (F/F_w). The permeate flux was calculated based on Equation 1.

$$F = \frac{m / \rho}{A \; x \; t} \tag{1}$$

F is the permeate flux, m is the mass of the permeate, ρ is the density of the overall permeate, A is the effective area of the membrane, and t is the interval time of permeate sampling.

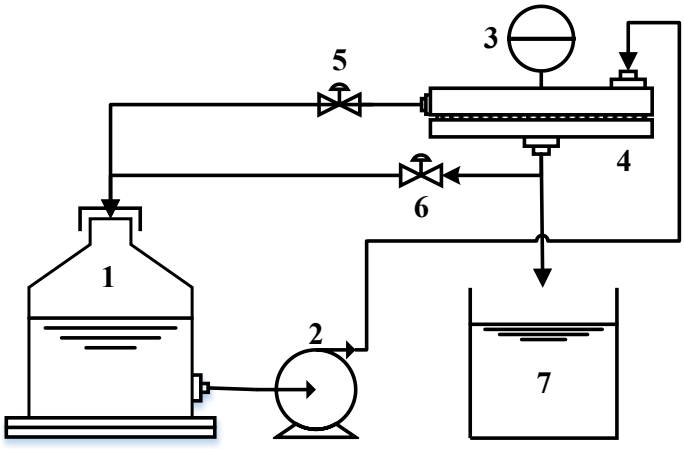
The performances of UF and MEUF to remove dye from the wastewater model solution were evaluated by dye rejection. The rejection was determined based on Equation (2).

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \text{ x } 100\% \tag{2}$$

where C_p is the permeate concentration and C_f is the feed concentration, respectively.

2.4. Analytical methods

The concentrations of dye pollutants in the retentate and the permeate were determined using Spectrophotometric UV-Vis (Shimadzu UV mini 1240). The maximum wavelength to analyze each sample (remazol dye, naphthol dye, and saponin) was determined by calibration methods [21], and a proper amount of sample was diluted to a specific concentration to match the spectrophotometer light specification. To determine the maximum wavelength, the absorbance of each sample was analyzedd at various wavelengths, ranging from 190–380 nm for ultraviolet light, and 380–750 nm for the visible light, with wavelength interval of 2 nm. The highest absorbance obtained from the analysis was determined as the maximum wavelength to conduct the concentration analysis.



1. Feed tank
2. Centrifugal pump
3. Pressure gauge
4. Ultrafiltration module
5. Flow control valve
6. Valve permeate
7. Open tank for permeate

Fig. 1. Schematic diagram of the cross-flow membrane filtration module

The calibration curve was obtained by plotting the sample concentration and the absorbance was used to determine the concentration of dye pollutants and the saponin content. A standard solution of remazol dye, naphthol dye, and saponin was prepared at various concentrations and then analyzed using a spectrophotometer at the maximum wavelength.

The samples of retentate and permeate solution were diluted with distilled water per the requirement of UV spectrophotometer analysis. Each solution was then analyzed using the spectrophotometer at the proper maximum wavelength. The absorbance was plotted at the calibration curve to determine the concentration, and the concentration was measured simultaneously in the mix component mode. The data of dye and saponin concentration on the retentate and permeate were then applied to calculate the percent of rejection and the micelle loading properties.

2.5. Micelle loading analysis

Micelle loading was interpreted as the concentration of solubilised dye on the surfactant micelle by the concentration of surfactant forming micelles [21]. The study of micelle loading was conducted to investigate the formation of surfactant micelle and its effect on the ultrafiltration process. In addition, the formation of surfactant micelles was known to enhance the effectiveness of the dye pollutant removal. The parameter was presented as the equilibrium distribution constant (K_d) and micelle loading (L_m) [22]. The determinations of K_d and L_m were based on the mass action law that is described by Equations 3 and 4.

$$K_d = \frac{D_r}{S_r - D_p} \tag{3}$$

$$L_m = \frac{D_r - D_p}{S_r - S_p} \tag{4}$$

D_r and S_r are the concentrations of the dye pollutant and surfactant in retentate, respectively, while S_p and D_p are the concentrations of the surfactant and dye pollutant in permeate.

