

KORESPONDENSI JURNAL**JUDUL ARTIKEL : FOULING MECHANISM OF MICELLE ENHANCED ULTRAFILTRATION WITH SDS SURFACTANT FOR INDIGOZOL DYE REMOVAL**

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1.	Submit Manuscript to International Conference "MST 2017"	5 September 2017	Email : Abstract Submission
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8.	PUBLISHED ONLINE	16 Mei 2018	Email : Notification of Publication on Jurnal Teknologi



Nita Aryanti <nita.aryanti@che.undip.ac.id>

Abstract of MST

1 message

N. Aryanti <nita.aryanti@gmail.com>

Tue, Sep 5, 2017 at 6:48 AM

To: mst2017@che.undip.ac.id

Dear organizing committee of MST 2017,

Please kindly find abstract submitted to MST 2017 attached.

Best wishes,

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Separation of Indigosol Dyes in Synthetic Wastewater using Micellar-enhanced Ultrafiltration

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Abstract

Micellar-Enhanced Ultrafiltration (MEUF) is a promising technology capable of separating reactive dyes in batik wastewater. In the MEUF, a surfactant having a concentration higher than its Critical Micelle Concentration (CMC) is added to the polluted aqueous solution. This technology is able to separate the solute which can not be separated by ultrafiltration membrane. This study was focused on determining ultrafiltration (UF), and MEUF performance for reactive dye separation Batik wastewater was modelled by the indigosol Brown VAT 1, Indigosol Pink IR, and Indigosol Blue O4B) at concentration of 90 mg/l. A flat sheet of Polyethersulphone (PES) membrane made from 12% wt PES, 83% wt N-methyl pyrrolidone, and 5% wt Polyethylene glycol was prepared. Sodium Dodecyl Sulphate (SDS) was selected as a surfactant at a concentration of 0 CMC (UF) and 1,5 CMC (MEUF). The research evaluated the performance of UF and MEUF by determining the flux profile and dyes rejection.



MST 2017 <mst2017@che.undip.ac.id>

Acceptance Letter

1 message

MST 2017 <mst2017@che.undip.ac.id>
To: Nita Aryanti <nita.aryanti@gmail.com>

Fri, Oct 27, 2017 at 6:27 AM

Dear Sir/Madam,

We are pleased to inform you that your abstract:

Title : Fouling Mechanism of Micellar Enhanced Ultrafiltration with SDS Surfactant for Indigozol Dye Removal
Author : Nita Aryanti, Andya Saraswati, Rangga Pratama Putra

has been accepted and will be presented for oral presentation in the 13th International Conference Of Membrane Science & Technology (MST) 2017 organized by Department of Chemical Engineering Diponegoro University. The MST 2017 will be held in Patra Jasa Hotel-Semarang on **15th -16th November 2017**. Please note that this acceptance letter is also considered as **an invitation letter**.

Hence, we would like you to submit the abstract and full-paper manuscript which have been formatted according to the templates together with the CV of the presenter (please kindly find the template files in the attachments). The files should be saved as **“name of first author-abstract”**, **“name of first author-paper”** and **“name of first author-cv”**, respectively. Please submit the files at the MST website (<http://mst2017.com/>) before **31st August 2017**. The manuscript will be peer-reviewed and the selected one from those are to published in SCOPUS indexed Journal, a Special Issue of **MATEC Proceeding Conference** or be also be considered for inclusion in **Jurnal Teknologi (Malaysia)**.

We would like to remind you that the final registration for accepted paper and the due date for early-bird payment is **23rd October 2017**.

We are looking forward to seeing you in Semarang.

--

Best regards,

Assoc. Prof. Dr. Tutuk Djoko Kusworo
Conference Chair, Organizing Committee
Diponegoro University

13th MEMBRANE SCIENCE TECHNOLOGY CONFERENCE

Website: <http://mst2017.com/>



Acceptance Letter of MST 2017 nita.docx

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SUBMISSION OF PAPER

1 message

Nita Aryanti <nita.aryanti@che.undip.ac.id>
To: MST2017@che.undip.ac.id

Mon, Nov 6, 2017 at 7:42 PM

Dear Committee,

Here we send our paper for the MST 2017
Thank you for your consideration

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

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Abstract. Membrane separation technology was proposed to confront the trouble to treat inorganic dye pollutant such as indigo sol dye. A modified ultrafiltration process known as micellar-enhance ultrafiltration (MEUF) was used to remove three kind of indigo sol dye (Pink IR, Blue O4B, and vat brown). Surfactant at concentration above CMC was added to form micelle structure and solubilize the dye molecule in the feed solution. Maximum dye rejection was obtain by MEUF of all three kind of indigo sol dye. % rejection of indigo sol pink IR, blue O4B, and brown VAT1 is 94,27%, 95,49% and 99,15%, respectively. Even though, MEUF system leading to higher membrane flux, compared with UF system. Different flux profile phenomena between the three indigo sol dyes also shown in the experiment result. Expectedly cause by the different of each dye molecular structure. The blocking mechanism was predicted by mathematical model based on hermia's model. Depict a mechanism of complete blocking on most UF process and cake formation on MEUF process. This result showing that MEUF system can definitely help to retain the dye molecule on membrane separation process. But, a comprehensive study is needed to increase the membrane flux.

Keywords: Membrane separation, Micellar-enhance ultrafiltration, wastewater, indigo sol dye, blocking mechanism.

1.0 INTRODUCTION

Indigo sol dye is a reactive synthetic dye commonly used as fabric dye. It is widely used to produce light and bright color. In Indonesia, indigo sol dye is one of the fabric dye for batik industry both on industrial scale or home scale industry. The dyeing process produce effluent water contains various types of dyes. The dye pollutant on wastewater need to be treat before discharge to the environment. Severe damage on the aquatic environment may happens due to the presence of inorganic or synthetic dyes in wastewater. Many of these dyes are toxic and prone to cause carcinogenic effect. Synthetic dye originally have a complex molecular structure, making them more stable and very difficult to be degraded [1]. Indigo sol dye is a synthetic inorganic reactive dye with high solubility on water.

The study on the removal of inorganic dyes from wastewater has been studied before. Major technologies available to process the dye wastewater are biodegradation [2], adsorption [3,4], oxidation [5], coagulation-flocculation [6,7] and membrane separation [8,9,10,11]. The process confront some trouble to treat inorganic dye pollutant. Conventional biodegradation treatment is not very effective to treat synthetic dye considering its non-biodegradable characteristic. Biological treatment also can barely removes most used dyes, and ineffectively decolorize the wastewater effluent. Oxidation methods only effective to remove organic compounds on very low concentration.

Adsorption is very dependable by solution equilibrium and having slow process performance [12].

Confronting this challenge, separation using membrane technology may be an alternative way to remove synthetic dye from wastewater. Membrane separation technology known for as a technically effective and commercially viable for wastewater treatment [13]. Membrane technology is a pressure driven process with several classification 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 are report to have low permeability, higher transmembrane characteristic and require high pressure condition. This restriction leading to higher working investment and restriction of its extensive use [15]. Therefore, the use of ultrafiltration is expect to have high better membrane performance, and low differential pressure.

Nevertheless, ordinary ultrafiltration system is limited for removal of some low molecular weight inorganic compound that soluble in water. Indigo sol dye molecular weight is slightly below the range of UF membrane molecular weight cut off (400-700 Da). In consequence, micellar-enhanced ultrafiltration (MEUF) is proposed as a more viable alternative process for effective removal of indigo sol 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. MEUF technique is conduct 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 make it easy to retain together with the pollutant particles bound in its core. Allowing permeate with higher purity to be obtained. The mechanism of micellar-enhance ultrafiltration is depict in the Figure 1. MEUF method has the characteristic of low working pressure, low energy requirement, better retaining efficiency and simple operating. Still, the shortcoming of membrane fouling and concentration polarization is unavoidable [11].

Although many studies of contaminant removal from wastewater has already done. Not many experimental study of indigo sol dye removal using UF and MEUF membrane separation is reported. It is very unfortunate as indigo sol dye is widely use as dye material on fabric industries. For that reason, this study will focus on the removal efficiency of various indigo sol dye (Pink IR, brown VAT1 and blue O4B) using ultrafiltration and MEUF system. Dye wastewater model solution was used to grant more understanding of the filtration phenomena. The main objective of this study is to examine different filtration phenomena between ultrafiltration system and MEUF system. Conduct by monitoring the flux profile, pollutant concentration on permeate and % rejection of the membrane. Evaluation of fouling phenomena also perform by a mathematical models based on Hermia's models. Depict four different fouling mechanism (complete blocking, standard blocking, intermediate blocking and cake/gel formation).

