

Fouling Mechanism of Micelle Enhanced Ultrafiltration with SDS Surfactant for Indigozol Dye Removal

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FOULING MECHANISM OF MICELLE ENHANCED ULTRAFILTRATION WITH SDS SURFACTANT FOR INDIGOZOL DYE REMOVAL

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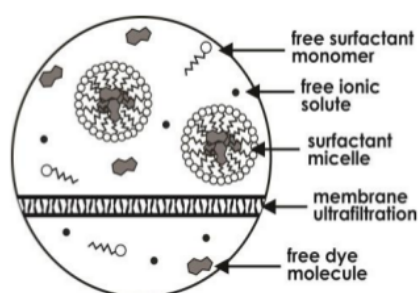
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Graphical abstract



Abstract

1.0 INTRODUCTION

Indigosol dye is a reactive synthetic dye commonly used as fabric dye and widely used to produce light and bright color. In Indonesia, indigosol dye is applied as one of the fabric dye for batik industry both on an industrial scale or home industry. The dyeing process produces effluent water containing various types of dyes. The dye pollutant on wastewater needs to be treated before being discharged to the environment. Severe damage on the aquatic environment may happen due to the presence of inorganic or synthetic dyes in wastewater. Many of these dyes are toxic and prone to cause carcinogenic effect. Synthetic dyes originally have a complex molecular

structure, making them more stable and very difficult to be degraded [1]. Indigosol dye is a synthetic inorganic reactive dye with highly soluble in water.

Investigation on the removal of inorganic dyes from wastewater has been found in the literature. Major technologies applied to process the dye wastewater were biodegradation [2], adsorption [3, 4], oxidation [5], coagulation-flocculation [6, 7] and membrane separation [8, 9, 10, 11]. However, there were some process challenges in inorganic dye pollutant treatment. Conventional biodegradation treatment is not very effective to treat synthetic dye considering its non-biodegradable characteristic. Biological treatment also can barely remove most used dyes, and ineffectively decolorise the

wastewater effluent. Oxidation methods are only effective to remove organic compounds at very low concentration. Adsorption is very dependable by solution equilibrium and having slow process performance [12].

In order to overcome this challenge, separation using membrane technology is an alternative method to remove synthetic dye from wastewater. Membrane separation technology is known as a technically effective and commercially viable for wastewater treatment [13]. Membrane technology is a **4**essure driven process with several classifications such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [14]. However, the small particles removal process such as reverse osmosis and nanofiltration were reported having low permeability, higher transmembrane characteristic and required high-pressure condition. This restriction leads to higher working investment and restriction of its extensive use [15]. Therefore, the use of ultrafiltration is expected to provide better membrane performance and low differential pressure.

Nevertheless, conventional ultrafiltration system is limited for removal of some low molecular weight inorganic compound that soluble in water. Indigosol dye molecular weight is slightly below the range of UF membrane molecular weight cut off (400-700 Da). As a consequence, micellar-enhanced ultrafiltration (MEUF) is proposed as a more viable alternative process for effective removal of indigosol dye on wastewater.

MEUF system is a promising physicochemical separation technique, with high effectiveness for removing small molecules [16, 17], heavy metals ions [18, 19, 20, 21], and reactive toxic dye [22, 23, 24] from wastewater. The MEUF technique is performed based on the surfactant characteristic in aqueous solution. At concentration above its critical micellar concentration (CMC), surfactant molecule prone to spontaneously aggregate to form micelles structure [25]. Micelles have large size and hence make them easy to retain together with the pollutant particles bound in its core and allowing permeate with higher purity to be obtained. The mechanism of micellar-enhance ultrafiltration is depicted in Figure 1. The MEUF method has the characteristic of low operation pressure, low energy requirement, better-retaining efficiency and simple operating. However, the shortcoming of membrane fouling and concentration polarization was unavoidable [11].

