Treatment of batik wastewater using plant derived surfactant-enhanced ultrafiltration membrane

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Treatment of batik wastewater using plant derived surfactant-enhanced ultrafiltration membrane

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Abstract. Saponin extract from pericarps of Sapindus rarak DC is utilized to replace synthetic surfactant in the surfactant-enhanced ultrafiltration process. The process conducts to treat real batik wastewater. The extraction by maceration methods was performed in the various ratio of solute to solvent. The extract with proper calculation is used in the wastewater treatment process in various CMC concentration. The highest yield is obtained at solute to solvent ratio of 1:40 (w/v). The flux value of solution without saponin is higher than the one with saponin addition.The flux value is decreased by the increase of saponin concentration on the feed solution. Thelowest average flux value of 31.35 L/m2.h was obtained from the feed solution with saponin concentration of 2 times CMC. Both processes with and without the addition of saponin exhibit permeate flux declined over time. This is due to the interaction of saponin molecule with the pollutant where the pollutant is covered by saponin molecules. The membrane performance shows that saponin is successfully worked to solubilize or bounded the heavy metal molecule, dyes molecules, and other pollutants on its micellar structure. This is proved by the decrease of Cr and COD concentration after the ultrafiltration process enhanced with saponin. Saponin at the concentration of 2 times CMC giving the best result with lowest Cr and COD concentration of 18.3 ppm and 108.4 ppm, respectively, and highest rejection of Cr and COD of 95.88% and 96.91% respectively.

1. Introduction

Indonesia is a country with high demand and production of textile. The textile industry in Indonesia keeps growing year by year. The textile industry in Indonesia shows a rapid growth, increased by 6% year on year from US$ 11,8 billion in 2016 [1]. One of the well-known textile industry is the industry of batik. Batik is a traditional fabric mainly comes from Java Island. Most of the production process is conduct in Indonesia, about 75% utilized. The production and processing of textile require a great number of chemical substances such as the dye. It is used in the process is usually contained the heavy metal such as Cr [2] and contain high COD materials. This substance is chemically un-degradable and appears as mutagenic and carcinogenic materials [3,4]. The liquid effluents produce from the textile industry was record a large amount with average water use rate being 40 m^3/ton of the product [5]. Hence, the treatment of this wastewater is an urgent need.

One of the promising advance methods to remove pollutant is surfactant-enhanced membrane ultrafiltration. This method is a modified ultrafiltration membrane separation process with a lower

operating pressure requirement compared to RO and NF and membranes of higher permeability. This process has shown advantages of high removal efficiency, high permeate flux, and lower energy consumption as compared to individual membrane processes [6,7]. This method is widely used to remove heavy metal ions such as chromate [8], Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+} [9]. It is also applied to remove reactive dyes such as Remazol dyes [10], Eriochrome Blue Black [11] and a mixture of Reactive Black and Orange [12]. The basic idea for surfactant-enhanced ultrafiltration is that a surfactant forms large amphiphilic aggregate micelles when it is added to aqueous streams at a concentration higher than its critical micelle concentration (CMC). This micellar formation generates an ionic flocculation which conducts before the ultrafiltration process. The process begins with a mixture of surfactants in the effluent. The surfactant interacts with the pollutant molecules through micellar solubilization. The solute, according to its affinity for the aqueous medium, is positioned within the micelle [11]. Micelles containing solubilized solute are larger in size, with aggregation number range from 50 to 100 [13]. Thus, the pollutant (dye) molecule inside the surfactant micelle can be rejected by the pores of the ultrafiltration membrane.

The surfactant used in the process is generally a synthetic surfactant. Several cationic, anionic, and the non-ionic surfactant has been utilized for MEUF processes, such as hexadecylpyridinium chloride (CPC), Hexavalent trimethyl ammonium bromide (CTAB) [14], Sodium dodecyl sulfate (SDS) [15,16], Brij, Tween 80, Marlophen NP5 [17] and many more. This surfactants are less biodegradable, persistent in nature and may cause chronic toxicity and estrogenic activity [18].