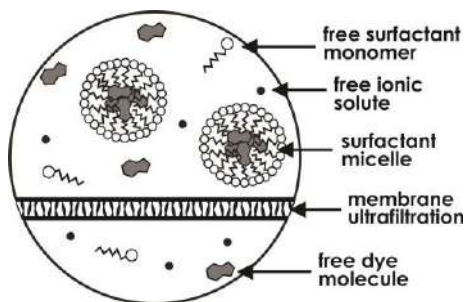


Figure 1 MEUF mechanism of inorganic dye removal

2.0 METHODOLOGY

2.1 Dye Model Solution

The dye wastewater model solution was prepared using analytical grade reagents and distilled water as the solvent. Indigo sol pink IR, indigo sol brown VAT1 and indigo sol blue O4B were used as the dye on the wastewater model solution. As much of 90 grams of each dyes was added into 1 liter 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. It's molecular weight was 288,372 gr/mol and the critical micelle concentration at 8,27 mMol [26]. Model 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 in to the MEUF system.

2.2 Ultrafiltration and MEUF system

The membrane used in this research is polyethersulfone (PES) membrane with molecular weight cut off 1 kDa, manufactured by Sterlitech. The MEUF experiments were conducted at laboratory-scale using UF membrane equipment. Fig 1 present

the MEUF system, which operated in cross-flow mode. The MEUF process 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 each 5 minutes for 120 minutes. 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. While the micellar-enhanced ultrafiltration was conducted with the addition of surfactant (model surfactant solution). The experiment was using total recycle system where permeate and the retentate were recycled into the feed tank. In each operation, permeate and the retentate at time of 0, 60, and 120 minutes was collected and analyzed.

2.3 Analysis of membrane rejection

Ultrafiltration and MEUF performance to remove dye from the wastewater model solution was evaluated by the 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 Spectrofotometric 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 the Hermia's model. Hermia's model comprising four different blocking mechanism models, complete blocking, standar blocking, intermediate blocking, and gel/cake formation. The pore blocking law on filtration process was expressed by equation 3

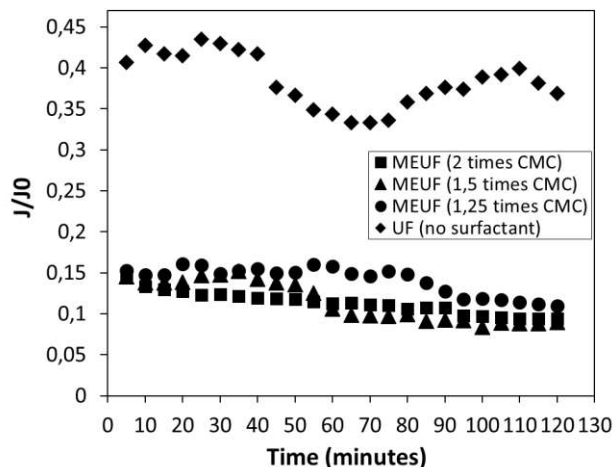
$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV} \right)^n \quad (3)$$

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 linearize equation according to equation (3) are given in Table 2 [27].

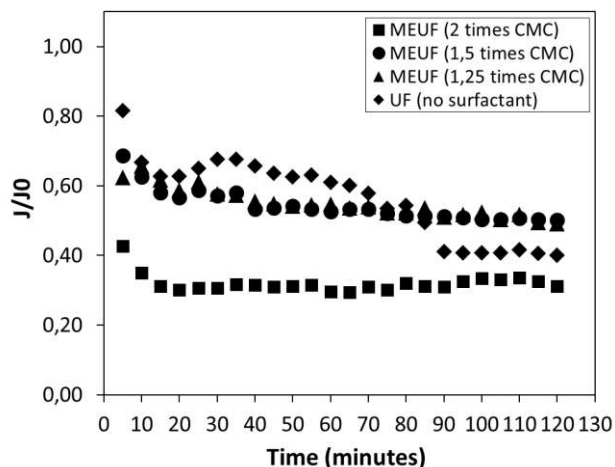
Table 2 Linearize equation of blocking/fouling models based on Hermia's model

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

(A)



(B)



(C)

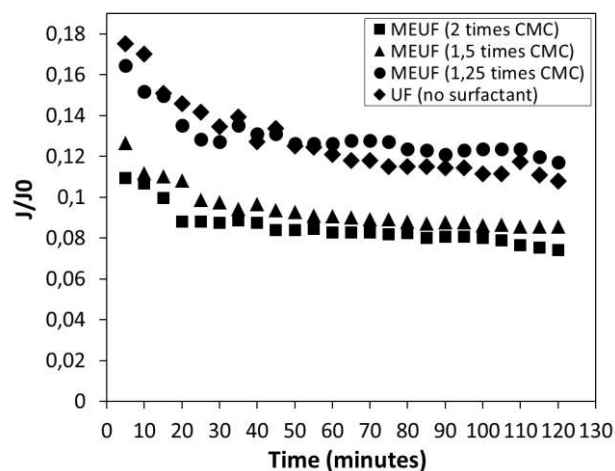


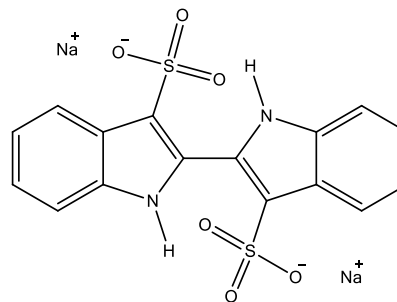
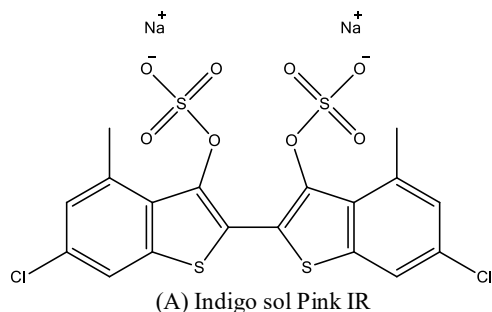
Figure 2. Flux profile of indigo sol dye filtration by ultrafiltration and MEUF for : (A) Indigo sol pink IR, (B) Indigo sol blue O4B and (C) Indigo sol brown VAT1

3.0 RESULTS AND DISCUSSION

3.1 Permeate flux Profile of UF and MEUF System

Various kind of indigo sol dyes were separated from the wastewater model solution using ultrafiltration and MEUF. Ultrafiltration process was conducted without the presence of surfactant, while MEUF was conducted by the presence of surfactant on various concentration. The flux profile at various time for filtration of indigo sol VAT brown, indigo sol Pink IR, and Indigo sol blue were shown in the Fig. 1.

Indigo sol dye is a leuco ester reactive dye having a specific ionic structure of ion Na^+ [31]. Each indigo sol dye has their own specific ion placement resulting in the difference of color appearance. In this study, three kinds of indigo sol dye were used, the molecular structure of each indigo sol dye is present in the Fig. 3



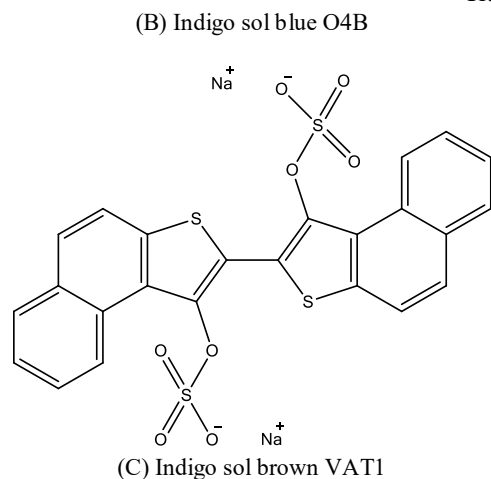


Figure 3 Molecular structure of indigo sol dye

Fig. 3 shows that indigo sol pink IR have a pair of Na^+ ion on the same side, as indigo sol blue and indigo sol VAT brown have the ion pairing on the opposite side. The different of ion disposition between the indigo sol dyes affecting its interaction with the surfactant molecules. Adding of surfactant on aqueous solution with concentration above its CMC generate the formation of surfactant micelle. In general, the internal core of the micelle is the hydrophobic region, having ability to solubilized hydrophobic or less polar molecule. While, the external polar or charged layer of micelle is having more hydrophilic characteristic. Based on the ion disposition, the ionic interaction between indigo sol pink and surfactant molecule mainly occur only on one side. Leaving the other side of dye molecule to have more hydrophobic characteristic. The hydrophobic side have a tendency to attach at the membrane because PES membrane is partly hydrophobic. Resulting on the accumulation of dye molecule on the membrane surface. Lowering the flux value compared with the process carried on without surfactant addition. Similar solubilization mechanism of hydrophobic and hydrophilic substances by surfactant micelle also reports in previous study for removal of emerging contaminants [25,32] and fractionated natural organic matter [33].