Although many studies of contaminant removal from wastewater have already carried out, not many experimental studies of indigosol dye removal using UF and MEUF membrane separation is reported. It is miserable as indigo sol dye is widely used as dye material on fabric industries. For that reason, this study is focused on the removal efficiency of various indigosol dye (Pink IR, brown VAT1 and blue O4B) using ultrafiltration and MEUF system. Dye wastewater model solution was used to provide more understanding of the filtration phenomena. The primary objective of this study is to examine different

filtration phenomena between ultrafiltration system and MEUF system. The study is conducted by evaluating the flux profile, pollutant concentration on permeate and % rejection of the membrane. Evaluation of fouling phenomena is also performed by a mathematical model based on Hermia's models, representing different fouling mechanism (complete blocking, standard blocking, intermediate blocking and cake/gel formation).

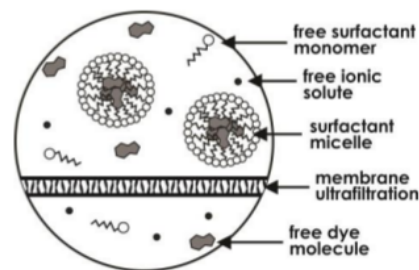


Figure 1 MEUF mechanism of inorganic dye removal

2.0 METHODOLOGY

2.1 Dye Model Solution

The dye wastewater model solutions were prepared using analytical grade reagents and distilled water as the solvent. Indigosol pink IR, indigo sol brown VAT1 and indigo sol blue O4B were used as the dye on the wastewater model solution. To make the dye solution, 90 grams of each dye was added to 1 litre of distilled water. The solutions were homogenized using magnetic stirrer without heat treatment. Sodium dodecyl sulphate (SDS) as the surfactant was provided by Sigma-Aldrich. The SDS has molecular weight of 288,372 gr/mol and the critical micelle concentration of 8,27 mMol [26]. Model of surfactant solution was prepared by adding surfactant at various CMC concentration (0; 1,25; 1,5; and 2 times of CMC). Then the solution was fed into the MEUF system.

2.2 Ultrafiltration and MEUF System

The membrane used in this research was flat sheet polyethersulfone (PES) membrane having molecular weight cut off 1 kDa (Sterlitech, USA). The MEUF experiments were conducted at laboratory-made UF membrane cell. Figure 2 presents the MEUF system, which operated in cross-flow mode. The MEUF experiments were carried out at room temperature ($\pm 29^{\circ}\text{C}$), and the transmembrane pressure (TMP) was maintained at 1 bar.

Each membrane was compacted before used in the ultrafiltration process. The compaction was conducted by filtering water through the membrane at pressure of 1 bar for 60 minutes. The weight of permeate collected at specific time was calculated

to get the initial membrane characteristic as pure water flux (J_0). Then, the dye wastewater model solution was feed into the filtration instrument. Permeate fluxes (J) were determined by weighing permeate collected every 5 minutes for 120 minutes.

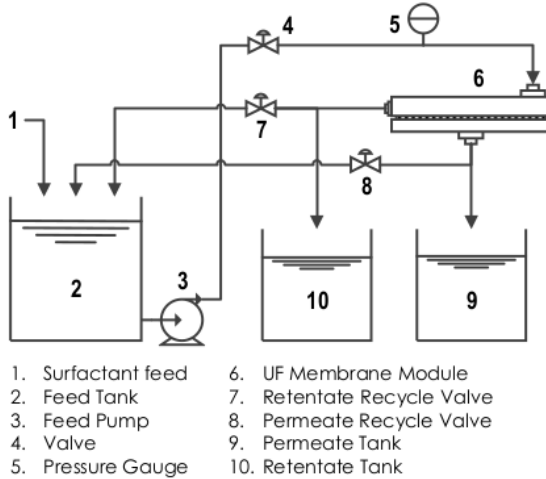


Figure 2 Cross flow micellar-enhanced ultrafiltration membrane system

The flux was calculated based on Equation (1).

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

Where W is the weight of permeate, A is the membrane area, and t is the time interval. Ultrafiltration was operated without any addition of surfactant in the feed solution. 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 were collected and analyzed at the time of 0, 60, and 120 minutes.