For the solution, a plant-derived saponin is introduced to replace the synthetic surfactant. The structure of saponin is consist of a hydrophobic triterpenoidal or steroidal backbone and one or two hydrophilic glycoside moieties attached to the backbone (Figure 1). This molecular structure gives saponin a specific characteristic of amphiphilic glycoconjugates with foaming properties in water [19]. The combination of the nonpolar sapogenin and water-soluble side chain is similar to the structure of most synthetic surfactants having lipophilic and hydrophilic molecular parts. Saponin found in the several plants grow in Indonesia such as binahong leaf, inggu leaf (*Ruta angustifolia L.*), white Oyster mushroom [20], sprouts of green beans. The most valuable investment of saponin is the pericarps of lerak (*Sapindus rarak DC.*) [21]. The extraction of saponin from the plant has already discussed in the previous report, such as extraction of saponin from chenopodium quinoa [22], Allium nigrum L. [23], quillaja saponin [24], and Panax notogingseng [25].

However, a limited number of study has discussions about the extraction of Sapindus rarak DC. The study ceased to be limited only to phytochemical analysis, and some physical properties analysis. Moreover, a limited number of study are found in investigating the utilization of saponin in the surfactant-enhanced ultrafiltration. To our best knowledge, only one study of plant-derived biosurfactant as a surfactant in the MEUF application is found, conduct by Samal et al. [26]. The study to find the green system of micellar-enhanced ultrafiltration using natural surfactant is an urgent need. Hence, this study is conducted to evaluate the application of plant-derived surfactant in the surfactant-enhanced membrane ultrafiltration. The main objective of this study examines different filtration phenomena between the ultrafiltration system and surfactant-enhanced UF system using saponin from Sapindus rarak DC. The study is conducted by extracting the saponin from Sapindus rarak DC, evaluating the flux profile, pollutant concentration on permeate and evaluating the system performance by % rejection of the membrane.

2. Materials and Methods

This research is designed for the obtained extract of saponin from Sapindus rarak with high purity. Also applied the saponin extract to replace synthetic surfactant in the surfactant-enhanced ultrafiltration. The research begins with the preparation of raw material and extraction of saponin from Sapindus rarak. The further study is to apply the saponin extract in the surfactant-enhanced ultrafiltration process, evaluation of the process and investigation of membrane fouling mechanism.

2.1. Materials

The raw materials used in this study is raw pericarps of Sapindus rarak DC purchased from Batik Zie, Semarang. Distilled water as the solvent is obtained from Laboratory of MeR-C, UPT, Undip, Semarang. Pure saponin in practical (P.A) grade is procured from Sigma Aldrich as the comparative standard. And the real batik wastewater is the effluent of batik production from Simbang Kulon batik industry, Pekalongan. For the ultrafiltration process, polyethersulfone (PES) membrane with molecular weight cut off 5 kDa, manufactured by Sterlitech is used. The membrane utilized in this work has an effective surface area of 9,6 cm^2.

