

# Reactive dyes decolourization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process

A.L. Ahmad\*, S.W. Puasa

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Penang, Malaysia

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## Abstract

This study was designed to investigate the removal of reactive dyes, C.I. Reactive Black 5 (RB5) and C.I. Reactive Orange 16 (RO16) using two-step, pre-treatment and micellar-enhanced ultrafiltration (MEUF). Coagulation was used as pre-treatment process and its optimum condition were identified. A cationic surfactant, cetylpyridinium chloride (CPC) was used for the MEUF and its effectiveness was investigated. Several operating conditions such as surfactant concentration and operating pressure were varied to find the optimum conditions for MEUF process. The optimum condition obtained from MEUF parameters study was used for treating the pre-treated solution obtained at pre-treatment process. Results obtained in this study shows that the combination pre-treatment and MEUF process achieved almost complete decolourization of both RB5 (99.75%) and RO16 (99.98%) from aqueous solution.

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**Keywords:** Coagulation; Micellar-enhanced ultrafiltration; Cationic coagulant; Reactive dye; Cationic surfactant; Ultrafiltration membrane

## 1. Introduction

The textile industry is one of the most complicated in manufacturing industry because of its fragmented and heterogeneous character. The main environmental impacts of the textile chain come from the so called “wet processes”, of the textile finishing industry. The effluent from the textile processing is often discharged into a municipal sewage treatment plant or directly into waterways [1].

Reactive dyes are being recognized as the best dye used for cotton and other cellulose fibers [2]. These dyes are extensively used in textile industry, fundamentally due to the ability of their reactive groups to bind textile fibers by covalent bond formation. These characteristics facilitate the interaction with the fiber and reduce energy consumption [3].

However in typical dyeing process, 50–100% of the dye fixed on the fiber, and the unfixed dyes are discharged in spent dye-baths or in wastewater from subsequent textile-washing operations [4]. The discharge of high colored waste is not

only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological process within a stream. In addition, many dyes are toxic to some organisms and may cause direct destruction of aquatic communities [5]. Furthermore, the chemical structure of dyes varies enormously, and some have complicated aromatic structures that resist degradation in conventional wastewater treatment process because of their stability to sunlight, oxidizing agents and microorganism [6]. The color of textile effluent is also unacceptable under environmental enforcement body besides the other parameter such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), total iron, etc. [7]. Due to these factors, the textile industry faces the challenge of balancing the environmental protection, its economic viability and sustainable development. There is an urgent need to find a way to preserve the environment while keeping the economic growing.

Rate-governed separation processes, such as membrane filtration, are becoming attractive for the separation of colored effluent containing various types of dye. Reverse osmosis (RO) and nanofiltration (NF) are readily recognized as the best available techniques for the separation of several commercial dyes. However, both RO and NF processes use relatively “dense” membranes. Permeability of these membrane is low and thus to get the desired throughput (permeate flux), a high operating pressure is required [8]. Ultrafiltration has been successfully

*Abbreviations:* MEUF, micellar-enhanced ultrafiltration; UF, ultrafiltration; RO16, C.I. Reactive Orange 16; RB5, C.I. Reactive Black 5; CPC, cetylpyridinium chloride

\* Corresponding author. Tel.: +60 4 594 1012; fax: +60 4 594 1013.

E-mail address: chlatif@eng.usm.my (A.L. Ahmad).

### Nomenclature

$A$	membrane area ( $\text{m}^2$ )
$C_{pc}$	permeate concentration of surfactant ( $\text{g/L}$ )
$C_{pd}$	permeate concentration of dye ( $\text{g/L}$ )
$C_{0d}$	feed dye concentration ( $\text{g/L}$ )
$C_{0c}$	feed surfactant (CPC) concentration ( $\text{g/L}$ )
$R_c$	percentage of surfactant rejection (%)
$R_d$	percentage of dye rejection (%)
$R_m$	membrane resistance ( $\text{m}^{-1}$ )
$v_w$	permeate flux ( $\text{m}^3/\text{m}^2 \text{ s}$ )

### Greek letters

$\Delta\pi$	osmotic pressure differential (Pa)
$\Delta P$	pressure differential (Pa)
$\Delta t$	time difference (s)
$\Delta V$	cumulative volume difference ( $\text{m}^3$ )
$\mu$	viscosity (Pa s)

applied in many industries, but it has not been widely accepted by the textile industry since it makes direct reuse impossible and will require further filtration by either NF or RO [5]. Therefore in order to get the desired throughput, a modified ultrafiltration membrane separation processes maybe an alternative where the operating pressure requirement is low compared to RO and NF, and membrane of higher permeability can be used. In this case, the modified ultrafiltration membrane separation which is micellar-enhanced ultrafiltration (MEUF) had been used to treat dye effluent. This method combines the high selectivity of reverse osmosis and the high flux of ultrafiltration [9].

As shown in Fig. 1, the basic idea for MEUF is that surfactant forms large amphiphilic aggregate micelles when it is added to aqueous streams at a concentration higher than its critical micelle concentration (CMC). Micelles thus formed were used to solubilize the organic solute (opposite charge ions) present in the solution [10]. The ions and dissolved organic compounds (solute) can be mostly trapped by the micelles if they tend to be strongly attracted by the micelle surface and will be solubilized in the micelle interior, respectively. The hydrodynamic size of the solutes increasing and the solutes can be retained after trap-

ping with the micelles, whereas the untrapped species readily pass through the ultrafiltration membranes [11]. Here, most of the dye molecule which known as solute in dyeing-containing effluent are solubilized in the micelles and these micelles being larger in size which would be rejected by ultrafiltration membrane. The permeate stream contains water and small amount of unsolubilized solutes and free surfactants [12].