As for indigo sol blue and indigo sol VAT brown, the flux of wastewater with surfactant addition is similar with the flux of dye only wastewater. Taking account that the surfactant-dye interaction take place more thoroughly on each opposite side of the dye molecule. Emerging a thorough hydrophilic external layer covering the dye molecule. This layer is prohibit the micelle molecule to attach on the membrane surface. The cross flow system of the filtration process inducing a vertical flow of solution through the membrane surface. 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 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. The substance with molecular weight greater than membrane pore size will be 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 expect to be water with relatively low impurities (dye molecules) content. Table 1 showing 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		
	Indigo Sol Blue O4B	Indigo Sol Pink IR	Indigo Sol 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

From Table 1, it is known that the dye concentration on the ultrafiltration system is higher than the MEUF. Showing 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 to the lower of impurities concentration on permeate. The surfactant was added at concentration higher that 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 charge micelles of SDS surfactant. Making it bigger than the membrane pore, so it can be retained by the ultrafiltration membrane. The use of SDS surfactant to form micelles on the wastewater treatment by MEUF has already done before. The successful result also reported by the previous study for removal of cadmium ions [28], chromium ions [34], boron ion [17] and zinc ions [35].

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

The pollutant concentration on permeate also affect the membrane rejection. Permeate with lower impurities concentration specify a better membrane rejection. The membrane rejection of various indigo sol filtration under ultrafiltration and MEUF system is exhibited on Fig. 4 which have conformity with the trend of impurities concentration on permeate.

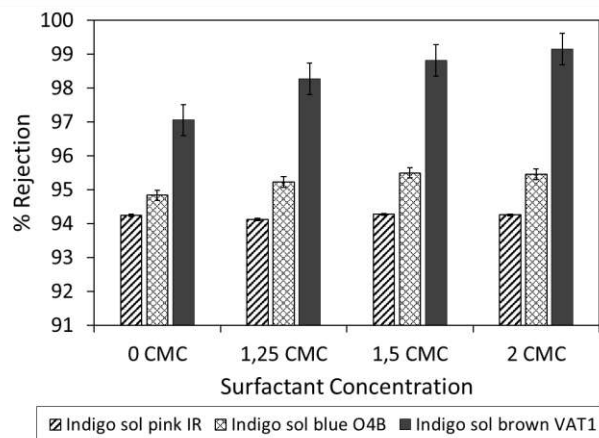


Figure 4 Rejection of indigo sol dye at various CMC, (A) Indigo sol pink IR, (B) Indigo sol blue O4B and (C) Indigo sol brown VAT1

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 indigo sol dye during ultrafiltration and MEUF was studied by application of Hermia's mathematical model. Hermia model provide 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 report 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 shows the befitting experimental data and the degree of model fitness (represent by R^2) based on Hermia's model. The value of corresponding correlation (R^2) was simply used to rationally determine the fitted blocking mechanism.

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 the befitting experimental data and the degree of model fitness (represent by R^2) based on Hermia's model. The value of corresponding correlation (R^2) was simply used to rationally determine the fitted blocking mechanism. The complete blocking mechanism fit to the experimental data for ultrafiltration of indigo sol blue and indigo sol pink IR. While ultrafiltration of indigo sol VAT brown is fit to the cake formation mechanism. The micellar-enhanced ultrafiltration of all indigo sol 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 is 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 is occurs when the foulant particles deposition already block the membrane pore and initiate cake formation [38].

As explain before, the molecular structure of indigo sol blue and pink IR is smaller than indigo sol vat brown. Hence, it is possible if there is a different blocking mechanism between indigo sol blue and pink IR with the indigo sol vat brown. Indigo sol vat brown have a bigger molecular structure allows it to highly deposit on the membrane surface and initiate cake formation. The filtration of indigo sol 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 propose to remove reactive indigo sol dye from wastewater. The process is compared with ordinary ultrafiltration system. The result showing better dye pollutant rejection by the addition of surfactant. The formation of surfactant micelle is expect to help the retaining of dye molecule. Although, addition of surfactant in MEUF system also lowering the membrane flux profile. The result also showing a different profile of membrane flux between each indigo sol dye. The different molecular structure of each indigo sol dye is expect to be the main factor of different flux and rejection profile. Fouling/blocking mechanism of UF and MEUF process to remove indigo sol dye is predict by mathematical model based on hermia's model. The fouling mechanism is predict to be complete blocking and gel/cake formation. The further work to study indigo sol dye removal by membrane separation is indeed still needed. Indigo sol dye is an easily oxidize reactive dye. Hence, the effect of oxidation support factor also need to be consider in the ultrafiltration and MEUF process.

Acknowledgement

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Letter of Acceptance

1 message

MST 2017 <mst2017@che.undip.ac.id>
To: Nita Aryanti <nita.aryanti@gmail.com>

Thu, Dec 14, 2017 at 3:31 PM

Dear Sir / Madam,

The committee of the MST 2017 would like to thank you for your participation in the conference and making the conference run successfully. Currently, we are processing the publication of the papers submitted to and presented at the conference.

Based on the review of the organizing committee, we are glad to inform you that your paper entitled "*Fouling Mechanism of Micelle Enhanced Ultrafiltration with SDS Surfactant for Indigozol Dye Removal*" has been SELECTED to be published in **Jurnal Teknologi**.

Regarding this information, as an author, you are required to prepare your revised paper following the guideline provided. Further review will be performed by the reviewer of Jurnal Teknologi, and the acceptance of the paper is decided by the Editor of Jurnal Teknologi.


Please submit your revised paper by December 27th, 2017.
Thank you for your cooperation.

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Best regards,

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

Nita Aryanti^{a*}, Andya Saraswati^a, Rangga Pratama Putra^a, Aininu Nafiunisa^a

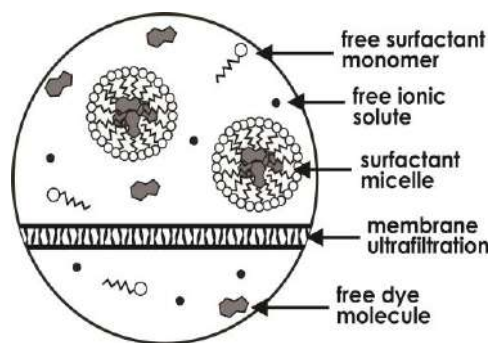
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Graphical abstract



Abstract

Membrane separation technology was proposed to confront the trouble to treat inorganic dye pollutant such as indigo sol dye. A modified ultrafiltration process known as micellar-enhance ultrafiltration (MEUF) was used to remove three kind of indigo sol dye (Pink IR, Blue O4B, and vat brown). Surfactant at concentration above CMC was added to form micelle structure and solubilize the dye molecule in the feed solution. Maximum dye rejection was obtain by MEUF of all three kind of indigo sol dye. % rejection of indigo sol pink IR, blue O4B, and brown VAT1 is 94,27%, 95,49% and 99,15%, respectively. Even though, MEUF system leading to higher membrane flux, compared with UF system. Different flux profile phenomena between the three indigo sol dyes also shown in the experiment result. Expectedly cause by the different of each dye molecular structure. The blocking mechanism was predicted by mathematical model based on hermia's model. Depict a mechanism of complete blocking on most UF process and cake formation on MEUF process. This result showing that MEUF system can definitely help to retain the dye molecule on membrane separation process. But, a comprehensive study is needed to increase the membrane flux.

Keywords: Membrane separation, Micellar-enhance ultrafiltration, wastewater, indigo sol dye, blocking mechanism.

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1.0 INTRODUCTION

Indigo sol dye is a reactive synthetic dye commonly used as fabric dye. It is widely used to produce light and bright color. In Indonesia, indigo sol dye is one of the fabric dye for batik industry both on industrial scale or home scale industry. The dyeing process produce effluent water contains various types of dyes. The dye pollutant on wastewater need to be treat before discharge to the environment. Severe damage on the aquatic environment may happens due to the presence of inorganic or synthetic dyes in wastewater. Many of these dyes are toxic and prone to cause carcinogenic effect. Synthetic dye originally have a complex molecular structure, making them more stable and very difficult to be degraded [1]. Indigo sol dye is a synthetic inorganic reactive dye with high solubility on water.