2.2. Extraction of saponin from Sapindus rarak DC.

The fruits of Sapindus rarak is prepared to get a clean and homogeneous sample before used in the extraction process. The dry pericarps are ground and sieved through 100 mesh sieve to obtain the homogeneous fine powder of Sapindus rarak. Ready to use dry Sapindus rarak powder is extracted by maceration extraction (ME). The dry powder of Sapindus rarak was mixed with distilled water as the solvent in various solute-solvent ratios. Based on the preliminary analysis the ratio of solute to solvent between 1:10 to 1:150 w/v was selected. The extraction with the ratio of solute to solvent below 1:10 has a very low yield and required more unnecessary raw material. While the extraction with the ratio of solute to solvent above 1:150 w/v showed that the yield had already stagnant. The solutions were homogenized using magnetic stirrer at 30 rad/s for 15 minutes. The homogeneous mixtures are then soaked for 12 hours at room temperature (25±2 ^oC). After the extraction, further post treatments were performed. The suspense containing solution is mixed using magnetic stirrer at 30 rad/s for 5 minutes to make a homogeneous suspension again. Then the solution is filtered using filter cloth and centrifuged at 4.500 rpm for 15 minutes to separate out the solid particles. The supernatant solution is analyzed by spectrophotometric methods to quantify the saponin concentration. The most common methods applied for saponin quantification is spectrophotometric analysis by using UV light scatter [26, 27]. Pure saponin purchase from Sigma, Aldrich is used as the standard solution reference to make the calibration curves. The maximum absorption wavelength is determined by UV-VIS Spectrophotometer. The preparation of the calibration curve is performed by analyzed the absorbance of pure saponin solution in various concentration (5000-100 ppm). Spectrophotometric analysis is performed by measuring the absorbance at the maximum absorption wavelength using reagent blank as a reference. The regression equation of the standard curve based on the concentrations (x) versus the absorbance value (y) is made and should have a linear correlation of more than 0,95.

2.3. Application of saponin extract for surfactant-enhanced ultrafiltration of batik wastewater treatment

The extract of Sapindus rarak DC with the highest concentration of saponin is chosen to use in the MEUF study. It is added to the wastewater by a suitable range of 0-2 times CMC, where the condition is no surfactant, with surfactant below CMC, and with surfactant above CMC. The CMC used is the CMC of pure saponin (0.1% weight) provide by the saponin's manufacturer, Sigma Aldrich. In this study, filtration is carried out using a cross-flow filtration cell. A schematic flow diagram of the ultrafiltration set-up is shown in Figure 1

In each experiment, the membrane is first placed in distilled water for 2 h before used to make sure that the membrane is clean. It is then compacted by place it in the cell and compress up to 200 kPa for approximately one hour using distilled water. To discover the membrane permeability, pure water fluxes were measured at various pressures. The weight of permeate collected at a specific time was calculated to get the initial membrane characteristic as pure water flux (J0).

After the ultrafiltration process, permeate flux and membrane rejection are calculate to distinguish the performance of the surfactant-enhanced ultrafiltration. The permeate fluxes (J) were determined by weighing permeate and calculated based on Equation (1).

The permeate was collected every 5 minutes for 120 minutes to get a comprehensive result of flux profile

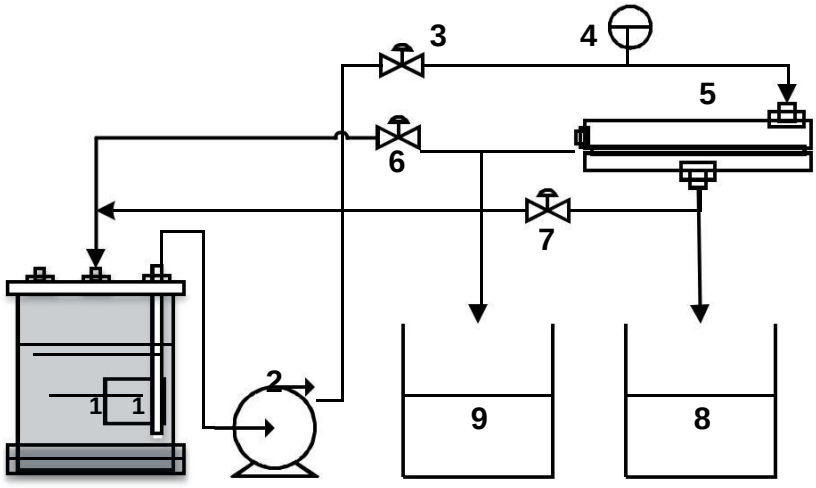
$$J = \frac{W}{A\ x\ t} \quad (1)$$

Where W is the weight of permeate, A is the membrane area, and t is the time interval. Ultrafiltration process without any addition of surfactant in the feed solution is conducted as the control variables. On the other hand, the micellar-enhanced ultrafiltration was conducted with the addition of surfactant (model surfactant solution). The experiment was a total recycle system where permeate and the retentate were recycled into the feed tank. In each operation, permeate, and retentate was collected and analyzed at the time of 0, 60, and 120 minutes.