The use of membrane technology in combination with another pre-treatment method was also demonstrated as practical solution for treating wastewater [13]. Petrov and Stoychev [14] studied the combination of precipitation and ultrafiltration method on purification of water contaminated with bifunctional reactive dyes. Al-Basaki and Banal [15] studied the combining of ultrafiltration and adsorption method for the treatment of colored waters. These researchers showed that combination process could obtain above 90% of dye removal. The combination of coagulation/MEUF present in this study has been recognized as new approach since no research has been done on this combination treatment.

Ahmad et al. [16] had done study on the removal efficiency of MEUF towards C.I. Reactive Orange 16 and C.I. Reactive Black 5. This previous study has been focused on the MEUF potential in removal reactive dyes from an aqueous solution. A comparison study has been done between normal ultrafiltration (UF) and MEUF. The results obtained prove that the dye rejection was higher for MEUF process compared to UF process. In addition, an investigation on effect of surfactant concentration and transmembrane pressure on the dye rejection and permeate flux have been studied as a function of operating time.

The objective of the current study is to use micellar-enhanced ultrafiltration (MEUF) membrane process to treat the reactive dye (C.I. Reactive Black 5 and C.I. Reactive Orange 16) in aqueous solution. In order to apply membrane separation technology, pre-treatment process was carried out to reduce high content of dyes in aqueous solution. This pre-treatment was important in reducing membrane fouling at membrane separation process. The pre-treatment process was tested using coagulation method where Nalco bio-based polymer was used as coagulant. Parameters including the effect of pH and coagulant dosages on dye removal have been studied and its optimum condition was identified. The optimum pre-treated solution will be further treated using micellar-enhanced ultrafiltration (MEUF). However, since the residual dye concentration of pre-treated solution for both dyes is not same, it is difficult to make comparison on the performance of dye rejection between these dyes. Here, a study on MEUF parameters was done on the same feed dye concentration of 0.050 g/L in order to identify the MEUF optimum condition. A cationic surfactant, cetylpyridinium chloride (CPC) was used in micellar-enhanced ultrafiltration (MEUF) process and its effectiveness was investigated. A thin film (TF) ultrafiltration membrane with 10,000 molecular weight cut-off (MWCO) was used under unstirred dead-end filtration. The unstirred condition has been chosen since this method is adequate to produce high rejection of dyes. The effects of feed surfactant concentration and operating pressure on the permeate flux, dye and surfactant rejection have been studied and its optimum condition was identified. The optimum condition obtained from MEUF parameters

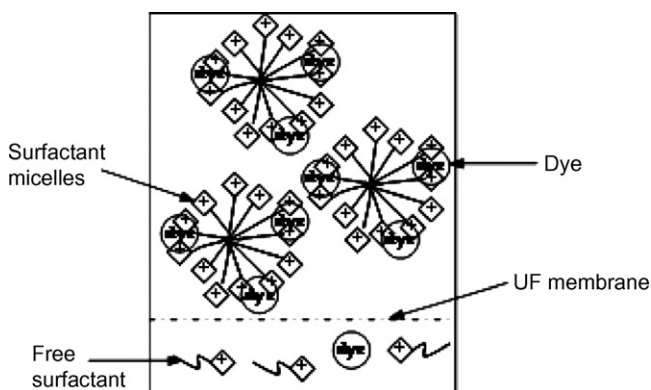


Fig. 1. Micellar-enhanced ultrafiltration (MEUF) phenomenon.

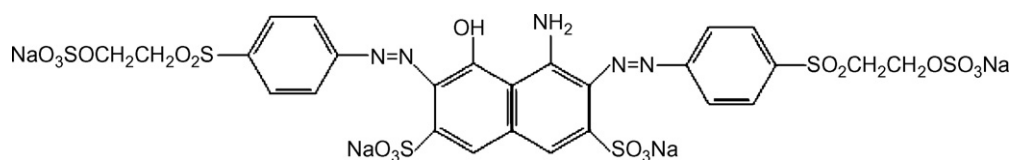


Fig. 2. Structure of Reactive Black 5 dye.

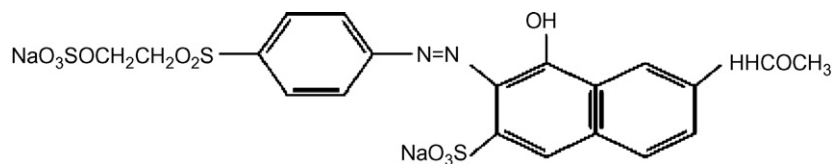


Fig. 3. Structure of Reactive Orange 16 dye.

Table 1  
Membrane specification

Type	GN
Membrane	TF (thin film) ultrafiltration membrane
Pore size (MWCO)	10,000
Typical operating pressure	276–1379 kPa
Recommended pH	Operating range: 2–11
Maximum temperature	50 °C

study will be used for treating the pre-treated solution obtained from pre-treatment experiment.

## 2. Materials and methods

### 2.1. Experimental materials

The Reactive Black 5 (MW 991.82), Reactive Orange 16 (MW 617.54) and surfactant CPC (MW 358.01) were purchased from Sigma–Aldrich (M) Sdn. Bhd., Malaysia. The chemical structures for these materials are presented in Figs. 2–4. The ULTIMER® 7751 Nalco cationic flocculant was obtained from Ondeo Nalco Chemical (M) Sdn. Bhd., Malaysia.