The study on the removal of inorganic dyes from wastewater has been studied before. Major technologies available to process the dye wastewater are biodegradation [2], adsorption [3,4], oxidation [5], coagulation-flocculation [6,7] and membrane separation [8,9,10,11]. The process confront some trouble to treat inorganic dye pollutant. Conventional biodegradation treatment is not very effective to treat synthetic dye considering its non-biodegradable characteristic. Biological treatment also can barely removes most used dyes, and ineffectively decolorize the wastewater effluent. Oxidation methods only effective to remove organic compounds on very low concentration. Adsorption is very dependable by solution equilibrium and having slow process performance [12].

Confronting this challenge, separation using membrane technology may be an alternative way to

remove synthetic dye from wastewater. Membrane separation technology known for as a technically effective and commercially viable for wastewater treatment [13]. Membrane technology is a pressure driven process with several classification 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 are report to have low permeability, higher transmembrane characteristic and require high pressure condition. This restriction leading to higher working investment and restriction of its extensive use [15]. Therefore, the use of ultrafiltration is expect to have high better membrane performance, and low differential pressure.

Nevertheless, ordinary ultrafiltration system is limited for removal of some low molecular weight inorganic compound that soluble in water. Indigo sol dye molecular weight is slightly below the range of UF membrane molecular weight cut off (400-700 Da). In consequence, micellar-enhanced ultrafiltration (MEUF) is proposed as a more viable alternative process for effective removal of indigo sol 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. MEUF technique is conduct 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 make it easy to retain together with the pollutant particles bound in its core. Allowing permeate with higher purity to be obtained. The mechanism of micellar-enhance ultrafiltration is depict in the Figure 1. MEUF method has the characteristic of low working pressure, low energy requirement, better retaining efficiency and simple operating. Still, the shortcoming of membrane fouling and concentration polarization is unavoidable [11].

Although many studies of contaminant removal from wastewater has already done. Not many experimental study of indigo sol dye removal using UF and MEUF membrane separation is reported. It is very unfortunate as indigo sol dye is widely use as dye material on fabric industries. For that reason, this study will focus on the removal efficiency of various indigo sol dye (Pink IR, brown VAT1 and blue O4B) using ultrafiltration and MEUF system. Dye wastewater model solution was used to grant more understanding of the filtration phenomena. The main objective of this study is to examine different filtration phenomena between ultrafiltration system and MEUF system. Conduct by monitoring the flux profile, pollutant concentration on permeate and % rejection of the membrane. Evaluation of fouling phenomena also perform by a mathematical models based on Hermia's models. Depict four different fouling mechanism (complete blocking, standard blocking, intermediate blocking and cake/gel formation).

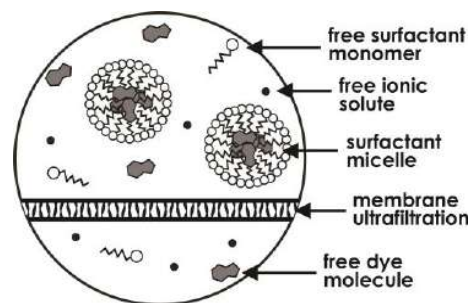


Figure 1 MEUF mechanism of inorganic dye removal

2.0 METHODOLOGY

2.1 Dye Model Solution

The dye wastewater model solution was prepared using analytical grade reagents and distilled water as the solvent. Indigo sol pink IR, indigo sol brown VAT1 and indigo sol blue O4B were used as the dye on the wastewater model solution. As much of 90 grams of each dyes was added into 1 liter 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. It's molecular weight was 288,372 gr/mol and the critical micelle concentration at 8,27 mMol [26]. Model 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 in to the MEUF system.

2.2 Ultrafiltration and MEUF system

The membrane used in this research is polyethersulfone (PES) membrane with molecular weight cut off 1 kDa, manufactured by Sterlitech. The MEUF experiments were conducted at laboratory-scale using UF membrane equipment. Fig 1 present the MEUF system, which operated in cross-flow mode. The MEUF process 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 each 5 minutes for 120 minutes. 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. While the micellar-enhanced ultrafiltration was conducted with the addition of surfactant (model surfactant solution). The experiment was using total recycle system where permeate and the retentate were recycled into the feed tank. In each operation, permeate and the retentate at time of 0, 60, and 120 minutes was collected and analyzed.

2.3 Analysis of membrane rejection

Ultrafiltration and MEUF performance to remove dye from the wastewater model solution was evaluated by the 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)

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

where, C_p is permeate concentration and C_f is the feed concentration respectively. The Concentration of dye was determined using Spectrofotometric 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 the Hermia's model. Hermia's model comprising four different blocking mechanism models, complete blocking, standar blocking, intermediate blocking, and gel/cake formation. The pore blocking law on filtration process was expressed by equation 3

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

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 linearize equation according to equation (3) are given in Table 2 [27].

Table 2 Linearize 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 Formattion	$\frac{1}{J^2} = \frac{1}{J_0^2} + K_{ef} t$	Pore blocking

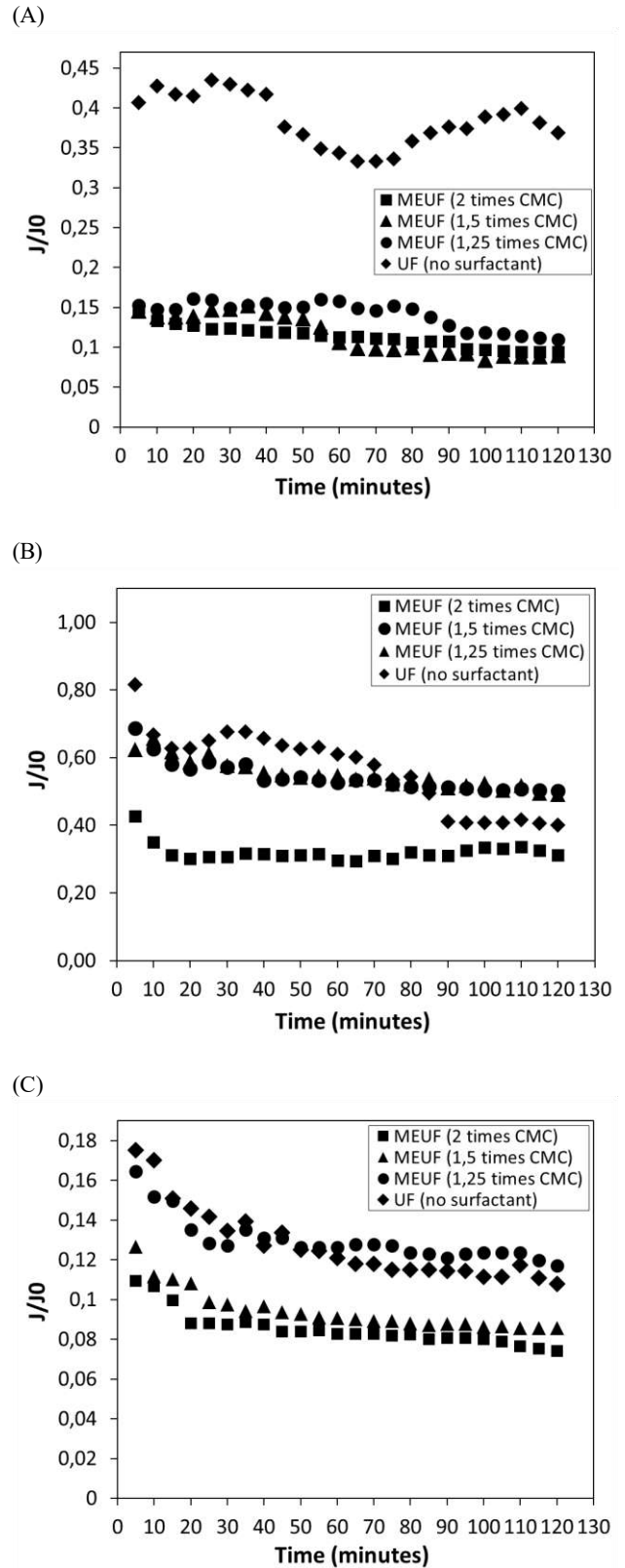


Figure 2. Flux profile of indigo sol dye filtration by ultrafiltration and MEUF for : (A) Indigo sol pink IR, (B) Indigo sol blue O4B and (C) Indigo sol brown VAT1

3.0 RESULTS AND DISCUSSION

3.1 Permeate flux Profile of UF and MEUF System

Various kind of indigo sol dyes were separated from the wastewater model solution using ultrafiltration and MEUF. Ultrafiltration process was conduct without the presence of surfactant, while MEUF was conduct by the presence of surfactant on various concentration. The flux profile at various time for filtration of indigo sol VAT brown, indigo sol Pink IR, and Indigo sol blue were shown in the Fig. 1.