3. Result and discussion

3.1. Effect of saponin concentration on the profile of permeate flux of various dyes

The ultrafiltration experiment for the removal of dye pollutants from wastewater was conducted with and without surfactant assistance. A total of six different dyes were used in this study. Three different remazol dyes (R. red Rb, R. Yellow G, and R. Turquoise Blue) and three different naphthalene-based azo dye (AS-OL, AS-BR, and AS-LB) present the various frequently used azo dye in fabric dyeing. The saponin was used as a surfactant to enhance the ultrafiltration process. In addition, the effect of saponin concentration on the permeate profile flux for removal of various dyes is presented in Figure 2 for remazol dyes and Figure 3 for naphthol dyes.

Figure 2 shows the permeate flux profile on the removal of remazol dye at various saponin concentrations. The figures depict that the permeate flux decreased by the time of filtration. The filtration of remazol Red Rb without the addition of saponin and with the addition of saponin at its CMC shows a rapid decline in the first 20 minutes of the filtration process. In contrast, the flux with a higher concentration of saponin shows a relatively stable flux profile. Compared to the other remazol dye, the remazol Red Rb has a more ionic charge group on the outside of its molecular structure (Table 1a). An ionic dye has good water solubility and provides a hydrophilic character [23]. This characteristic caused the remazol red solution to easily go through the PES membrane and has a partly hydrophilic characteristic [24]. Even with the addition of saponin with concentration right at the CMC, the remazol red solution is still processing the same characters. However, the flux also declined over time, just like the other feed solution with higher saponin concentration. This was commonly found on the membrane filtration where the flux declines over time, which generally was caused by the polarisation of pollutant concentration at the membrane surface [12]. It was observed that without adding any saponin as the surfactant, the flux declined because the dye pollutant itself has a potency to create a blocking on the surface or pores of the membrane. The previous study of methylene blue removal using the ultrafiltration membrane also showed a similar result where the dye lowered the flux as the time increased [25].

Figure 2 also shows the shortcoming of the saponin addition to the ultrafiltration process. The addition of saponin to the feed solution decreases the permeate flux for all kinds of the remazol dyes, and as the saponin concentration increases, the permeate flux decreases. Adding saponin at concentrations two times the CMC shows the lowest normalised flux. This phenomenon was less expected because the saponin formed a large aggregate when added to a solution at a concentration higher than its CMC [13]. At concentrations higher than the CMC, saponin formed a micelle structure that grew its molecular weight until 10–15 times [26]. The structure of micelle was a hydrophilic head on the outside and the hydrophobic tail on the inside [10]. The hydrophilic head of the micelle tends to bind to each other, creating a layer of cake that potentially blocks the membrane pore. The result of this phenomenon is a decreased permeate flux by the addition of saponin as the surfactant. A similar trend was also observed in the previous study of micellar-enhanced ultrafiltration for boron removal, where a lower flux was found when the surfactant was added [27]. However, the study found that the concentration polarization was not mainly caused by the addition of surfactant and rather than due to the characteristic of the membrane pore, as the flux decline was also found on the membrane filtration without any surfactant [27].

Figure 3 shows the effect of surfactant addition to the membrane performance at various naphthalene-based dyes. Similar to the ultrafiltration process for remazol dyes removal, the decline of normalized flux occurs in almost all processes. The decline of flux indicated that the membrane started to foul, and a concentration polarization of the pollutant occurred on the membrane surface [28]. This kind of phenomena is very common in the filtration operation using membrane, where some of the retaining substance generates foulant with various kinds of fouling mechanisms [29].

