



# **Influence of Recirculation Rate on Performance of Membrane Bioreactor Coupling with Ozonation Treating Dyeing and Textile Wastewater**

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## **ABSTRACT**

Membrane fouling is a limitation of widespread application of membrane bioreactor (MBR) for wastewater treatment. This research focused on organics removal and fouling control by adding alum into MBR sludge to improve permeate quality and prolong the filtration time. The ozonation followed by the MBR treatment and the recirculation rate (RR) from ozonation reactor returning to MBR was studied to enhance the non-biodegradable matters. The applied dosage was 104 mg O<sub>3</sub>/h and the RR was at 1 and 1.5. It is observed that the removal efficiency of COD and color in single MBR was 87 ± 3% and 86 ± 5% respectively. When coupling with ozonation, the removal efficiency of COD was 90 ± 2% and 96 ± 1% for RR at 1 and 1.5. Those of color were 93 ± 4% and 95 ± 5% at the respective recirculation rate. The results indicate that the higher recirculation rate enhanced the COD and color removal. In addition, the fouling rate increased approximately 1.9 and 7.2 times when the membrane flux was double and triple, respectively.

*Keywords:* Membrane Bioreactor (MBR); fouling; fouling rate; ozonation; alum

## **1. INTRODUCTION**

Nowadays, MBR is widely applied in municipal and industrial wastewater treatment. Advantages of MBR include long sludge retention time (SRT) of 5 – 50 days, high MLSS and low F/M ratio (Dvorak et al., 2011; Nguyen et al., 2013; Visvanathan et al., 2000). The flocs size in MBR is often smaller than those in conventional activated sludge process. The smaller flocs allow easy diffusion of nutrients and oxygen into the core of flocs (Gender et al., 2000). The presence of the membrane could prevent the washout of the nitrifying micro-organism at the short SRT and HRT (Soriano et al., 2003) and encourage the rise of the slow-growing bacteria.

Membrane fouling causing reduction of the permeate flux is inevitable. Therefore membrane must be backwashed or chemically cleaned regularly. This is one of the drawbacks of the MBR applications in practice. The main problem is extracellular polymeric substances (EPS) which enter and deposit on membrane surface, thus causing fouling (Al-Halbouni et al., 2008; Dvorak et al., 2011; Thanh et al., 2008). Furthermore, suspended particles cover the membrane surface to form cake layers which also cause flux reduction after a certain operating period (Thanh et al., 2008; Visvanathan et al., 2000).

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MBR is very effective for the removal of biodegradable organic matters. However, single MBR process is not so effective to eliminate hardly biodegradable compounds, thus it should be coupled with advanced oxidation process such as ozonation (Muza et al., 2013; Wu et al., 2012). Moreover, ozonation is widely used not only for degradation of large COD compounds but also sludge minimization and control of membrane fouling in MBRs (Hwang et al., 2010; Muza et al., 2013).

To avoid membrane fouling, the mechanism of making colloids and sludge particles aggregate to bigger flocs in the MBR was investigated in this study. The flocs can absorb soluble organic matters and thus fouling could be controlled (Siddiqui et al., 2000). In this research, a dosage of alum coagulant was introduced into membrane bioreactor to observe the fouling improvement and treatment performance (in terms of COD and color removal).

Besides, the composition of dyeing and textile wastewater is very diverse and complex. The major contaminants are persistent organics, surface-active agents, dyes, etc that are not able to be removed by a single biological process (Thanh et al., 2011). In practice, the secondary effluent of dyeing and textile wastewater does not comply with standard limits of Viet Nam national technical regulation for dyeing and textile wastewater (column B, QCVN 13:2008/BTNMT). To meet the demand of industrial water reuse, MBR process is used in the combination with advanced ozonation to remove persistent organic matters (non-biodegradable dyes). In this study, different recirculation ratio (RR = 1 and RR = 1.5) from ozonation reactor returning to MBR was investigated. The permeate quality and fouling propensity were characterized during study period.

## 2. MATERIALS AND METHOD

### 2.1 Components of wastewater

Wastewater was taken from a dyeing and textile company in Ho Chi Minh city. The components of the wastewater are presented in Table 1. The COD of dyeing and textile wastewater varies and depends on the products and/or dyes used.

### 2.2 Alum

Alum was added into the MBR at the concentrations of 0.04 g Al/L sludge. This dosage was previously optimized by Zaisheng et al. (2009). The reactor working volume was 22 L, thus 7.87 g Alum was initially added. After every 3 days another 0.375 g Alum was added to compensate the loss through excess sludge removal.

### 2.3 Seed sludge

Seed sludge was taken from the conventional activated sludge process with initial MLSS concentration of 3,000 mg/L.