Indigo sol dye is a leuco ester reactive dye having a specific ionic structure of ion Na^+ [31]. Each indigo sol dye have their own specific ion placement resulting to the difference of color appearance. In this study, three kind of indigo sol dye were used, the molecular structure of each indigo sol dyes are present in the Fig. 3

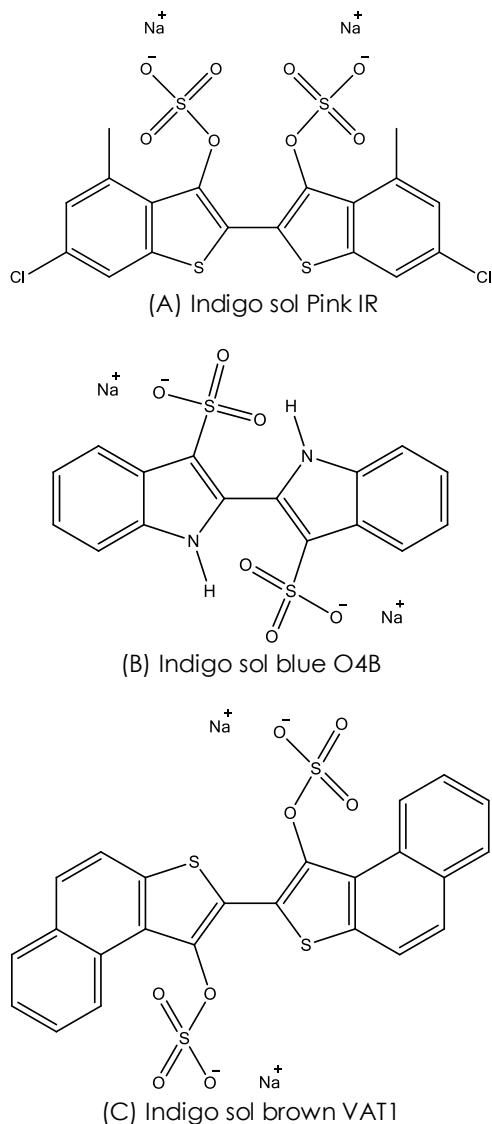


Figure 3 Molecular structure of indigo sol dye

Fig. 3 shows that indigo sol pink IR have a pair of Na^+ ion on the same side, as indigo sol blue and indigo sol VAT brown have the ion pairing on the opposite side. The different of ion disposition between the indigo sol dyes affecting its interaction with the surfactant molecules. Adding of surfactant on aqueous solution with concentration above its CMC generate the formation of surfactant micelle. In general, the internal core of the micelle is the hydrophobic region, having ability to solubilized hydrophobic or less polar molecule. While, the external polar or charged layer of micelle is having more hydrophilic characteristic. Based on the ion disposition, the ionic interaction between indigo sol pink and surfactant molecule mainly occur only on one side. Leaving the other side of dye molecule to have more hydrophobic characteristic. The hydrophobic side have a tendency to attach at the membrane because PES membrane is partly hydrophobic. Resulting on the accumulation of dye molecule on the membrane surface. Lowering the flux value compared with the process carried on without surfactant addition. Similar solubilization mechanism of hydrophobic and hydrophilic substances by surfactant micelle also reports in previous study for removal of emerging contaminants [25,32] and fractionated natural organic matter [33].

As for indigo sol blue and indigo sol VAT brown, the flux of wastewater with surfactant addition is similar with the flux of dye only wastewater. Taking account that the surfactant-dye interaction take place more thoroughly on each opposite side of the dye molecule. Emerging a thorough hydrophilic external layer covering the dye molecule. This layer is prohibit the micelle molecule to attach on the membrane surface. The cross flow system of the filtration process inducing a vertical flow of solution through the membrane surface. 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 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. The substance with molecular weight greater than membrane pore size will be 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 expect to be water with relatively low impurities (dye molecules) content. Table 1 showing the dye concentration on permeate after filtration.

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

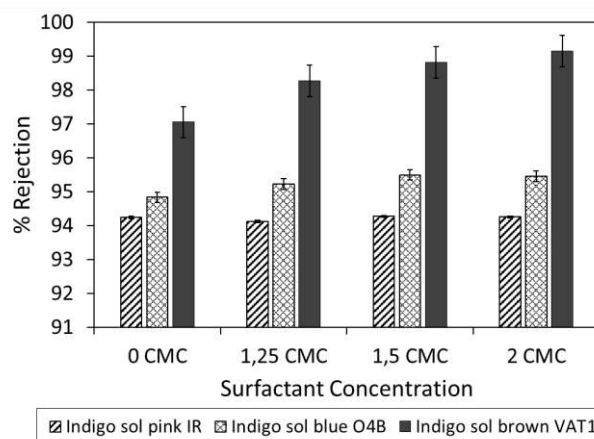
Surfactant Concentration	Dye Concentration on Permeate		
	Indigo Sol Blue O4B	Indigo Sol Pink IR	Indigo Sol Brown VAT1
0 cmc	4651,29	5186	2653,14
1,25 cmc	4297,18	5188,5	1553,14
1,5 cmc	4090,12	5172,25	1062,94
2 cmc	4057,18	5157,25	766,86

From Table 1, it is known that the dye concentration on the ultrafiltration system is higher than the MEUF. Showing 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 to 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 charge micelles of SDS surfactant. Making it bigger than the membrane pore, so it can be retained by the ultrafiltration membrane. The use of SDS surfactant to form micelles on the wastewater treatment by MEUF has already done before. The successful result also reported by the previous study for removal of cadmium ions [28], chromium ions [34], boron ion [17] and zinc ions [35].

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

The pollutant concentration on permeate also affect the membrane rejection. Permeate with lower

impurities concentration specify a better membrane rejection. The membrane rejection of various indigo sol filtration under ultrafiltration and MEUF system is exhibited on Fig. 4 which have conformity with the trend of impurities concentration on permeate.

**Figure 4** 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 indigo sol dye during ultrafiltration and MEUF was studied by application of Hermia's mathematical model. Hermia model provide 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 report 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 shows the befitting experimental data and the degree of model fitness (represent by R^2) based on Hermia's model. The value of corresponding correlation (R^2) was simply used to rationally determine the fitted blocking mechanism.

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 the befitting experimental data and the degree of model fitness (represented by R^2) based on Hermia's model. The value of corresponding correlation (R^2) was simply used to rationally determine the fitted blocking mechanism. The complete blocking mechanism fit to the experimental data for ultrafiltration of indigo sol blue and indigo sol pink IR. While ultrafiltration of indigo sol VAT brown is fit to the cake formation mechanism. The micellar-enhanced ultrafiltration of all indigo sol 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].

As explain before, the molecular structure of indigo sol blue and pink IR is smaller than indigo sol vat brown. Hence, it is possible if there is a different blocking mechanism between indigo sol blue and pink IR with the indigo sol vat brown. Indigo sol vat brown have a bigger molecular structure allows it to highly deposit on the membrane surface and initiate cake formation. The filtration of indigo sol 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 propose to remove reactive indigo sol dye from wastewater. The process is compared with ordinary ultrafiltration system. The result showing better dye pollutant rejection by the addition of surfactant. The formation of surfactant micelle is expect to help the retaining of dye molecule. Although, addition of surfactant in MEUF system also lowering the membrane flux profile. The result also showing a different profile of membrane flux between each indigo sol dye. The different molecular structure of each indigo sol dye is expect to be the main factor of different flux and rejection profile. Fouling/blocking mechanism of UF and MEUF process to remove indigo sol dye is predict by mathematical model based on hermia's model. The fouling mechanism is predict to be complete blocking and gel/cake formation. The further work to study indigo sol dye removal by membrane separation is indeed still needed. Indigo sol dye is an easily oxidize reactive

dye. Hence, the effect of oxidation support factor also need to be consider in the ultrafiltration and MEUF process.

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Fwd: QUALITY CONTROL RESULTS: MST 2017

2 messages

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3 March 2018 at 04:21

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Subject: QUALITY CONTROL RESULTS: MST 2017

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Cc: "Quality Penerbit Penerbit UTM" <qpenerbit@utm.my>, "ROSLI BIN MD. ILLIAS TNCPI" <r-rosli@utm.my>

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Based on the JT Quality Control Workshop for Special Issue: MST 2017 on 21 February 2018, the committee has decided as follows:

9 Accepted 9 Rejected

Therefore, the total number of accepted paper are: **9 only**. For all accepted articles, please improve, reformat and return to us by **15 March 2017 (Thursday)**. The correction should be highlighted in colour.