The rejection (R) was calculated for each sample collected at time 0, 60, and 120 minutes. The calculation was carried out according to Equation (2)

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where, CP is the concentration of heavy metal or COD of the permeate and CF is the concentration of the feed respectively. The COD concentration analysis was conducted by spectrophotometric methods and COD kit with suitable reagent. While the Cr concentration analysis was performed using conductometric methods.



1. Feed Tank
2. Feed Pump
3. Feed Valve
4. Pressure Gauge
5. UF Membrane Module
6. Retentate Recycle Valve
7. Permeate Recycle Valve
8. Permeate Tank
9. Retentate Tank

Figure 1. Schematic Picture of Membrane Ultrafiltration

3. Results and discussions

3.1. Extraction of Saponin

The extraction of saponin from pericarps of Sapindus rarak DC. has been conducted using distilled water as the solvent. Water has been frequently used as a solvent for saponin extraction and proved to give better results than another polar solvent such as ethanol or aqueous ethanol [28]. This part of the study is performed to investigate the concentration and yield of saponin extracted from the dried-ground

pericarp of Sapindus rarak DC. The yield of saponin is calculated on the material dry basis. The results are present in Figure 2.

Figure 2 shows that the yield of extracted saponin is increased by the increase of solvent ratio. It was ascribed to the fact that more extraction solvent exposes to the raw material can boost the extraction process. It is the nature of the extraction process where the greater the solute-solvent ratio increases the concentration gradient and the driving force during mass transfer in solids. This system has an effect on an increase of the substance diffusion from the solid component to the solvent. Furthermore, extraction was influenced by how fast the component was dissolved and the equilibrium of solute solubility in the liquid solution was achieved [29]. From this study, the equilibrium of saponin extraction using distilled water as the solvent was achieved at a solute-solvent ratio of 1:40 (w/v). With the maximum yield of 22.54%. The further increase of solvent ratio did not make any significant difference where the yield of
22.51% and 22.53% is obtained from the solute-solvent ratio of 1:80 and 1:150 (w/v) respectively. On the other hand the extraction with a ratio of 1:10 and 1:20 (w/v) showing a lesser yield. It indicates that the solvent was already saturated and unable to solubilize more saponin substance. The similar results were found in the extraction of steroid saponin from Dioscorea zingiberensis C.H. Wright [30], extraction of dioscin and protodioscin from T. terrestris [31].

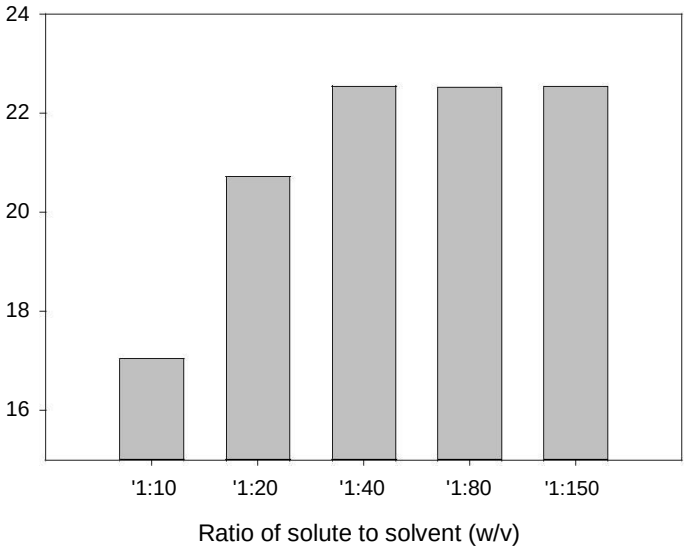


Figure 2. Concentration of saponin in extract solution and yield of extracted saponin