### 2.4 Ozonator

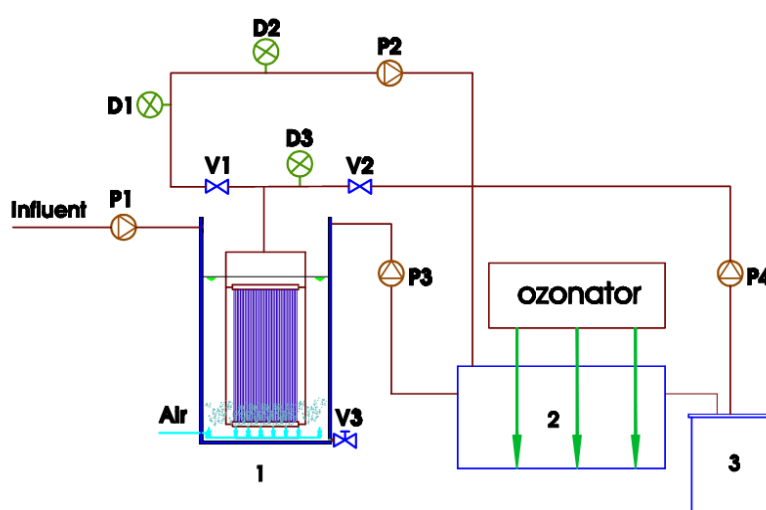
The ozone generating machine used was produced by Viqua (Canada). The ozone generation rate is 104 mg/h. Ozone was introduced to the bottom of ozone contactor through a stone diffuser.

### 2.5 Membrane Bioreactor coupling with Ozonation Process

The system was operated at three following stages, namely control MBR, MBR-RR1 and MBR-RR15 which corresponded to (1) single MBR process, (2) MBR coupling with ozonation reactor at recirculation rate (RR) of 1 and (3) MBR coupling with ozonation at RR of 1.5, respectively.

**Table 1** Composition of raw dyeing and textile wastewater

Parameter	Unit	Value
Temperature	$^{\circ}\text{C}$	60 – 80
pH	-	4 – 13
COD	mg/L	1,500 – 5,000
Color	mg/L	400 – 5,000
Turbidity	mg/L	18 – 592
SS	mg/L	0 – 50
$\text{PO}_4^{3-}\text{-P}$	mg/L	0.15 – 0.20
TKN	mg/L	9 – 16



(1) MBR:  $L \times W \times H = 0.4\text{m} \times 0.1\text{m} \times 0.7\text{m}$ ; (2) Ozonation tank; (3) Effluent container ; P1, P2, P3, P4: Feed, permeate, recirculation and backwash pump; V1, V2, V3: Solenoid valves and bottom valve; D1, D2, D3: Pressure gauge

**Figure 1** Experimental set-up of MBR coupling with ozonation

For the system operation, wastewater was pumped into MBR and controlled by a level sensor. Air was introduced to bottom of the reactor and underneath of the membrane module by stone diffusers. Aeration was controlled with DO at around 4 mg/L. Permeate was sucked semi-continuously with the cycle of 8 minutes on and 2 minutes off. In the case of coupling with ozonation, the permeate from the MBR was pumped into the ozonation tank. Here, a portion of ozonated wastewater was recirculated to the MBR and the remaining was discharged into an effluent container. The

recirculation rates (RR) at 1.0 and 1.5 times were investigated in this study.

The trans-membrane pressure (TMP) was recorded daily through digital pressure gauge to evaluate the membrane fouling. When the TMP value reached over 43 kPa, the backwash pump was operated automatically to push out the cake layer attaching on membrane. The hollow fibre membrane used was produced by MOTIMO company (China). Membrane is made from PVDF with the surface area of  $1\text{ m}^2$  and pore size of  $0.2\ \mu\text{m}$ .

**Table 2** Operating conditions of the system

Parameter	Unit	MBR	MBR-RR1	MBR-RR1.5
Flux	L/m <sup>2</sup> ·h	2.0	3.9	5.6
SRT	days		60	
OLR	kg COD/m <sup>3</sup> ·d		1.1 – 1.7	
HRT	h		10.5 -11.5	
Alum	g Al/L <sub>sludge</sub>		0.04	

## 2.6 Analytical parameters

MBR was operated at organic loading rate (OLR) varying from 1.1-1.7 kg COD/m<sup>3</sup>·day, depending on the real wastewater characteristics. Samples of feed wastewater, permeate and sludge were collected every two days. Analyzed parameters of wastewater quality were COD and color. The sludge was characterized by MLSS, MLVSS, SVI<sub>30</sub>, and microscopic observation. The analytical methods were according to standard methods (APHA, 1998). Membrane fouling was investigated by trans-membrane pressure (TMP) and membrane resistance. Membrane was cleaned after each operation period (when changing the recirculation rate) by chlorine and sodium hydroxide according to Thanh et al. (2008). The TMP values were used to control the operating duration. The single MBR reach TMP of -4 kPa for 35 days without any physical cleaning. The MBR-RR1 and MBR-RR2 reached the same TMP value for 10 days and 6 days, respectively.