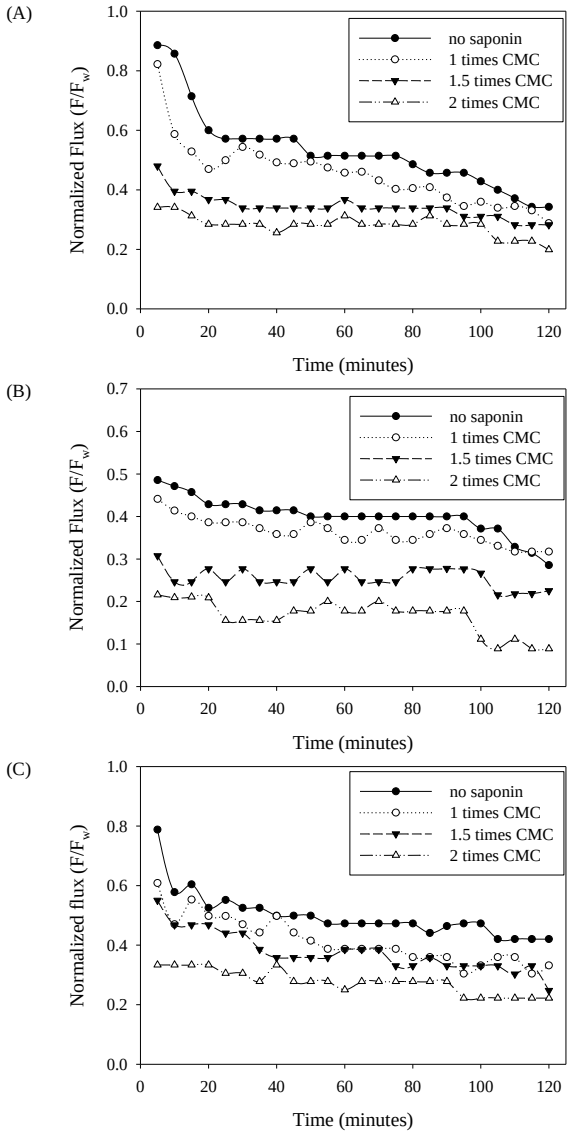


Fig. 2. Profile of permeate flux on various saponin concentrations for the removal of (A) remazol red RB, (B) remazol yellow G, (C) remazol Turquoise Blue.

In this study, the retaining substances consist of free monomer dyes, free monomer saponin, dye molecule attached to the saponin micelle, or an empty saponin micelle, and these components had the potential to become foulants on the membrane surface. The pollutant started to deposit on the membrane surface and detained the water from going through the membrane.

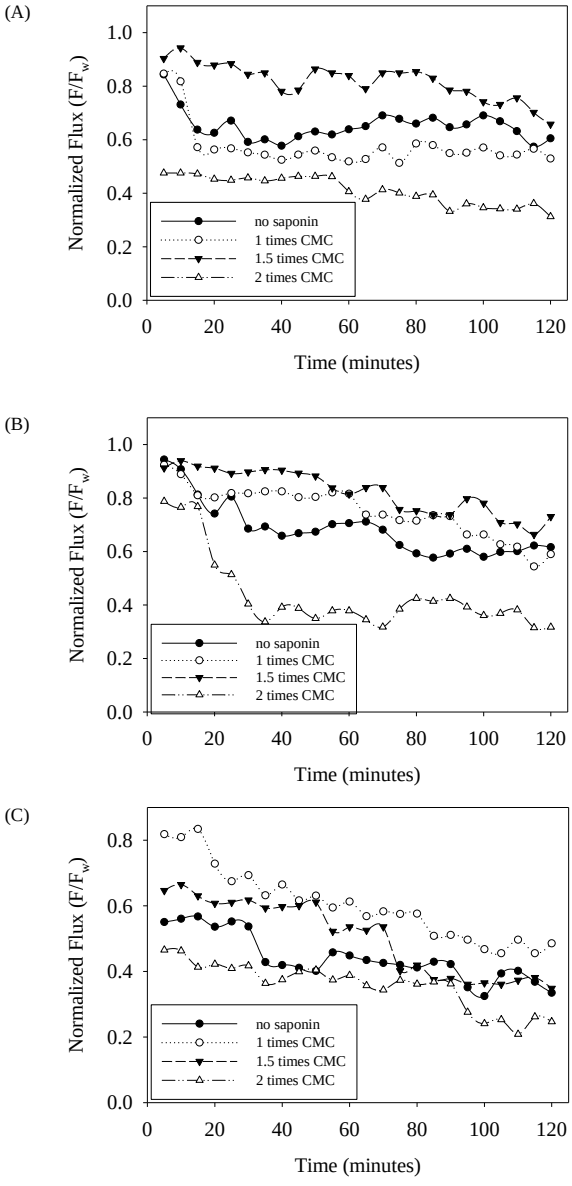


Fig. 3. Profile of permeate flux on various saponin concentration for the removal of (A) Naphthol AS-LB (B) Naphthol AS-BR, (C) Naphthol AS-OL.