### 2.2. Membranes

A GN polymeric membrane of molecular weight cut-off 10,000, obtained from Osmonics was used for the experiments. The pure water permeability of the membrane was  $5.870 \times 10^{-11}$  m/Pa s. Properties of this membrane were given in Table 1.

### 2.3. Ultrafiltration cell

Membrane stirred cell, model Sterlitech™ HP4750, USA, has been used to conduct under unstirred dead end filtration experiments. The capacity of the cell is 300 mL and the mem-

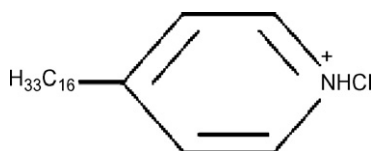


Fig. 4. Structure of cetylpyridinium chloride (CPC).

brane diameter is 49 mm and the effective membrane area is  $14.6 \text{ cm}^2$ . The maximum operating pressure is 6900 kPa.

### 2.4. Experimental procedure

#### 2.4.1. Pre-treatment experiments

The basis dye concentration used in this study was 0.500 g/L. The optimal pH and amount of Nalco to be used as coagulant were determined using jar-test. Diluted solutions of HCl and NaOH were added to adjust the pH of the solution to the desired value. Nalco coagulant was added and mixed for 2 min under rapid mixing condition (250 rpm). The solution was mixed at slow flocculation (40 rpm) for 15 min after rapid mixing. Residual dye concentration was measured after settling for 60 min. The coagulation process was conducted by varying the initial pH (3–9) and the coagulant concentration (1–10 g/L). The treated solution obtained at optimum condition in the pre-treatment experiments will be further treated in MEUF experiments.

#### 2.4.2. MEUF experiments

The cell was pressurized using a nitrogen gas cylinder. The membrane was compacted using distilled water at pressure of 500 kPa for 3 h. During compaction of membrane, water flux was measured continuously until a constant flux condition was achieved. Water flux was measured at different operating pressures and from the slope of the flux versus pressure curve, the membrane permeability ( $L_p$ ) was determined.

Filtration experiments were carried out in unstirred dead end filtration containing mixture of surfactant and dye. Duration of MEUF experiments were about 60 min. Experiments were designed to observe the effects of feed surfactant concentration and operating pressure on the rejection of dye and permeate flux. The CMC of CPC in aqueous medium was 0.322 g/L [12].

**2.4.2.1. MEUF parameters study.** For MEUF parameters study, a feed dye concentration of 0.050 g/L was selected for each experiment. Feed solution for each experimental was prepared by weighing amounts of dye and surfactant and dissolving them in distilled water. After filling the feed solution, the cell was pressurized at the operating pressure using a pressure regulator. Permeate from the bottom cell was collected, where the cumulative weight was continuously measured with the help of

an electronic balance. The cumulative weight were converted to cumulative volume and the permeate flux could be measured. The permeate concentrations were measured using UV–vis spectrophotometer.

After each run, the cell and membrane were washed thoroughly with distilled water. The membrane permeability was checked and it has been observed that the permeability varies within  $\pm 2\%$  of its initial measured value. All the experiments were conducted at room temperature ( $32 \pm 2^\circ\text{C}$ ). A schematic of the experimental set up is shown in Fig. 5.

For the effect of surfactant concentration experiments, the operating pressure remained constant at 300 kPa while the surfactant concentrations were varied at CPC-to-dye concentration ratio of 10, 12, 13, 15 and 20. For effect of operating pressures experiments, the operating pressures were varied at 300, 350, 400, 450 and 500 kPa while the initial surfactant solution was remained constant at 0.750 g/L. The optimum condition obtained from MEUF parameters study has been used for treating the pre-treated solution obtained from the pre-treatment experiment.

**2.4.2.2. MEUF for pre-treated solution.** The optimum condition obtained from MEUF parameters study had been used for treating the pre-treated solution obtained at pre-treatment process. The experiments were conducted at optimum operating pressure. Feed solution for these experiments was prepared by weighing amounts surfactant at optimum CPC/dye concentration ratio and dissolving them in pre-treated solution. Permeate from the bottom cell was collected and its concentration were measured using UV–vis spectrophotometer.

## 2.5. Analysis

Feed and permeate concentrations of dye and surfactant were measured by a UV–vis Spectrophotometer (Thermo Spectronic, USA; model: GENESYS 2). The wavelengths at which maximum absorption occur were 259 nm for cetylpyridinium chloride (CPC), 592 nm for Reactive Black 5 and 493 nm for Reactive

Orange 16. Dye rejection, CPC rejection and permeate flux can be calculated using equation:

$$R_d = \left(1 - \frac{C_{pd}}{C_{0d}}\right) \times 100\% \quad (1)$$

$$R_c = \left(1 - \frac{C_{pc}}{C_{0c}}\right) \times 100\% \quad (2)$$

$$v_w = \frac{\Delta V}{\Delta t A} \quad (3)$$

where  $C_{0c}$  is the feed surfactant concentration,  $C_{pc}$  the permeate concentration of surfactant,  $C_{0d}$  the feed dye concentration,  $C_{pd}$  the permeate concentration of dye,  $R_c$  the percentage of surfactant rejection,  $R_d$  the percentage of dye rejection,  $\Delta t$  the time difference,  $\Delta V$  the cumulative volume difference,  $A$  the membrane area and  $v_w$  is the permeate flux.

## 3. Results and discussions

This section is divided into three parts: (i) pre-treatment, (ii) parameter study for micellar-enhanced ultrafiltration and (iii) combination pre-treatment and MEUF process.