2.3 Analysis of Membrane Rejection

Ultrafiltration and MEUF performances to remove dye from the wastewater model solution were evaluated by dye rejection. 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, C_p is permeate concentration and C_f is the feed concentration respectively. The concentration of dye was determined using Spectrophotometric UV-Vis at maximum wavelength by calibration methods.

2.4 Model of Membrane Fouling Mechanism

Mathematical models were used to describe the fouling phenomena, based on Hermia's model. Hermia's model comprises four different blocking mechanism models, complete blocking, standard blocking, intermediate blocking, and gel/cake formation. The pore blocking law on filtration process was expressed by equation (3).

$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV}\right)^n \quad (3)$$

Where t is the filtration time, V is the permeate volume at specific time, n is a constant to indicate the fouling mechanism. The n value for complete blocking, standard blocking, intermediate blocking, and gel/cake formation is 2, 1.5, 1, and 0, respectively. After taking account of the n value and the condition on each fouling mechanism, the linearised equation according to equation (3) are given in Table 2 [27].

Table 2 Linearisation equation of blocking/fouling models based on Hermia's model

Model of Blocking Mechanism	Linearize Equation	Physical Concept
Complete Blocking	$\ln J = \ln J_0 - K_c t$	Formation of surface deposit
Standard Blocking	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + K_s t$	Pore blocking and surface deposit
Intermediate Blocking	$\frac{1}{J} = \frac{1}{J_0} + K_i t$	Pore constriction
Gel/Cake Formation	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{ef} t$	Pore blocking

3.0 RESULTS AND DISCUSSION

3.1 Permeate Flux Profile of UF and MEUF System

Various kinds of indigosol dyes were separated from the wastewater model solution using ultrafiltration and MEUF. Ultrafiltration process was conducted without the presence of surfactant, while MEUF was carried out by the presence of surfactant on various concentration. Flux profiles at a various time for filtration of indigosol VAT brown, indigosol Pink IR, and Indigosol blue were shown in Figure 3.