A different phenomenon was found on the removal of naphthol dyes compared to those of the removal of the remazol dye. Adding saponin as the surfactant on the feed solution provided a positive effect on the permeate flux and increased the permeate flux. The highest flux was achieved while saponin is added as much of 1.5 times CMC for naphthol AS-LB (black) and AS-OL (blue) and naphthol AS-BR (purple). On the MEUF of naphthol dyes, the flux was increased as saponin was added. This effect was because of the solubilization of the dye molecule on the surfactant micelle. The structure of surfactant micelles that have a hydrophilic head on the outside and a hydrophobic tail on the inside allowed pollutant substances such as dyes to be solubilized on it [5]. The solubilization of dyes allowed the dye molecule to grow in size and to be retained by the membrane pores [3]. Unlike the small molecule dyes that easily block the inner side of the membrane pores, a saponin micelle molecule is larger than the membrane pores. This structure enables the micelle to be retained on the surface of the membrane and let the water solvent go through the membrane. However, the flux was dropped by further adding saponin at a concentration 2 times that of CMC. In addition, naphthalene-based dyes have a relatively smaller molecular size than remazol dye (Table 1). As a result, a smaller concentration of saponin is required to solubilize the naphthol dye. Excess addition of surfactant on the ultrafiltration feed solution generates extra foulant that can clog the membrane pores [27]. A micelle of the surfactant is mostly structured as the head of the hydrophilic group on the outer side. These hydrophilic head groups are easily attached and create a layer of foulant, lowering the ability of the water solvent to go through the membrane. The different flux profile trend between the remazol dyes and naphthol dyes shows that each dye has unique micellar characteristics. The difference might be caused by the various properties of each dye pollutant such as polarity, ion charges, molecular structure and molecular size.

3.2. Rejection of dyes pollutant

The efficiency of the ultrafiltration process can be characterized by the rejection of each pollutant. The rejection is denoted as the amount of substance retained by the membrane pores relative to the initial substance concentration on the feed and usually present in a percent value [4,9]. In this study, the effect of saponin concentration on the rejection percentage of the dyes was investigated, and all experiments were conducted under the room temperature with a transmembrane pressure of 150 kPa. The concentration of dye pollutants on the feed solution remains the same for all experiments at 300 ppm of dyes. The rejection values correspond to the solute concentration on permeate (dye pollutants and remaining saponin). Figure 4 and Figure 5 show dye concentration and saponin concentration in the permeate, respectively. According to those figures, the concentration of dye pollutants declines with the addition of saponin for both remazol dyes and naphthol dyes. The lowest dye concentration is found at the addition of saponin at 2 times CMC, and the addition of saponin at the feed solution allows the solubilization of dyes on the surfactant micelles. The micelles of saponin can solubilize the dye pollutant, although it is a nonionic surfactant. This was because the micelle possesses both hydrophilic and hydrophobic sides that can solubilize the hydrophilic dyes with a mechanism of like dissolved like [2,17]. The previous study also shows a similar result where the micellar solubilization and adsorption of dye molecule on the agglomerate of a nonionic surfactant was responsible for the higher retention of the dye pollutant. The study shows that a nonionic NPE_9 and Berol 535 were able to solubilize Sudan I and quinizarin dyes [2]. Tehrani-Bagha et al. demonstrated that a nonionic surfactant has higher solubilization power than anionic and cationic surfactants [2]. A nonionic surfactant also has a lower CMC than the ionic surfactant, making the nonionic surfactant more economic [26].