### 3.1. Pre-treatment

In this study, coagulation pre-treatment using Nalco coagulant had been suggested in order to reduce dye concentration before it further treated by membrane filtration process. The basis concentration of dyes used in this study is 0.500 g/L.

#### 3.1.1. Effect of pH

The removal of C.I. Reactive Black 5 (RB5) and C.I. Reactive Orange 16 (RO16) from a 0.500 g/L dye solution by ULTIMER<sup>®</sup> 7751 Nalco (Bio-based polymer) has been studied at various pH conditions (pH 3–9). A fixed Nalco dosage of 5.0 g/L was chosen for these experiments. The results are shown in Fig. 6. From this figure, it can be observed that a very good removal of all dyes can

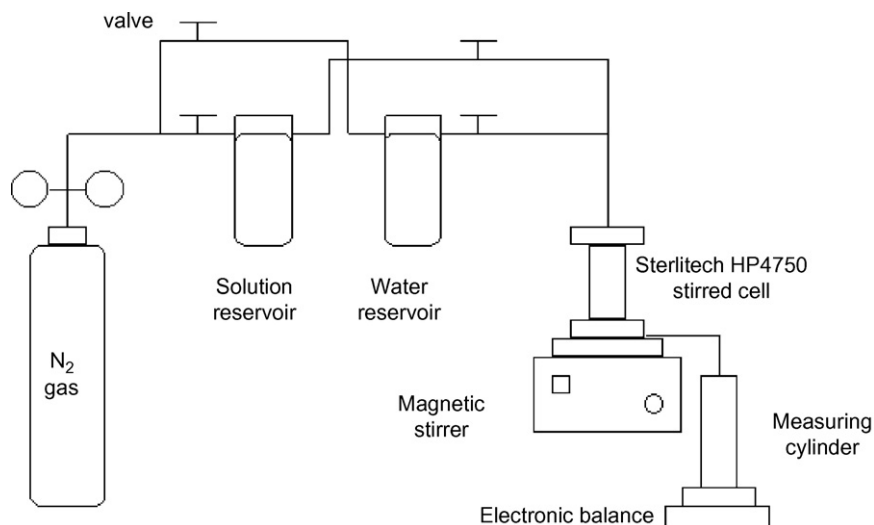


Fig. 5. Schematic diagram of the experimental rig.



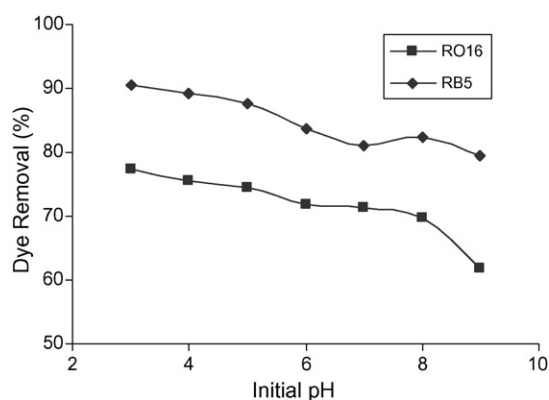


Fig. 6. Effect of initial pH on the percentage of dye removal for RB5 and RO16 at Nalco dosage of 5.0 g/L.

be achieved in the pH range of 3–5. The maximum removal for RB5 and RO16 were 90.64 and 77.50%, respectively at pH 3. As the pH increases towards alkaline value, the removal becomes poorer. Removal of both RB5 and RO16 dye reduced from 90.64 and 77.50% at pH 3–79.59 and 61.72% at pH 9, respectively.

The best performance of Nalco coagulant within the acid pH range is due to the increasing of its cationic charge flocculant in acidic pH, which means positive charges increased at low pH values. With increased positive charges in the matrix, coagulation becomes more effective in removal highly negative charge of reactive dyes. However as the pH increased, the charge concentration in the Nalco will be decreased thus resulting in low removal of dyes [17].

The performance of dye removal by chemical coagulation also can be explained depends upon the solubility of the dyes. Dyes with high solubility cannot be well removed by coagulants. Solubility differences are attributed to different chemical structures. Reactive dyes are characterized by azo bonds (N=N). Reactive dyes also have  $-\text{SO}_3^-$ ,  $-\text{COO}^-$ ,  $-\text{OH}$  group where this bond contributed to increase the solubility of the dyes [17]. Papic et al. [5] reported that the appearance of the maximum in dye removal could be explained by the effect of the ionization of sulpho, amino and hydroxyl groups in the dye molecule, which increases with pH. From this explanation, it can be summarized that the solubility of the dye increased as the pH of solution increased. As stated above, dyes with high solubility cannot be well removed by coagulants. Results in Fig. 6 proof that as the pH increased, the solubility of the dyes will be increased thus resulting in low removal of dyes.

The difference of dye removal performance for both RB5 and RO16 was investigated. From Fig. 6, it can be observed that the removal of RB5 dye was higher than RO16 dye. This could be explained depends on the differences of molecular structure for both dyes. The chemical structure for RB5 and RO16 dye is shown in Fig. 2 and Fig. 3. From these figures, it can be observed that RB5 consist of four sulphonic acid ( $\text{SO}_3^-$ ) group with molecular weight of 991.82 while RO16 consist of only two sulphonic acid ( $\text{SO}_3^-$ ) group with molecular weight of 617.54. Although RO16 consists smaller sulphonic acid group compared to RB5, but RO16 consists of smaller aromatic structure and molecular weight compared to RB5. The removal using coag-

ulation process is more effective on RB5 as this dye heavier where it can easily sediment compared to RO16 by using Nalco coagulant. Kim et al. [18] reported the removal of Reactive Yellow 84 (RY84) and Reactive Blue 49 (RB49) by coagulation using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as coagulant. They also indicated that the removal of RY84 with four  $\text{SO}_3^-$  group were higher than RB49 with three  $\text{SO}_3^-$  group, which present the same explanation on dye molecular structure with the result obtained in this current study.