3.2. Permeate flux profile of surfactant-enhanced ultrafiltration system

Ready to use the extract of saponin obtained from the extraction process was used for the surfactant-enhanced ultrafiltration to treat wastewater. The real batik wastewater is slightly diluted using distilled water (addition of 10% of water) to avoid direct fouling on the membrane. The operation of ultrafiltration was carried out without and with the presence of surfactant at a concentration below the CMC until above the CMC. Flux profile at various time for filtration of batik wastewater is present in Figure 3.

Saponin is a natural plant-derived substance with a combination of nonpolar sapogenin and a water-soluble side chain. This characteristic is similar to the structure of most synthetic surfactants having lipophilic and hydrophilic molecular parts [32]. Figure 3 shows the flux profile of textile effluent treatment using surfactant-enhanced ultrafiltration on a various concentration of saponin surfactant material. The flux value of solution without saponin is higher than the one with saponin addition. The flux value is decreased by the increase of saponin concentration on the feed solution. The lowest average flux value of 31.35 L/m^2.h was obtained from the feed solution with saponin concentration of 2 times CMC. The process without the addition of saponin exhibit permeates flux

declined over time. However, ultrafiltration process with the addition of saponin above CMC only slightly declined and almost stable, then the process without saponin or saponin below CMC. This is due to the interaction of saponin molecule with the pollutant where the pollutant is covered by saponin molecules. The free monomer of dye molecule has a tendency to block the pore of the membrane, resulting in the significant flux decline. Where the dye molecule covered by saponin molecules has a bigger size and rarely goes inside the pore of the membrane. Resulting in a more stable flux profile.

Addition of saponin as surfactant molecule in the feed solution at a concentration above the CMC generates the formation of surfactant micelles [33]. In general, the micelle structure is the hydrophobic region in the internal core, and hydrophilic region in the external side. The hydrophobic core had the ability to solubilize hydrophobic or less polar molecule. As for the polar or charged layer of the external side, micelle has the more hydrophilic characteristic [34]. Based on this fact, the pollutant molecule will be trapped in the core of the micelle, where it is covered by a hydrophilic molecule. This hydrophilic side of surfactant micelle had the tendency to attached one to each other in low aqueous solution. This micelle forming a layer, blocking the water to get through the membrane, resulting in the lower of flux. This layer is rather not permanent and can be disturbing again by the feed flow, proved by the tendency of flux profile to be constant.

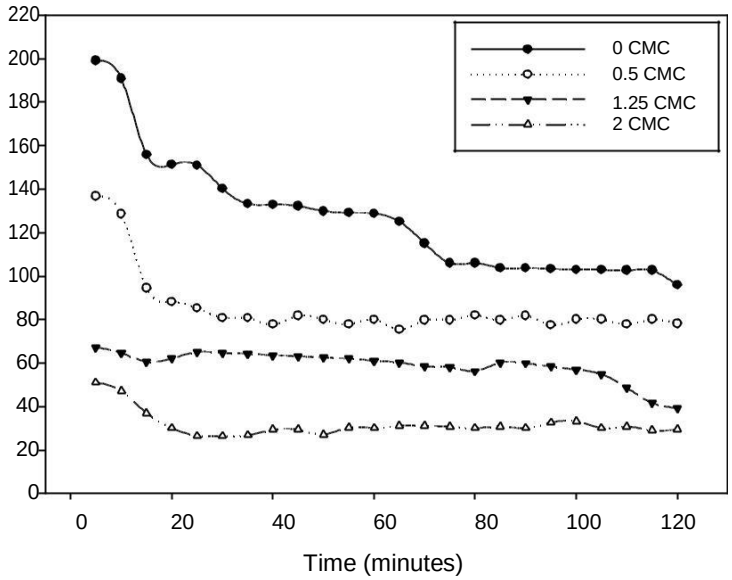


Figure 3. Flux profile of batik wastewater treatment by surfactant-enhanced ultrafiltration at various CMC