Figure 5 presents the concentration of saponin on the permeate flows. Although saponin forms a micelle structure at the concentration above CMC, some free monomer saponin might also exist on the feed solution. This is because the addition of saponin near the CMC places the solution into an aggregation state. When both molecule aggregates and a monomer exist, this state is also known as a metastable premicelles state [30]. The transport process and the flow of a surfactant contain solution also affect the release of surfactant monomer from the micelle structure [31]. The surfactant content on permeate is undesirable because it contaminates the clean permeate. Although saponin is easily degradable, the minimum amount of loss saponin is still preferable. Based on Figure 5a, the saponin concentration on permeate increases by adding saponin for all of the naphthol dyes, and this is because there is an excess amount of saponin added into the solution than needed to solubilize the dye pollutant. This result also corresponds to the flux profile of naphthol dye where the permeate flux at the saponin concentration 2 times CMC shows a decline.

The concentration of saponin on the permeate of remazol feed is shown in Figure 5b. The saponin content on the permeate flux reduced by the addition of saponin on the feed solution. Remazol dyes have a larger molecular size than the naphthol dyes, so these dyes need more surfactant to solubilize each molecule of remazol dye. The aggregation number of the surfactant is affected by the amount of solubilized materials (pollutant solutes). The solute materials with larger molecule size require a higher aggregation number of a surfactant to make a stable complete micelle [30]. This increase can lead to a metastable state of the remaining free monomer of the surfactant. The metastable state commonly occurs at the concentration of a surfactant near the CMC. At the metastable state, the free monomer of surfactant is easily detached from the micelle structure, allowing it to go through the membrane pore into the permeate flows [31].

Corresponding to the concentration of the dyes pollutant on the permeate flux, the rejection values are calculated to ensure the ultrafiltration performance related to the addition of saponin. A better membrane rejection is obtained at the higher saponin concentration, and the rejection of various

dye pollutants is presented in Table 2. The rejection of dyes pollutant increases by the addition of saponin for all kinds of dyes, and the addition of saponin at a concentration 2 times CMC achieves a higher rejection percentage with the highest rejection of 98.89% for the removal of remazol yellow G and Turquoise Blue. In contrast, the ultrafiltration process in the absence of saponin shows a low rejection percentage with the lowest one is obtained on the removal of remazol yellow G, which only rejects 48% of the dye molecules.

3.3. Study of surfactant micelle loading on the MEUF of dye-polluted solutions

The last investigation in this study is to analyze the performance of the saponin as the surfactant on the micellar-enhance ultrafiltration process of dye wastewater. The study was conducted based on the values of micelle loading capacity (L_m) and the equilibrium distribution coefficient (k_d). An amphiphilic compound has the loading ability to associate with a solute substance because of both endo- and exo-complexes formation [32]. Micelle loading was denoted as the amount (mM) of the dyes associates on the micelle aggregate by the amount (mM) of the surfactant that formed the micelle [33]. The micelle loading can also be interpreted in the mass ratio (g/g), which is expressed as the amount (in grams) of solubilized dye in the micelle and the amount (in grams) of the micellised surfactant [21]. The ratio of solute on the micelle and in the solution is known as the equilibrium distribution coefficient [4]. The micelle loading capacity and the equilibrium distribution coefficient of the various micellar-enhance process is presented in Table 3.

The micelle loading capacity of the remazol dye is lower than the naphthol dye, and this was caused by the bigger molecular size of remazol dyes; therefore, only a small amount of dye was solubilized on the part of the surfactant molecule [22]. The addition of saponin on the remazol and naphthol dyes solution decreases the micelle loading capacity, and this was due to there being more formation of micelles at a high concentration of saponin on the solution while the amount of dyes remain the same. The low value of micelle loading indicated that there is excess surfactant to solubilize the dye pollutant. Consequently, there is still capacity to solubilize more dyes.

The equilibrium coefficient of naphthol dye is smaller than the remazol dyes, confirming that there is more remazol dye that solubilizes inside the micelle compared to the naphthol dyes. The equilibrium coefficient increases as saponin is added, showing that the concentration of dyes on the micelle is increased by the addition of saponin. Adding saponin assists dyes molecule to solubilize and grow in size so the small molecule of dye pollutants can be retained by the membrane pores.