### 3.1.2. Effect of coagulant concentration

Dye removal as a function of coagulant concentration is shown in Fig. 7. The removal efficiencies for both dye increasing as the coagulant dosage increases. Between coagulant dosage 1.0 and 4.0 g/L, the differences of removal efficiencies were relatively significant for both RB5 and RO16. The maximum removal efficiencies for RB5 and RO16 were 95.61 and 79.39%, and these were achieved at coagulant concentration of 4.5 and 9.0 g/L at initial pH of 3. The removal efficiencies of the RB5 dye were higher than those of the RO16, and the coagulant concentrations needed to achieve maximum removal efficiency were lower for the RB5 dye than for the RO16 dye. As discussed earlier, higher dosage was needed for RO16 as this dye has lower molecular weight compared to RB5. Nalco coagulant shows a reversal effect at too high dosages. This was due to the charge reversal phenomenon of coagulation, where colloidal stability will restabilise if the coagulant charge concentration is higher than total charge of colloids [17].

### 3.2. Parameter study for micellar-enhanced ultrafiltration (MEUF)

From Ahmad et al. [16] previous study on removal of reactive dyes from an aqueous solution using MEUF, it has been proven that the dye rejection for UF process was too low compared to MEUF process. The comparison between the UF and MEUF processes indicates that in MEUF process, the dyes were solubilized within the surfactant micelles and these micelles were larger in size. Most of the micelle particles were retained over the membrane surfaces and were subsequently rejected by the ultrafiltration membrane.

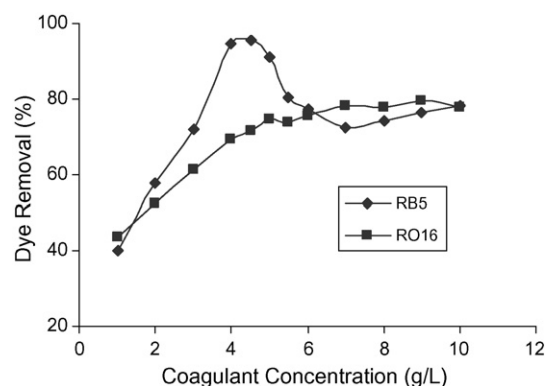


Fig. 7. Effect of Nalco concentration on the percentage of dye removal for RB5 and RO16 at initial pH of 3.

The variation of permeate flux for filtration of MEUF over the time operation was also presented in this previous study [16]. It can be observed that the permeate flux declines over the time operation. For the case of MEUF, the permeate flux drop was due to the formation of deposited layer of micelle [16]. As a result, the osmotic pressure at the membrane solution interface would increase and therefore reduce the driving force for the permeating solution. This leads to a decline of the permeate flux with the time operation [16]. From this previous study, Ahmad et al. [16] has clearly shown some evidence of the build up of micelles or solid material at the membrane surface.

### 3.2.1. Effect of feed CPC (surfactant) concentration

#### 3.2.1.1. Effect of CPC concentration on the dye rejection.

Fig. 8(a) shows the effects of CPC concentration for fixed dye concentration on the dye rejection. From the figure, it is obvious that the observed dye rejection increases with CPC concentration. It can be observed from the figure that the highest dye rejection for RB5 and RO16 dye were 99.33% and 99.89% at CPC-to-dye concentration ratio of 20. This is quite obvious, as the number of concentration of the micelles will be more with increasing CPC concentration, resulting into an increase of the amount of dye solubilized in the micelles [19]. Koyuncu [20] reported that highest maximum removal (>99.5%) of RB5 and RO16 by using nanofiltration membrane (MWCO: 150–300 Da) were obtained at operating pressure of 2400 kPa. However by using MEUF process, highest maximum removal of both dyes could be obtained by using high molecular weight of membrane (MWCO: 10,000) at low pressure driven (300 kPa). It is evident that the advantages of MEUF process are a relatively low energy requirement and low pressure driven [21].

It can be observed from Fig. 8(a) that the dye rejection of RO16 and RB5 dyes increases rapidly and then gradually with increase in feed CPC concentration. As discussed earlier, the number of micelles in the solution increasing as the feed CPC concentration increased, hence enhances the overall dye solubilization. At higher CPC concentration, the feed solution starts getting saturated by the micelles. Therefore, the dye solubilization attains almost a constant value at higher CPC concentration [22].