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As decided by the JT Quality Control Committee, rejected articles **are not replaceable**. Minimum articles in one slot that can be published is 8 articles. If articles accepted are less than that, we will not proceed with the publication. The cost of publication is pervolume and not perarticle. If you decided to proceed, we will issue the invoice. Kindly provide the proof of payment which has a computer generated statement.

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1_001	<p>INNOVATIVE DESIGN OF SOLAR-POWERED DESALINATION (SPD) SYSTEM USING VACUUM -MULTI EFFECT MEMBRANE DISTILLATION (V-MEMD) PROCESS</p>	<p>Achmad Chafidz^{a,*}, Faisal RM^a, Irfan Wazeer^b, Esa D. Kerme^c, Saeed M. AlZahrani^b</p>	<ul style="list-style-type: none"> • This paper does not up to the standard of indexed Preliminary/Technical Report/Survey paper • Title does not represent the strength of the study/research • Abstract: Does not fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (iv) conclusion • Graphical abstract should represent the content of the article • Does not follow the journal's format: (1) Introduction (2) Methodology (3) Results and Discussion (4) Conclusion • Not enough Results and Discussion • Conclusion is repeating the results only • References does not follow the in-house style of Jurnal Teknologi • Minimum references 15 (7 only) 	<p>REJECTED</p>
2_002	<p>REMOVAL OF REFRACTORY COMPOUNDS FROM LANDFILL LEACHATE BY USING NANOFILTRATION</p>	<p>Titik Istirokhatun^{a,b}, Desinta Aswin Amalia^a, Wiharyanto Oktiawan^a, Arya Rezagama^a, M. Arief Budihardjo^a, Nofiana^b, Heru Susanto^{b,c}</p>	<p>ARTICLE HISTORY Please provide complete date</p> <p>ABSTRACT</p> <ul style="list-style-type: none"> • Please fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (missing) (iv) conclusion • Remove/delete Malay abstract <p>GRAPHICAL ABSTRACT Provide graphical abstract. Must represent the study</p> <p>FIGURES & TABLES</p> <ul style="list-style-type: none"> • Caption should be centered if only one row, but aligned if has two or more rows. Example: Figure 4 Nitrogen content of <i>C. vulgaris</i> at three light intensity (3 000 lux, 4 000 lux, 5 000 lux) and media (Walne, Formulation, NPK). Each value is the mean of three sample • Improve the quality/visibility of all Figure 1. Make 	<p>ACCEPTED WITH CORRECTION</p>

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3_003	<p>DEVELOPMENT OF ANTIFOULING POLYETHERSULFONE (PES)-NANO ZNO MEMBRANE FOR PRODUCED WATER TREATMENT</p>	<p>Tutuk Djoko Kusworo^{*a}, Nita Aryanti^a, Qudratun^b, Via Dolorosa Tambunan^a, and Natalia Rosa Simanjuntak^a</p>	<p>FORMAT Please follow the original templete of Jurnal Teknologi. This article is in different margin</p> <p>ARTICLE HISTORY Please provide complete date</p> <p>ABSTRACT</p> <ul style="list-style-type: none"> • Please fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (missing) (iv) conclusion <p>CONTENT</p> <ul style="list-style-type: none"> • Enter two times before starting with Introduction (Original templete has a break) • Enter two times before starting with the new MAIN TOPIC <p>FIGURES & TABLES</p> <ul style="list-style-type: none"> • Caption should be centered if only one row, but aligned if has two or more rows. Example: Figure 4 Nitrogen content of <i>C. vulgaris</i> at three light intensity (3 000 lux, 4 000 lux, 5 000 lux) and media (Walne, Formulation, NPK). Each value is the mean of three sample • Improve the quality/visibility of all Figures. Make sure the label/line is sharp and not blur • Enter two times after Tables or figures before starting with new paragraph • Caption size 8 pt not 9 pt 	<p>ACCEPTED WITH CORRECTION</p>

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4_004	OPTIMUM PARAMETERS FOR TREATING COOLANT WASTEWATER USING PVDF-MEMBRANE	Erna Yuliwati ^a , Ahmad Fauzi Ismail ^{b*} , Amrifan Saladin Mohruni ^c , Agung Mataram ^c	<ul style="list-style-type: none"> • This paper does not up to the standard of indexed journal: Preliminary/Proceeding paper • Equation 3 not clear and poor quality/visibility of Figure 4 • Not enough Results and Discussion 	REJECTED
5_005	REMOVAL OF CD ²⁺ AND PB ²⁺ HEAVY METALS IN WATER BY USING ADSORPTION-ULTRAFILTRATION HYBRID PROCESS	Sri Syawaliahb Mulyatia*,	ARTICLE HISTORY Please provide complete date ABSTRACT <ul style="list-style-type: none"> • Single enter/spacing before keywords CONTENT <ul style="list-style-type: none"> • Enter two times before starting with the new MAIN TOPIC • All Sub topic should be bold and Title Case • All Sub sub topic should be bold, italic and Title Case FIGURES & TABLES <ul style="list-style-type: none"> • Enter two times after Tables or figures before starting with new paragraph 	ACCEPTED WITH CORRECTION
6_006	A STUDY OF FOULING IN ULTRAFILTRATION OF ELECTROPLATING WASTEWATER	Danu Ariono ^a , Anita Kusuma Wardani ^a , Putu Tapa Prihartini Aryanti ^b , Ahmad Nurul Hakim ^a , and I Gede Wenten ^{1,*}	TITLE Refine. Title should represent the strength of the study/research AFFILIATION Single spacing after last affiliation and the red line ARTICLE HISTORY	ACCEPTED WITH CORRECTION

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7_007	FINE PARTICLE REMOVAL USING HYDROPHOBIC MICROPOROUS POLYMERIC MEMBRANES	Anita Kusuma Wardani, Ivan, Ivan Ruben Darmawan, Khoiruddin, and I Gede Wenten*	<p>REVIEW PAPER</p> <p>SUGGESTED BY THE COMMITTEE TO BE PUBLISHED IN JURNAL TEKNOLOGI NORMAL ISSUE. To be submitted by the author in https://jurnalteknologi.utm.my. Will undergone normal process of publication (rely very much on the progress of the article). Charges RM530 for local</p>	REJECTED

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8_008	FOULING MECHANISM OF MICELLE ENHANCED ULTRAFILTRATION WITH SDS SURFACTANT FOR INDIGOZOL DYE REMOVAL	Nita Aryanti^a, Andya Saraswati^a, Rangga Pratama Putra^a, Aininu Nafiunisa^a, Dyah Hesti Wardhani^a	ARTICLE HISTORY Please provide complete date CONTENT <ul style="list-style-type: none"> • Enter two times before starting with the new MAIN TOPIC • All Sub topic should be bold and Title Case. No need to italic FIGURES & TABLES <ul style="list-style-type: none"> • Caption should be centered if only one row, but aligned if has two or more rows. Example: Figure 4 Nitrogen content of C. vulgaris at three light intensity (3 000 lux, 4 000 lux, 5 000 lux) and media (Walne, Formulation, NPK). Each value is the mean of three sample • Enter two times after Tables or figures before starting with new paragraph REFERENCES Single spacing between the text and not exactly	ACCEPTED WITH CORRECTION
9_009	EVALUATION OF BACTERIAL CELLULOSE-SODIUM ALGINATE FORWARD OSMOSIS MEMBRANE FOR WATER RECOVERY	Ngan T. B. Dang^a, Liza B. Patacsil^b, Aileen H. Orbecido^a, Ramon Christian P. Eusebio^c, Arnel B. Beltran^{a*}	ARTICLE HISTORY Please provide complete date ABSTRACT <ul style="list-style-type: none"> • Please fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (missing) (iv) conclusion CONTENT	ACCEPTED WITH CORRECTION

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10_01 0	CO₂ DESORPTION FROM ACTIVATED DEA BY USING MEMBRANE CONTACTOR WITH VACUUM REGENERATION TECHNOLOGY	Nidia Intan Listiyana, Yeni Rahmawati*, Siti Nurkhamidah, Hafan Rofiq Syahnur, and Yusuf Zaelana	<ul style="list-style-type: none"> This paper does not up to the standard of indexed journal: Preliminary/Proceeding paper Not enough Results and Discussion 	REJECTED
11_01 1	PHARMACEUTICAL COMPOUND REMOVALS DURING MIXED LIQUOR FILTRATION IN MEMBRANE BIOREACTOR OPERATED UNDER LONG SLUDGE AGE	Sirilak Prasertkulsak^a, Chart Chiemchaisri^{a*}, Wilai Chiemchaisri^a	<p>AFFILIATION If the author from the same affiliation, no need to use ^{a,b}. Only * for the corresponding author</p> <p>ARTICLE HISTORY Please provide complete date</p> <p>ABSTRACT</p> <ul style="list-style-type: none"> Please fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (missing) (iv) conclusion <p>GRAPHICAL ABSTRACT Replace. Must represent the study</p>	ACCEPTED WITH CORRECTION