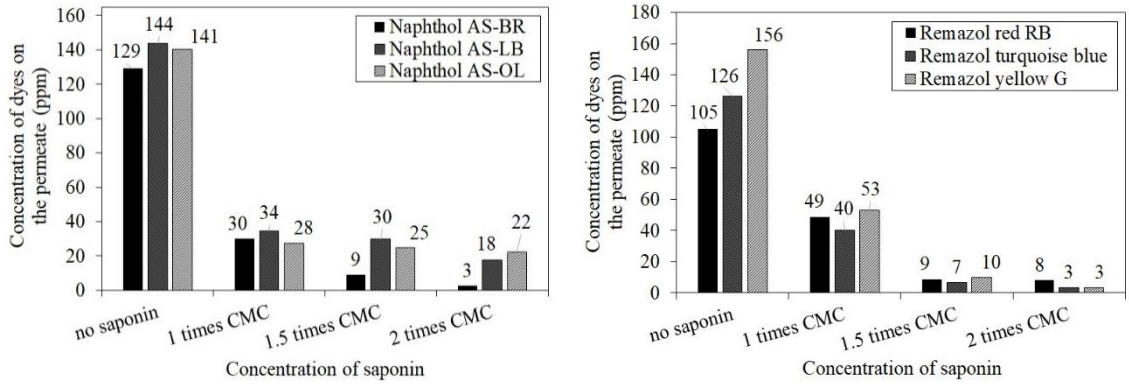


Fig. 4. The concentration of dye on the permeate under room temperature, 150 kPa transmembrane pressure, 300 ppm of dye pollutant on the feed and various saponin concentration for various dye type, (a) Naphthol dyes, (b) Remazol dye.

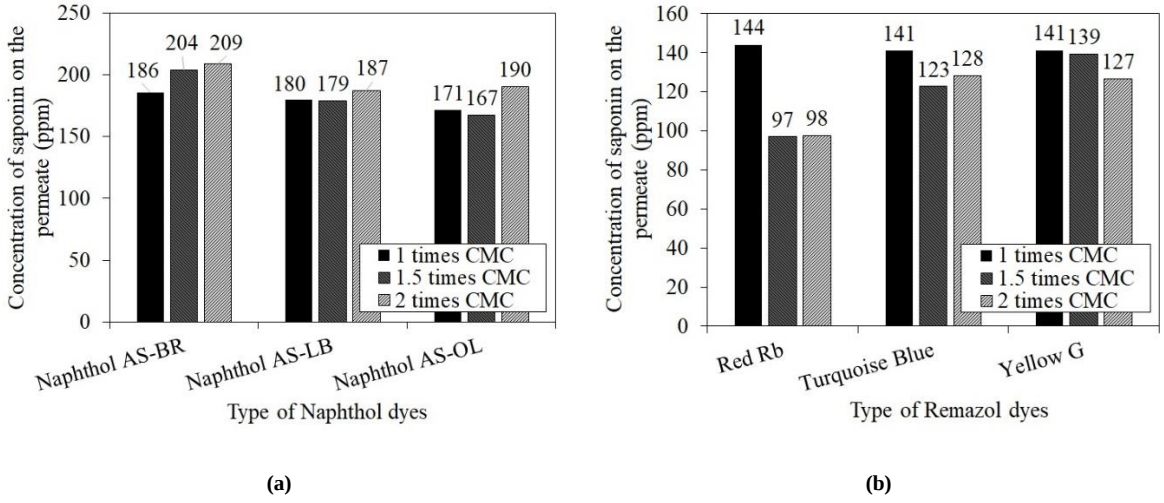


Fig. 5. The concentration of saponin on the permeate under room temperature, 150 kPa transmembrane pressure, 300 ppm of dye pollutant on the feed and various saponin concentration for various dye type, (a) Naphthol dyes, (b) Remazol dye.

Table 2
Rejection of remazol and naphthol dye at room temperature, 150 kPa transmembrane pressure, 300 ppm of dye pollutant on the feed and various saponin concentration.