From Fig. 8(a), it is clearly seen that the dye rejection of RO16 dye is higher compared to RB5 dye. This comparison could be explained on the differences solubilization of dyes into the micelles. As stated earlier, the solubility differences are attributed to different chemical structures. Reactive dyes are characterized by azo bonds (N=N). Reactive dyes also have  $-\text{SO}_3^-$ ,  $-\text{COO}^-$ ,  $-\text{OH}$  group where this bond contributed to increase the solubility of the dyes [18]. As stated earlier, RB5 consist of four sulphonic acid ( $\text{SO}_3^-$ ) group while RO16 consist of only two sulphonic acid ( $\text{SO}_3^-$ ), which means RB5 dye has higher water solubility compared to RO16 dye. Komesvarakul et al. [23] stated that in micellar solution, the solute with a low water solubility shows a greater solubilization constant than the solute with a higher water solubility. This statement prove that RO16 dye have greater solubilization ability in the micelles compared to RB5 dye. This resulted in the higher dye

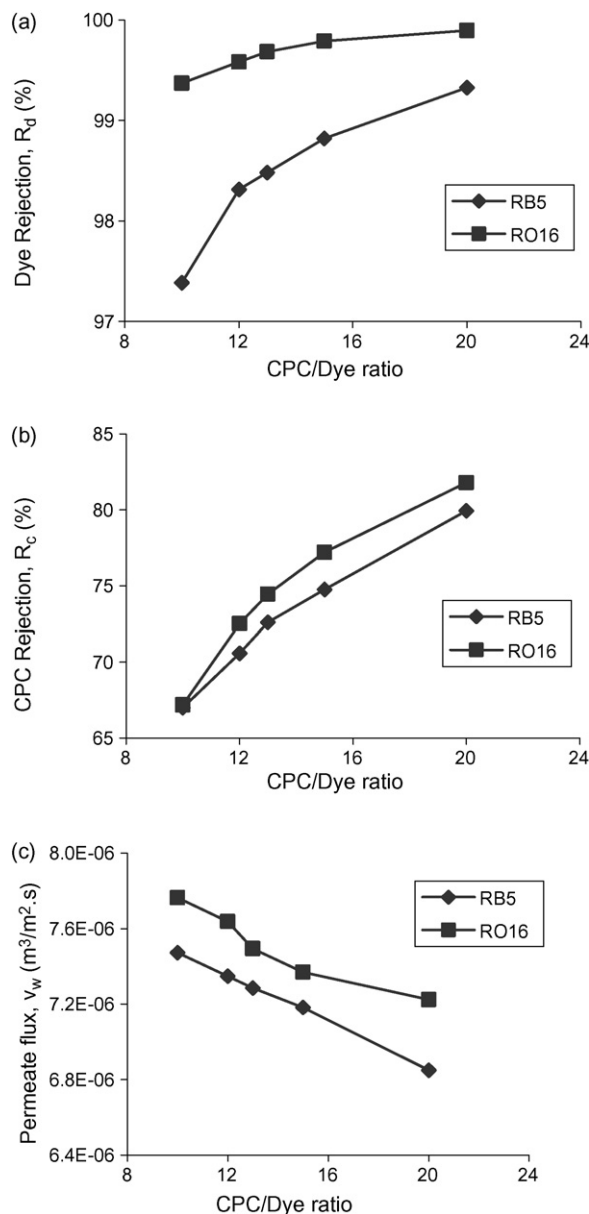


Fig. 8. Effect of CPC/Dye concentration ratio on (a) dye rejection, (b) CPC rejection and (c) permeate flux for MEUF of RB5 and RO16 after 1 h experiments at 300 kPa. Feed dye concentration: 0.050 g/L; CPC-to-dye ratio: 10, 12, 13, 15 and 20.

rejection of RO16 dye compared to that RB5 dye. Ahmad et al. [16] has done study for effect of feed CPC concentration on dye rejection and permeate flux. However in this current research, the study has focused on detailed study for effect of CPC concentration in term of CPC-to-dye concentration ratio on of dye rejection, CPC rejection and permeate flux.

#### 3.2.1.2. Effect of CPC concentration on the CPC rejection.

Although most of the surfactant (CPC) monomer form micelles when it is added to solution at concentration above its critical micelle concentration (CMC), there were still few of CPC monomer did not form micelles. Since the size of free CPC monomer is quite too small (MW of free CPC monomer is 358.01) compared to membrane pore size (MWCO of mem-

brane is 10,000), these free monomer can easily pass through the membrane to the permeate side.

The rejection of CPC at the end of the experiment is presented in Fig. 8(b). It is observed from the figure that there is an increasing trend in rejection of CPC with increased feed CPC concentration. Since all the feed CPC concentrations are quite above the CMC value (CMC of CPC is 0.322 g/L), the CPC micelles formed were retained by the membrane and the free CPC monomer which its concentration around or below CMC value will passed through the membrane. Here it can be concluded that although the feed CPC concentration ( $C_{0c}$ ) was increased, the permeate CPC concentration ( $C_{pc}$ ) which consist of free CPC monomer still remained at around or below CMC value [12]. As a result, the ratio ( $C_{pc}/C_{0c}$ ) decreases as the feed CPC surfactant increased, which resulted an increment in CPC rejection with feed CPC concentration [12].

However, there would be CPC left in the permeate solution since the CPC rejection was only about 70–80%. The CPC contains in the filtrate is actually has been recovered using precipitation method which has been presented in other paper. Furthermore, Purkait et al. [12] have done study on recovery of CPC from MEUF permeate. The results obtained proof that CPC can be recovered from MEUF filtrate and reuse in MEUF process.

**3.2.1.3. Effect of CPC concentration on permeate flux.** Permeate flux decreases with feed CPC concentration at fixed operating pressure of 300 kPa (Fig. 8(c)). For example for RB5 dye filtration, the permeate flux decreased from  $7.47 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$  to about  $6.85 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$  when CPC-to-dye concentration ratio increased from 10 to 20. In MEUF process, most of the micelles were retained over the membrane surface. By addition of surfactants above the critical micelle concentration (CMC), surfactant micelles were formed as large aggregates. This generates a deposited layer on the membrane surface and consequently, increases the resistance against the solvent flux through the membrane. This results in a decrease in the permeate flux [8]. Jadhav et al. [10] suggested the same trend in their study of removal phenol and aniline by micellar-enhanced ultrafiltration. They reported that an increase in feed surfactant concentration results in decrease of flux, which due to concentration polarization.