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12_01 2	<p>DEVELOPMENT OF NANO-HYBRID CELLULOSE ACETATE/TiO₂ MEMBRANE FOR EUGENOL PURIFICATION FROM CRUDE CLOVE LEAF OIL</p>	<p>Tutuk Djoko Kusworo*, Danny Soetrisnanto, and Dani Puji Utomo</p>	<ul style="list-style-type: none"> • This paper does not up to the standard of indexed journal: Preliminary/Proceeding paper • Not enough Results and Discussion • Minimum references is 15 (12 only) 	<p>REJECTED</p>
13_01 3	<p>SIMULTANEOUS METHYL ESTER PRODUCTION AND CAROTENE RECOVERY FROM CRUDE PALM OIL USING MEMBRANE REACTOR</p>	<p>I Gusti Bagus Ngurah Makertihartha^a, Khoiruddin^a, Eryk Bone Pratama Nabu^a, Putu Teta Prihartini Aryanti^b, I Gede Wenten^{a,*}</p>	<p>REVIEW PAPER</p> <p>SUGGESTED BY THE COMMITTEE TO BE PUBLISHED IN JURNAL TEKNOLOGI NORMAL ISSUE. To be submitted by the author in https://jurnalteknologi.utm.my. Will undergone normal process of publication (rely very much on the progress of the article). Charges RM530 for local author and RM630 international author.</p> <ul style="list-style-type: none"> • Abstract: Does not fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (missing) (iv) conclusion. 	<p>REJECTED</p>

ID Paper	TITLE	AUTHOR	COMMENTS	RESULT
14_01 4	THERMODYNAMIC STUDY OF POLYMER ELECTROLYTE MEMBRANE PREPARATION BY NON-SOLVENT INDUCED PHASE SEPARATION	Endah R Dyartanti. ^{1,2*} , Agus Purwanto ² , I Nyoman Widiasta ¹ and Heru Susanto ¹	<p>ARTICLE HISTORY Please provide complete date</p> <p>CORRESPONDING AUTHOR Must be the person who has an official email/organizational email/the supervisor. Do not use gmail/yahoo</p> <p>ABSTRACT</p> <ul style="list-style-type: none"> • Please fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (missing) (iv) conclusion <p>CONTENT</p> <ul style="list-style-type: none"> • Main Topic should be UPPERCASE & 11 pt, Sub topic TITLE CASE, 9 pt, Sub sub topic TITLE Case, italic and 9 pt <p>FIGURES & TABLES</p> <ul style="list-style-type: none"> • Caption should be centered if only one row, but aligned if has two or more rows, size 8 pt. Example: Figure 4 Nitrogen content of <i>C. vulgaris</i> at three light intensity (3 000 lux, 4 000 lux, 5 000 lux) and media (Walne, Formulation, NPK). Each value is the mean of three sample 	ACCEPTED WITH CORRECTION
15_01 5	PHYSICAL AND MECHANICAL PROPERTIES OF MEMBRANE POLYVINILIDENE FLOURIDE WITH THE ADDITION OF SILVER NITRATE	Agung Mataram ^a , S. Rizal ^{b*} , Estu Pujiono ^a	<ul style="list-style-type: none"> • This paper does not up to the standard of indexed journal: Preliminary/Proceeding paper • Abstract: Does not fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (iv) conclusion (missing) • Not enough Results and Discussion • Poor quality of figures • Does not follow in house style of Jurnal Teknologi • References less than 15 (10 only) 	REJECTED

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16_01 6	PREPARATION AND CHARACTERIZATION OF POROUS CERAMIC MEMBRANES FOR MICRO-FILTRATION FROM CLAY/CuZn USING EXTRUSION METHODS	Muh Amin ^{a*} , Muhammad Subri ^a	<ul style="list-style-type: none"> This paper does not up to the standard of indexed journal: Preliminary/Technical Report/Survey Abstract: Does not fulfill the element of: (i) Introduction (ii) problem statement (iii) quantitative results (iv) conclusion (missing) Not enough Results and Discussion Poor quality of figures Does not follow in house style of Jurnal Teknologi 	REJECTED
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Manuscript's Title	<i>Fouling Mechanism of Micelle Enhanced Ultrafiltration with SDS Surfactant for Indigozol Dye Removal</i>
Authors	Nita Aryanti*, Andya Saraswati, Rangga Pratama Putra, Aininu Nafiunisa, Dyah Hesti Wardhani

A. Reviewer Decision

Please give a (√)	
The manuscript could be published without revision	[.....]
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B. Comments on the manuscript

Comments about the Content

(please give brief comments about: (1) the originality of the paper, (2) the clarity of methodology, (3) the clarity of results, (4) scientific contribution)

- Paper content is acceptable

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(please indicate which part should be corrected)

- Some grammatical errors are found. Please check and revise.

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- Figure 1 of Schematic Diagram is stated in the text, however only Figure 1 of MEUF schematic is found.

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ID Paper	TITLE	AUTHOR	COMMENTS	RESULTS
8_00 8	FOULING MECHANISM OF MICELLE ENHANCED ULTRAFILTRATIO N WITH SDS SURFACTANT FOR INDIGOZOL DYE REMOVAL	Nita Aryanti ^{a*} , Andya Saraswati ^a , Rangga Pratama Putra ^a , Aininu Nafiunisa ^a , Dyah Hesti Wardhani ^a	<p>ARTICLE HISTORY Please provide complete date</p> <p>CONTENT</p> <ul style="list-style-type: none"> • Enter two times before starting with the new MAIN TOPIC • All Sub topic should be bold and Title Case. No need to italic <p>FIGURES & TABLES</p> <ul style="list-style-type: none"> • Caption should be centered if only one row, but aligned if has two or more rows. Example: Figure 4 Nitrogen content of C. vulgaris at three light intensity (3 000 lux, 4 000 lux, 5 000 lux) and media (Walne, Formulation, NPK). Each value is the mean of three sample • Enter two times after Tables or figures before starting with new paragraph <p>REFERENCES Single spacing between the text and not exactly</p>	ACCEPTED WITH CORRECTION

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

Nita Aryanti^{a*}, Andya Saraswati^a, Rangga Pratama Putra^a, Aininu Nafiunisa^a, Dyah Hesti Wardhani^a

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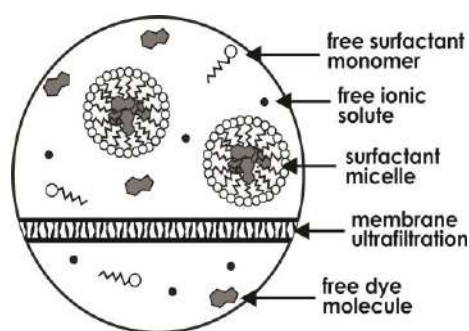
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Graphical abstract



Abstract

Membrane separation technology was proposed to confront the problem of inorganic dye pollutant treatment such as an indigosol dye. A modified ultrafiltration process known as micellar-enhance ultrafiltration (MEUF), was applied to remove three kinds of indigosol dye (Pink IR, Blue O4B, and vat brown). Surfactant at concentration above CMC was added to form micelle structure and solubilize the dye molecule in the feed solution. Maximum dye rejection was achieved by the MEUF of all three kinds of indigosol dye. The rejection of indigosol pink IR, blue O4B, and brown VAT1 were 94,27%, 95,49% and 99,15%, respectively. In this research, it was found that the MEUF system leads to higher membrane flux, compared to the ultrafiltration system as shown in flux profiles. The difference was expected due to different dye molecular structure. Blocking mechanism was predicted by a mathematical model based on Hermia's model and depicted a mechanism of complete blocking on most UF process and cake formation on MEUF process. This result confirmed that the MEUF system certainly retained the dye molecule on membrane separation process. However, a comprehensive study is required to increase the membrane flux.

Keywords: Membrane separation, Micellar-enhance ultrafiltration, wastewater, indigo sol dye, blocking mechanism.

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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 treat before being discharged to the environment. Severe damage on the aquatic environment may happens 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 pressure 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 Fig. 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).