3.3. Rejection of Cr and COD

The performance of membrane ultrafiltration is determined by its ability to retain a particular component. This performance was measured by the value of % rejection. It is an important parameter to present the membrane selectivity which means the ability of the membrane to retain or let pass a particular species. Membrane selectivity depends on the interfacial interaction between the membrane surface to the species that pass through it, the size of the species and the membrane pore size. Substances with molecular weight bigger than the membrane pore size are retained on the membrane surface, whereas the smaller-molecular-weighted species will pass through the membrane.

In this study, the rejection of Cr and COD was investigated. Chrome is one of the heavy metal commonly found in textile industries effluent. The preliminary analysis was conducted to know the Cr concentration on the raw real batik wastewater. Cr concentration of the raw batik wastewater is 615 ppm. The source of Cr heavy metal is the dye and preservative compound used in the production of finished textile [35]. While COD is an important parameter to determine wastewater quality.

The COD corresponds to an oxygen required to degrade biodegradable and non-biodegradable organic compounds. Figure 4 (a) and (b) presents the concentration of Cr and COD level at the various condition, while Figure 4 (c) and (d) presents the percent rejection of Cr and COD on the ultrafiltration membrane system.

Figure 4 presents a decrease of the Cr and COD concentration after the ultrafiltration process. The concentration of Cr and COD is also rather lower in the ultrafiltration process enhanced with saponin. And the % rejection of both Cr and COD was increased as the increase of saponin concentration above CMC. Saponin at a concentration of 2 times CMC giving the best result with lowest Cr and COD concentration of 18.3 ppm and 108.4 ppm, respectively. However, the addition of saponin as surfactant below the CMC was not significantly made any difference. The feed with saponin as much of 0.5 times CMC has a similar concentration of Cr and COD with the pure wastewater feed. Addition of saponin was definitely helped to reject the pollutant molecules from the effluents if only added above CMC. Surfactant at the concentration above its CMC tends to form micellar structure promptly, but below CMC, the surfactant molecules were in monomer state [13].