### 3.2.2. Effect of operating pressure on the dye rejection

**3.2.2.1. Effect of operating pressure on the dye rejection.** The effect of operating pressure on the dye rejection for MEUF of RB5 and RO16 for fixed dye and CPC concentration is presented in Fig. 9(a). It is clearly seen that the dye rejection decreases with the increase in operating pressure. It can be observed the dye rejections for RB5 and RO16 dyes decreased from 98.82 and 99.79% at 300 kPa to 97.39 and 99.05% at 500 kPa. Sabate et al. [24] also observed that as the operating pressure increased, the permeate concentration of phenol would be increased; hence decreasing the phenol rejection with operating pressure. The decreasing dye rejection may be due to the fact that at higher operating pressure, a micelle may be compacted and therefore decrease the micelle solubilization capability. Less amount of

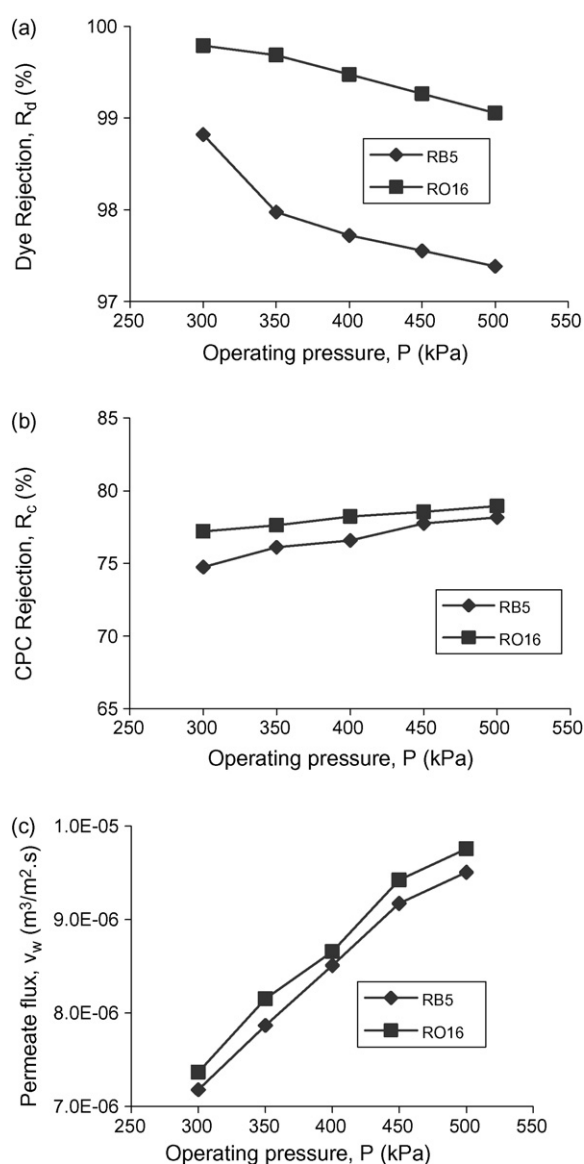


Fig. 9. Effect of operating pressure on (a) dye rejection, (b) CPC rejection and (c) permeate flux for MEUF of RB5 and RO16 after 1 h experiments at CPC concentration of 0.750 g/L. Feed dye concentration: 0.050 g/L; operating pressure: 300, 350, 400, 450, and 500 kPa.

dye solubilized in the micelles at a higher operating pressure [12]. Furthermore, the final feed concentration in the cell at 500 kPa would be higher than at 300 kPa. The permeate concentration would also follow the same trend. This could be the cause of a lower apparent dye rejection at a higher pressure.

**3.2.2.2. Effect of operating pressure on the CPC rejection.** The rejection of CPC with different operating pressure at the end of the experiment is presented in Fig. 9(b). It is observed from the figure that there is an increasing trend in rejection of CPC when the operating pressure increased. For example, the CPC rejections for MEUF of RB5 and RO16 increased from 74.75 and 77.20% at 300 kPa to 78.17 and 78.94% at 500 kPa. As the operating pressure increased, the effective driving force will drive the free CPC monomer to the membrane surface, hence would result

and accumulation of CPC monomer at the membrane surface. The CPC monomer concentration in the gel layer can exceed the CMC value and micelles can exist in this region [11]. Therefore, the increase of the operating pressure will increase the gel layer as reported by Gzara and Dhahbi [25], hence will increase the rejection of CPC at permeate stream.

As discussed in Section 3.2.2.1, the dye rejection decreased with operating pressure due to less amount of dye solubilized in the micelles. Although the dye rejection was decreased with operating pressure, but the differences of the dye rejection was too small as the operating pressure increased from 300 to 500 kPa (1.43% for RB5 and 0.74% for RO16). As the gel layer increased, some of the unsolubilized dye would be retained on the membrane surface, hence reducing the amount of free dyes pass through the permeate stream. This results the small differences of dye rejection for both MEUF of RB5 and RO16 although the operating pressure has been increased from 300 to 500 kPa.