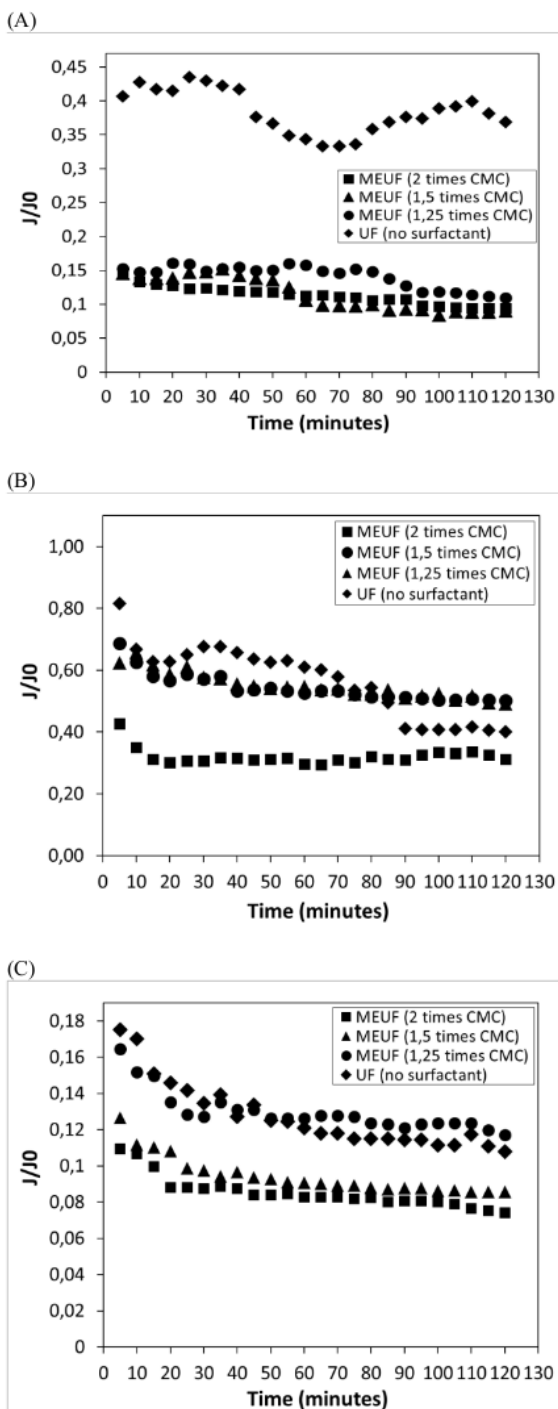


Figure 3 Flux profile of indigosol dye filtration by ultrafiltration and MEUF for: (A) Indigo sol pink IR, (B) Indigo sol blue O4B and (C) Indigo sol brown VAT1

Indigosol dye is a leuco ester reactive dye having a specific ionic structure of ion Na^+ [31]. Each indigosol dye has their own specific ion placement resulting to

the difference of colour appearance. In this study, three kinds of indigosol dyes were used, and molecular structure of each indigosol dyes are presented in Figure 3.

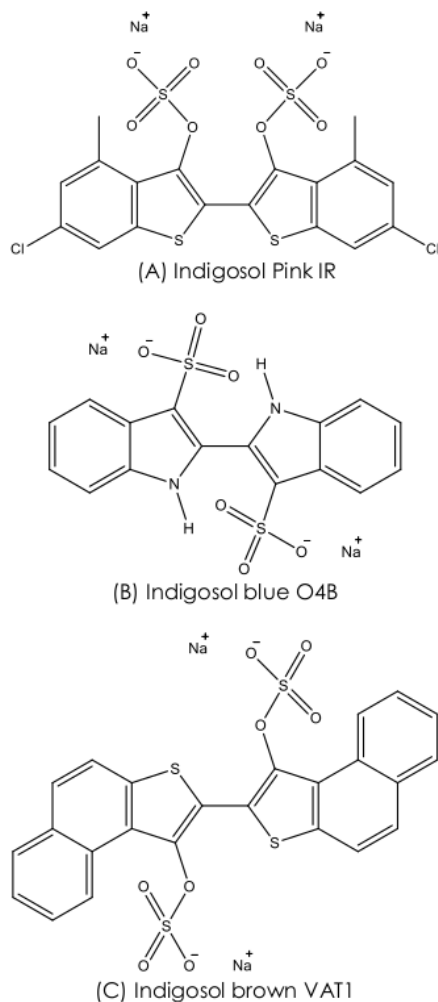


Figure 4 Molecular structure of indigo sol dye

Figure 4 shows that indigosol pink IR have a pair of Na^+ ion on the same side, as indigosol blue and indigosol VAT brown have the ion pairing on the opposite side. The different of ion disposition between the indigosol dyes affecting its interaction with the surfactant molecules. Adding of surfactant to an aqueous solution at concentration above its CMC generates the formation of surfactant micelle. In general, the internal core of the micelle is the hydrophobic region, having the ability to solubilise hydrophobic or less polar molecule. In contrast, the external polar or charged layer of micelle has the more hydrophilic characteristic. Based on the ion disposition, the ionic interaction between indigosol pink and surfactant molecule mainly occur only on

one side and leaving the other side of dye molecule to have the more hydrophobic characteristic. The hydrophobic side has a tendency to attach to the membrane because the PES membrane is partly hydrophobic. This result in the accumulation of dye molecule on the membrane surface and lower the flux value compared to those process without surfactant addition. Similar solubilisation mechanism of hydrophobic and hydrophilic substances by surfactant micelle was also reported in the previous study for removal of emerging contaminants [25, 32] and fractionated natural organic matter [33].

As for indigosol blue and indigosol VAT brown, the flux of wastewater with surfactant addition is similar to the flux of dye only wastewater. It is expected that the surfactant-dye interaction takes place more thoroughly on each opposite side of the dye molecule. Emerging thorough hydrophilic external layer covering the dye molecule. This layer prohibits the micelle molecule attached to the membrane surface. In addition, a cross flow system of the filtration process inducing a vertical flow of solution through the membrane surface and generate a concentration gradient on the membrane film and diffuse the micelle back to the feed bulk.