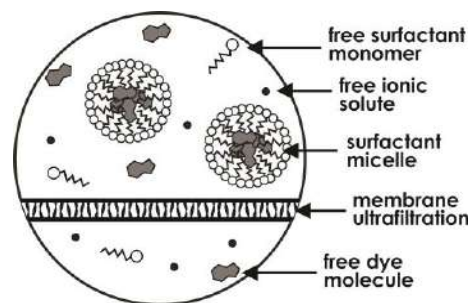


Figure 1 MEUF mechanism of inorganic dye removal

2.0 METHODOLOGY

2.1 Dye Model Solution

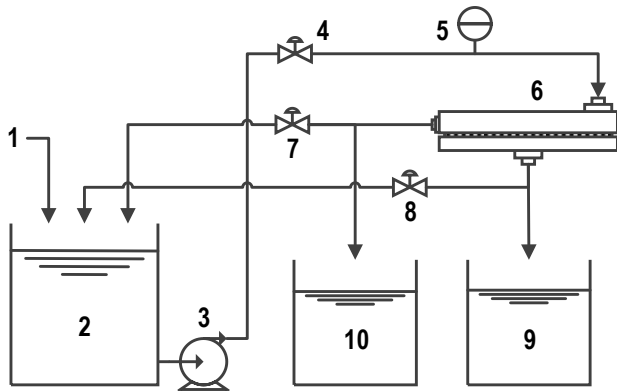
The dye wastewater model solutions were prepared using analytical grade reagents and distilled water as the solvent. Indigosol pink IR, indigo sol brown VAT1 and indigo sol blue O4B were used as the dye on the wastewater model solution. To make the dye solution, 90 grams of each dye was added to 1 litre 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. Fig. 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.



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

Figure 2 Cross flow micellar-enhanced ultrafiltration membrane system

The flux was calculated based on Equation (1).

$$J = \frac{W}{A \times t} \tag{1}$$

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)

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

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, standar blocking, intermediate blocking, and gel/cake formation. The pore blocking law on filtration process was expressed by equation (3).

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

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].

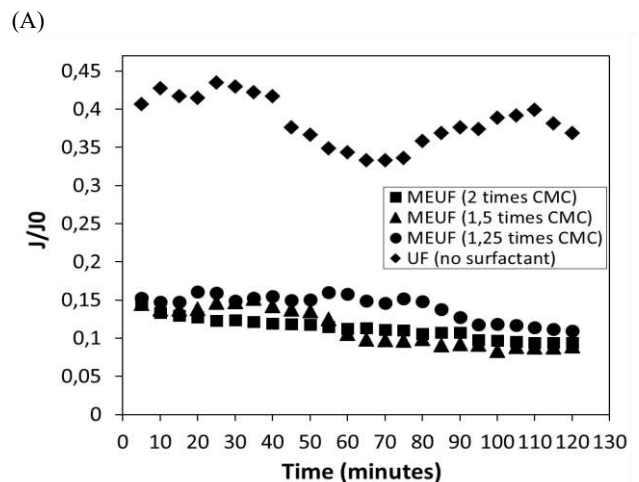
Table 2 Linearisation equation of blocking/fouling models based on Hermia's model

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 Fig. 3.



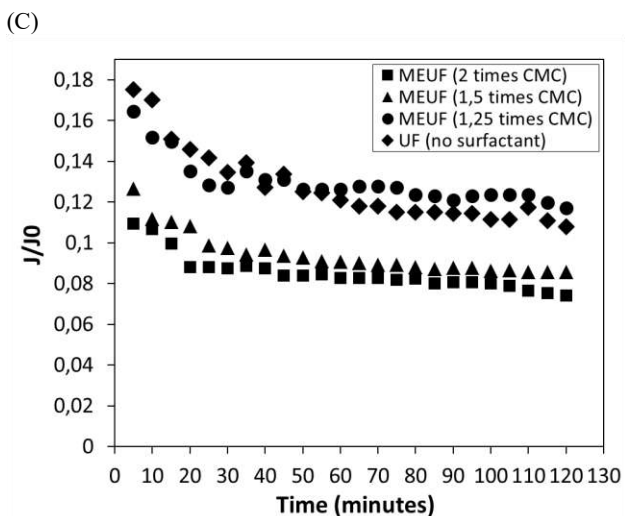
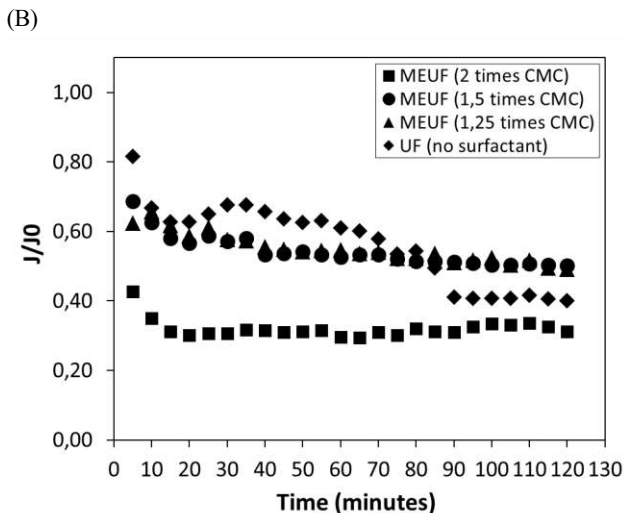
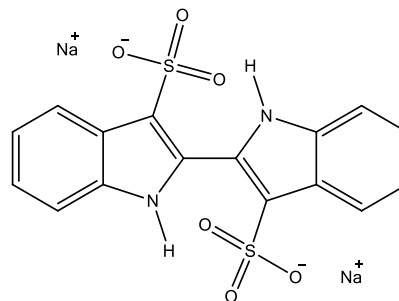
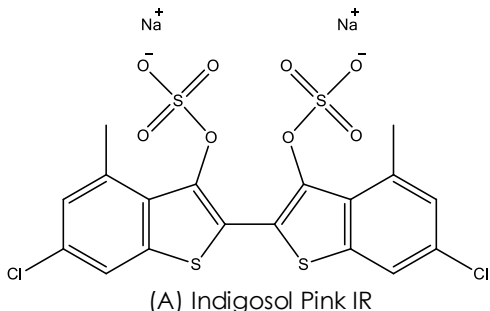
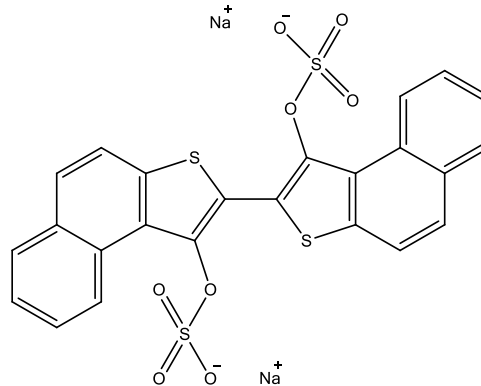


Figure 3. Flux profile of indigosol dye filtration by ultrafiltration and MEUF for : (A) Indigo sol pink IR, (B) Indigo sol. blue O4B and (C) Indigo sol brown VAT1

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 Fig. 3



(B) Indigosol blue O4B



(C) Indigosol brown VAT1

Figure 4 Molecular structure of indigo sol dye

Fig. 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 deposition 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 through 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 Fig. 5 which have conformity with the trend of impurities concentration on permeate.

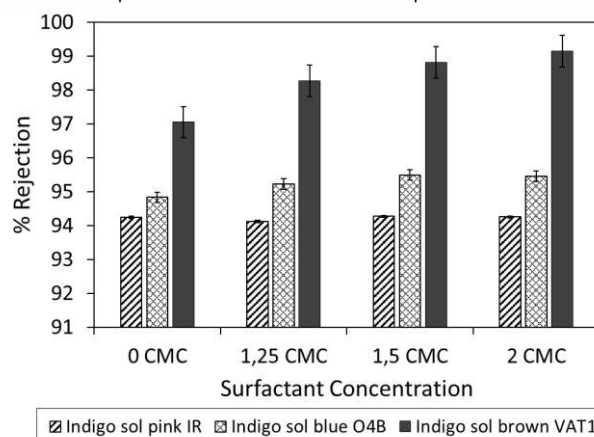


Figure 5 Rejection of indigo sol dye at various CMC, (A) Indigo sol pink IR, (B) Indigo sol blue O4B and (C) Indigo sol brown VAT1

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 (represented by R²) based on Hermia's model. The value of corresponding correlation (R²) was simply used to determine the fitted blocking mechanism rationally. The best fitting experimental data and the degree of model fitness (represented 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 fits 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-enhanced 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.

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