**3.2.2.3. Effect of operating pressure on the permeate flux.** The effect of operating pressure for fixed dye and CPC concentration on the permeate flux is presented in Fig. 9(c). It is evident from the figure that the flux increases with pressure. The permeate flux was slightly increased from  $7.18 \times 10^{-6}$  to  $9.51 \times 10^{-6}$  m<sup>3</sup>/m<sup>2</sup> s for RB5 and from  $7.37 \times 10^{-6}$  to  $9.76 \times 10^{-6}$  m<sup>3</sup>/m<sup>2</sup> s for RO16 dye when the operating pressure was increased from 300 to 500 kPa. In an osmotic pressure controlled UF system, the flux can simply be related to the pressure as follows:

$$v_w = \frac{\Delta P - \Delta\pi}{\mu R_m} \quad (4)$$

where  $v_w$  is the permeate flux (m<sup>3</sup>/m<sup>2</sup> s),  $\Delta P$  the pressure differential (Pa),  $\Delta\pi$  the osmotic pressure differential (Pa),  $\mu$  the viscosity (Pa s) and  $R_m$  is the membrane resistance (m<sup>-1</sup>), respectively. With increasing in pressure, the effective driving force for the solvent transport is higher for a fixed feed concentration [22]. Furthermore, the increase in driving force will overcome the membrane resistance. Therefore, increasing the pressure would force more water to pass through the membrane which would result in a higher permeate flux.

Flux decline is the major problem in UF. Various models have been developed to analyze and predict UF flux behavior during separation/fractionation of macromolecular solute. All

Table 2  
Results obtained at optimum pre-treatment run

Dye	pH	Nalco concentration (g/L)	Residual dye concentration (g/L)
RB5	3.0	4.5	0.0219
RO16	3.0	9.0	0.1031

of them can be classified as osmotic-pressure-controlled models, gel polarization models and resistance-in-series models [8]. In this study, the flux decline of MEUF is actually has been analyzed using Resistance-in-series models which will be presented in other paper.

### 3.3. Combination pre-treatment and MEUF process

As discussed in pre-treatment section (Section 3.1), coagulation process using ULTIMER<sup>®</sup> 7751 Nalco as coagulant shows high removal of RB5 and RO16 dyes from aqueous solution. However, the dyes are visible even at very low concentration. Therefore, the treatment process has to provide complete removal of dye from aqueous solution. In this present work, micellar-enhanced ultrafiltration (MEUF) using cationic surfactant, CPC was applied as a finishing and a polishing step after coagulation process. The results obtained at optimum pre-treatment run are shown in Table 2, which was selected for further treatment by MEUF process. It can be concluded from Section 3.2 that an optimum condition from MEUF parameters study was obtained at CPC-to-dye concentration ratio of 20 and operating pressure of 300 kPa. Hence, this optimum condition (Table 3) was selected for treating the selected pre-treated solution (Table 2).

Almost complete removal of RB5 and RO16 dye from aqueous solution was achieved by coagulation pre-treatment followed by micellar-enhanced ultrafiltration using ULTIMER<sup>®</sup> 7751 Nalco as coagulant and cetylpyridinium chloride (CPC) as surfactant (Table 4). With a single coagulation treatment (treatment 1), 95.62 and 79.38% removal of RB5 and RO16 dye was obtained. This removal was improved further after the MEUF finishing step with 99.75 and 99.98% removal of RB5 and RO16 dye. The most significant result is that the combination of both treatment resulted in water quality where the dye was

Table 3  
Optimum condition for MEUF process

Dye	CPC/dye ratio	CPC concentration (g/L)	Dye concentration (g/L)	Operating pressure (kPa)
RB5	20	0.438	0.0219	300
RO16	20	2.062	0.1031	300

Table 4  
Results for combination RB5 and RO16 dye treatment

Dye	Dye concentration before pre-treatment (g/L)	Dye concentration after pre-treatment (g/L)	Dye concentration after MEUF (g/L)	Dye removal for pre-treatment process (%)	Dye removal for combination pre-treatment and MEUF (%)
RB5	0.500	0.0219	$1.26 \times 10^{-3}$	95.62	99.75
RO16	0.500	0.1031	$1.05 \times 10^{-4}$	79.38	99.98



no longer visible (i.e.  $<0.001$  g/L). These results prove that the applied process Nalco coagulation/CPC MEUF achieved complete decolorization and almost total elimination ( $>99\%$ ) of both RB5 and RO16 dyes from aqueous solution.

#### 4. Conclusion

The applied process of Nalco coagulation as pre-treatment process has been studied and this process achieved removal of 95.61% RB5 and 79.39% RO16 dye at coagulant dosages of 4.5 g/L (RB5) and 9.0 g/L (RO16), respectively at pH 3 for 0.5 g/L of dye concentration. However, since the presence of dye in wastewater can be observed at very low dye concentration, 0.001 g/L is visible, it is necessary to achieve the complete dye removal using an efficient treatment process, micellar-enhanced ultrafiltration.

Micellar-enhanced ultrafiltration (MEUF) of RB5 and RO16 dye in CPC solution using 10,000 MWCO thin film ultrafiltration membranes has been studied over a feed CPC-to-dye concentrations ratio range of 10–20 and pressure range of 300–500 kPa at a constant dye concentration of 0.050 g/L. The experiments had been conducted under unstirred dead end ultrafiltration. Flux, CPC and dye rejection characteristic of RB5 and RO16 dye at different experimental conditions have been investigated and analyzed. The reactive dyes were successfully removed from aqueous solution by MEUF process at lower operating pressure and higher membrane MWCO. The optimum CPC-to-dye concentration ratio and operating pressure obtained from MEUF parameters study were 20 and 300 kPa. The combination pre-treatment and MEUF process achieved almost complete decolorization of both RB5 (99.75%) and RO16 (99.98%) from aqueous solution.

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