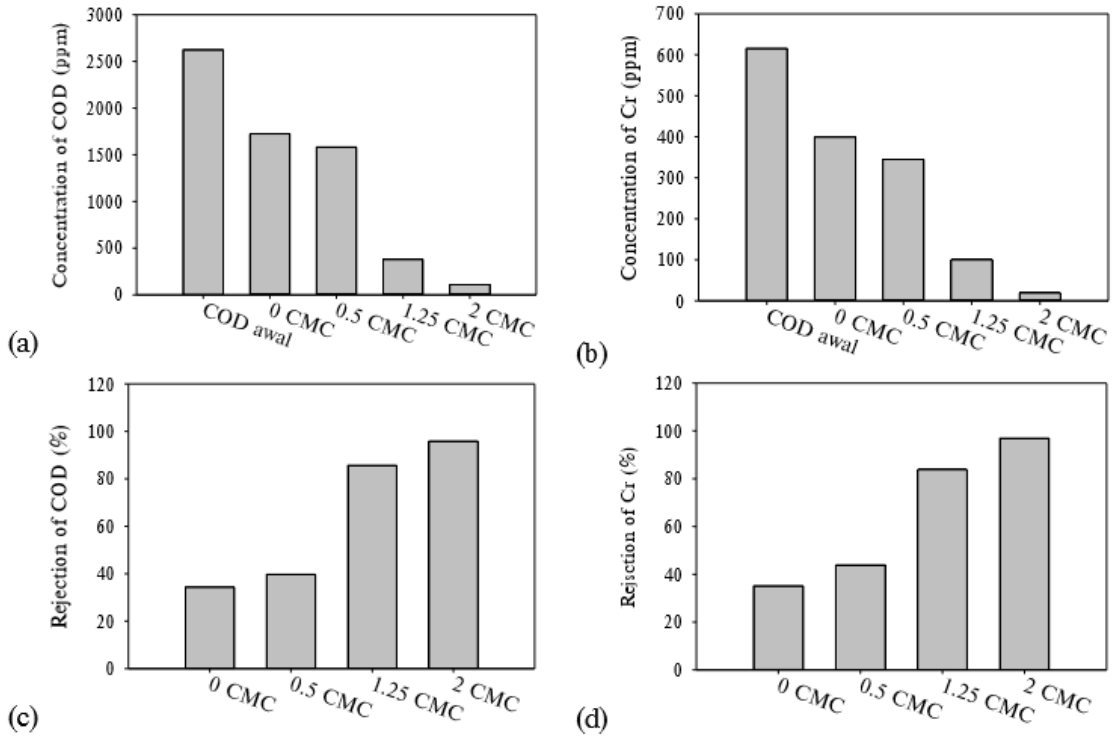


Figure 4. Membrane performance analysis (a) Concentration of COD before and after process, (b) Concentration of Cr before and after process, (c) Rejection of COD, (d) Rejection of Cr.

Low level of Cr and COD in permeate indicates that saponin is worked to solubilized or bounded the heavy metal molecule, dyes molecules, and other pollutants on its micellar structure. The bigger molecules formed by the interaction of surfactant micelle and pollutant was further retained by the membrane. Consequently, a smaller concentration of dye, pollutant, and surfactant was found, which were characterized by low levels of COD and Cr [11, 36]. As present in figure 4 (a) and (b), the concentration of Cr and COD was decreased by the increase of saponin concentration. The % of rejection was calculated by equation 2 where the concentration of a pollutant in the permeate compared to the concentration of a pollutant in the feed. The % of rejection showing how well the system ability to reject the pollutant. Figure 4 shows that with the addition of saponin as natural surfactant the concentration of Cr and COD level in the permeate was significantly decrease, resulting in the increase of % rejection.

High % rejection showing that the pollutant was well rejected from the wastewater after MEUF process. In the previous study, the surfactant-enhanced ultrafiltration has been applied for treatment of soil washing solution and the results show a reduction of COD level around 80%. The previous study of MEUF process using polyethersulfone membrane with a similar molecular weight cut-off also shows a similar result. The addition of ODA (octadecylamine acetate) and CPC (cetylpyridinium chloride) will decrease the final concentration of fluoride and increase the % of rejection up to 95-99% [37]. The other similar study to remove cadmium and zinc ion by MEUF process with SDS (sodium dodecyl sulfate) [15, 38] also shows the same trend of results. Even though the previous study is applying synthetic surfactant to support the filtration process, but the result was similar to the outcome of this study.

4. Conclusions

Saponin from pericarps of Sapindus rarak Dc is successfully extracted by maceration methods. The highest yield is obtained at solute to solvent ratio of 1:40 (w/v). The flux value of solution without saponin is higher than the one with saponin addition. The flux value is decreased by the increase of saponin concentration on the feed solution. The lowest average flux value of 31.35 L/m^2.h was obtained from the feed solution with saponin concentration of 2 times CMC. The process without the addition of saponin exhibit permeates flux declined over time. On the other hand, the ultrafiltration process with the addition of saponin above CMC only slightly declined and almost stable. This is the impact of saponin molecule interaction with the pollutant. Where the pollutant covered by saponin molecules has a bigger size and rarely goes inside the pore of the membrane. The membrane performance shows that saponin is successfully worked to solubilize or bounded the heavy metal molecule, dyes molecules, and another pollutant on its micellar structure. This is proved by the decrease of Cr and COD concentration after the ultrafiltration process enhanced with saponin. Saponin at a concentration of 2 times CMC giving the best result with lowest Cr and COD concentration of 18.3 ppm and 108.4 ppm, respectively, and highest rejection of Cr and COD of 95.88% and 96.91% respectively.

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