Dyes	Rejection of dyes at various saponin concentration (%)			
	No saponin	1 times CMC	1.5 times CMC	2 times CMC
Naphthol AS-BR	56.95	89.97	96.98	99.08
Naphthol AS-LB	52.16	88.53	90.10	94.16
Naphthol AS-OL	53.16	90.82	91.76	93.59
Remazol Red Rb	64.91	83.78	97.05	97.32
Remazol Yellow G	48.00	82.25	96.67	98.89
Remazol Turquoise Blue	58.00	86.59	97.82	98.89

Table 3
The micelle loading parameters for remazol and naphthol dye.

Dyes	Saponin Concentration	Micelle Loading Capacity (L_m) (mM/mM)	Equilibrium Distribution Coefficient (K_d) (mM/mM)
Naphthol AS-BR	1 Times of CMC	0.429	1.209
	1.5 Times of CMC	0.410	1.011
	2 Times of CMC	0.037	1.679
Naphthol AS-LB	1 Times of CMC	0.697	1.853
	1.5 Times of CMC	0.515	1.722
	2 Times of CMC	0.484	3.691
Naphthol AS-OL	1 Times of CMC	0.691	3.442
	1.5 Times of CMC	0.654	2.353
	2 Times of CMC	0.525	2.907
Remazol Red Rb	1 Times of CMC	0.171	13.365
	1.5 Times of CMC	0.188	32.210
	2 Times of CMC	0.163	31.842
Remazol Yellow G	1 Times of CMC	0.398	11.260
	1.5 Times of CMC	0.369	37.970
	2 Times of CMC	0.290	91.276
Remazol Turquoise Blue	1 Times of CMC	0.123	22.399
	1.5 Times of CMC	0.108	39.208
	2 Times of CMC	0.103	95.567

4. Conclusions

The ultrafiltration of six different dye pollutants was conducted with the presence and absence of saponin as a natural nonionic surfactant. The UF and MEUF performance results show that the flux profile decreased by the time along the filtration process. The addition of saponin decreases the normalized flux at the removal of remazol dyes and results in a higher normalized flux of the UF process than the MEUF. In contrast, adding saponin on the removal of naphthol shows a successful result. The addition of saponin up to 1.5 times CMC increases the normalized flux and then the flux decreases as saponin is added to as much as 2 times CMC. The addition of saponin demonstrates the improvement of dye pollutant removal, confirmed by a significant increase of rejection percentage by the addition of saponin on all kinds of dye pollutants. The highest rejection percentage of 98.89% and 99.08% achieved at the removal of remazol and naphthol dyes, respectively, obtained at the saponin concentration of two times CMC. The analysis of L_m and K_d showed that adding saponin can solubilize the dye pollutant and that further adding saponin lowers the value of micelle loading (L_m). The highest K_d of 95.567 mM/mM was achieved on the removal of remazol Turquoise Blue at the saponin concentration of 2 times CMC. In addition, the highest L_m of 0.697 mM/mM was achieved on the removal of naphthol AS-LB at the addition of saponin right at the CMC. An investigation of membrane performance under different dye concentrations on the feed and various transmembrane pressures is suggested for further study.

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Nomenclature

A	effective area of the membrane
C_f	Feed concentration
CMC	Critical micelle concentration
C_p	Permeate concentration
CPC	Cetylpyridinium chloride
CTAB	Cethyl trimethyl ammonium bromide
D_p	Dye concentration in permeate
D_r	Dye concentration in the retetante
F	Permeate flux
F_w	Flux of pure water

F/F_w	Normalised flux
K_d	Equilibrium distribution constant
L_m	Micelle loading
m	Mass of permeate
MEUF	Micellar-enhanced ultrafiltration membrane
NF	Nanofiltration
PES	Polyethersulphone
R	Rejection
RO	Reverse osmosis
S_p	Surfactant concentration in permeate
S_r	Surfactant concentration in the retentate
SDS	Sodium dodecyl sulfate
t	Interval time
UF	Ultrafiltration
ρ	Density of the overall permeate

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