3.2 Dye Molecule Rejection

Membrane performance is determined by its ability to retain a particular component expressed as percent of rejection. Membrane rejection is an important parameter to present the selectivity of the membrane. Membrane selectivity is used to measure the membrane ability to retain or let pass a particular species. Membrane selectivity depends on the interfacial interaction between membrane surface to the species that pass through it, the size of the species and the membrane pore size. Substances having molecular weight higher than membrane pore size is retained on the membrane surface as retentate, whereas the smaller-molecular-weighted species will pass through the membrane as permeate. In this experiment, permeate is expected to be water with relatively low impurities (dye molecules) content. Table 1 shows the dye concentration on permeate after filtration.

Table 1 Concentration of dye impurities on the permeate after membrane separation

Surfactant Concentration	Dye Concentration on Permeate		
	Indigosol Blue O4B	Indigosol Pink IR	Indigosol Brown VAT1
0 cmc	4651,29	5186	2653,14
1,25 cmc	4297,18	5188,5	1553,14
1,5 cmc	4090,12	5172,25	1062,94
2 cmc	4057,18	5157,25	766,86

Based on Table 1, the dye concentration of the ultrafiltration system is higher than the MEUF. This corresponds to more dye impurities transfer into

permeate on the ultrafiltration system whether caused by direct pass through the membrane film or convective transfer of solute particles. The addition of surfactant into the polluted aqueous wastewater resulting in the lower of impurities concentration on permeate. The surfactant was added at concentration higher than CMC, where the surfactant molecule aggregates and forming micelles. The surfactant used in this study is SDS, an anionic surfactant having specific negative charge on the aqueous solution. The dye impurities bind with the negatively charged micelles of SDS surfactant and make it bigger than the membrane pore. As a result, it can be retained by the ultrafiltration membrane. The use of SDS surfactant to form micelles on the wastewater treatment by MEUF has already investigated. The successful result is also reported by the previous study for removal of cadmium ions [28], chromium ions [34], boron ion [17] and zinc ions [35].

As seen in Table 1, the indigosol VAT brown permeate have lower concentration of dye impurities compared with other indigosol dye. Based on the molecular structure of each indigosol dye used in this experiment, the indigosol VAT brown has a bigger molecular structure with 4 hexagonal aromatic group. While the indigosol pink IR and indigosol blue only have 2 hexagonal aromatic group. This more prominent structure of indigosol brown allows molecules to retain easily on the membrane than other smaller molecules. Moreover, aggregation of surfactant to form micelles and solubilise dye molecule on the micelles structure making it to have bigger molar volume.

The pollutant concentration on permeate also affects the membrane rejection. Permeate with lower impurities concentration specify a better membrane rejection. The membrane rejection of various indigosol filtration under ultrafiltration and MEUF system is exhibited in Figure 5 which have conformity with the trend of impurities concentration on permeate.

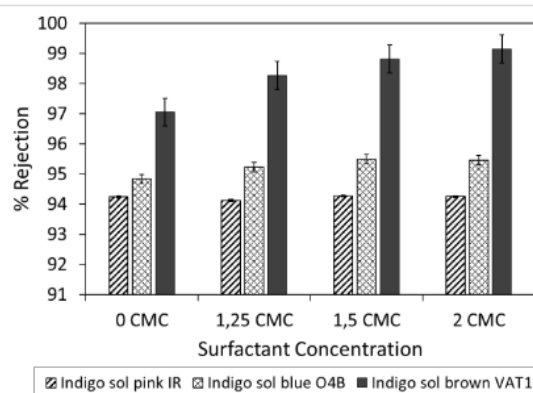


Figure 5 Rejection of indigo sol dye at various CMC, (A) Indigo sol pink IR, (B) Indigo sol blue O4B and (C) Indigo sol brown VAT1

3.3 Model of Blocking Mechanism

Mathematical model can be useful to accurately predict the fouling phenomena on the membrane filtration process. Blocking mechanism of indigosol dye during ultrafiltration and MEUF was studied by application of Hermia's mathematical model. Hermia model provides a comprehensive fouling prediction models, well equipped with four different fouling

mechanisms [33]. The experimental filtration data is fit to the empirical fouling models by Hermia to identify well suited fouling mechanisms. Previous study reported a well fitted result of Hermia's model with the experimental data for removal of polysaccharides [36], organic pollutant [27], and remazol dye [37] from wastewater.

Table 2 Mathematical model parameter of UF and MEUF blocking phenomena on indigo sol dye removal

Indigo sol dye	Filtration system	Complete Blocking (n=2)		Intermediate Blocking (n=1)		Standard Blocking (n=3/2)		Cake Formation (n=0)	
		R ²	Kc	R ²	Ki	R ²	Ks	R ²	Kfc
Pink IR	Ultrafiltration	0,8863	-0,0024	0,8784	0,0014	0,8826	0,0009	0,8681	0,0017
	MEUF	0,8589	-0,0057	0,8691	0,0026	0,8646	0,0019	0,8748	0,0023
Blue O4B	Ultrafiltration	0,8645	-0,0057	0,8463	0,0026	0,8567	0,0019	0,821	0,0024
	MEUF	0,8812	-0,002	0,8972	0,0008	0,8896	0,0006	0,9099	0,0006
Brown VAT1	Ultrafiltration	0,8741	-0,0028	0,8722	0,0017	0,8555	0,0012	0,8998	0,0017
	MEUF	0,8096	-0,002	0,808	0,0012	0,7886	0,0009	0,8436	0,0011

Table 2 shows fitting experimental data and the degree of model fitness (represent by R²) based on Hermia's model. The value of corresponding correlation (R²) was simply used to determine the fitted blocking mechanism rationally. The befitting experimental data and the degree of model fitness (represent by R²) based on Hermia's model. The value of corresponding correlation (R²) was merely used to determine the fitted blocking mechanism rationally. The complete blocking mechanism fit the experimental data for ultrafiltration of indigosol blue and indigosol pink IR. While ultrafiltration of indigosol VAT brown is fit to the cake formation mechanism. The micellar-enhanced ultrafiltration of all indigosol dye used in this study also shows a fitting to cake formation mechanism.

Complete blocking is the blocking mechanism resulting a reduction of open pores without deposition of foulant particles on the membrane surface. This blocking occurs when the foulant particle size is similar with the membrane pore size. Cake formation is the most severe blocking mechanism on the membrane filtration. This blocking occurs when the foulant particles deposition already block the membrane pore and initiate cake formation [38, 39].

As explained before, the molecular structure of indigosol blue and pink IR is smaller than indigo sol vat brown. Hence, it is possible if there is a different blocking mechanism between indigosol blue and pink IR with the indigosol vat brown. Indigosol vat brown has a more significant molecular structure, allowing it to deposit on the membrane surface and initiate cake formation highly. The filtration of indigosol dye by MEUF system is fitted to the cake formation mechanism. Theoretically, the dye-surfactant micelle has a bigger molecular structure compared with the monomer structure of surfactant

only or dye only. The micelle will deposit on the membrane surface, causing fouling over the time of filtration, and induce membrane pore blocking.

4.0 CONCLUSION

In this study, micellar-enhance ultrafiltration system is aimed to remove reactive indigosol dye from wastewater. The process was compared to the common ultrafiltration system. Results show better dye pollutant rejection by the addition of surfactant. The formation of surfactant micelle is expected to help the retaining of dye molecule. However, the addition of surfactant in the MEUF system also lowered the permeate flux. In addition, different profiles of membrane flux between each indigosol dye were shown. The different molecular structure of each indigosol dye is presumed as the primary factor of different flux and rejection profile. Fouling/blocking mechanism of UF and MEUF process to remove indigo sol dye is predicted by mathematical model based on Hermia's model. Based on the model, fouling mechanism was complete blocking and gel/cake formation. Further experimental work to study indigosol dye removal by membrane separation is indeed still required. Indigosol dye is an easily oxidize reactive dye. Hence, the effect of oxidation support factor also needs to be considered in the ultrafiltration and MEUF process.

Acknowledgement

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