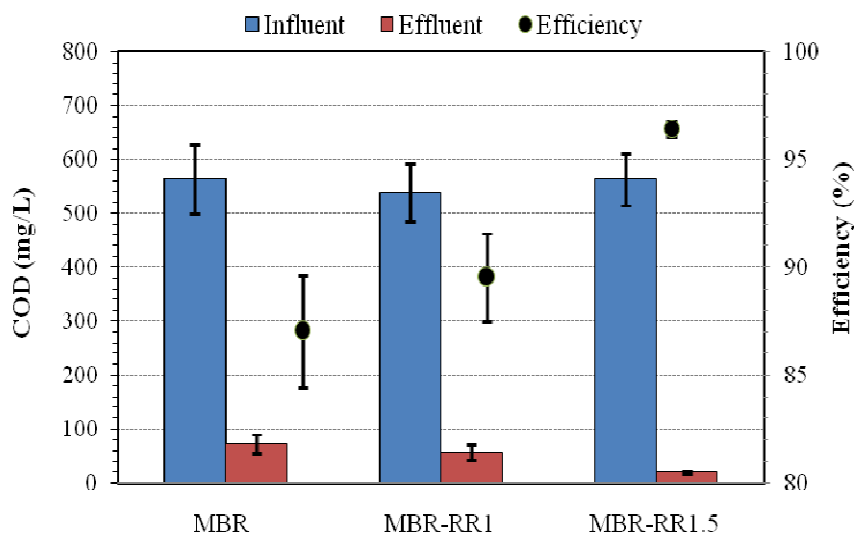
## 3. RESULTS AND DISCUSSION

### 3.1 Pollution removal

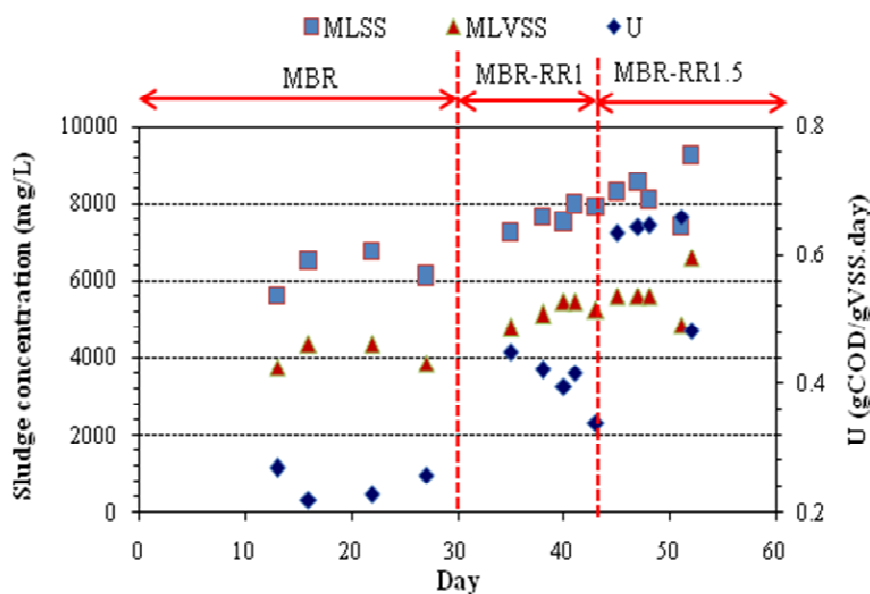
#### 3.1.1 COD removal

Figure 2 shows the COD removal of the three operating conditions (control MBR, MBR-RR1 and MBR-RR1.5). The results show that

without ozonation the average effluent COD was  $73 \pm 17$  mg/L while it was  $57 \pm 15$  mg/L and  $20 \pm 3$  mg/L for MBR-RR1 and MBR-RR1.5 respectively. The removal efficiency was  $87 \pm 3\%$ ,  $90 \pm 2\%$  and  $96 \pm 1\%$  for MBR, MBR-RR1 and MBR-RR1.5 respectively. This indicates the ozonation improved the COD removal clearly. The higher recirculation rate makes the better COD removal. It can be explained that the ozonation could cause the breakage of macromolecules (dye structure), making them biodegradable (Muza et al., 2013; Wu et al., 2012). When recycling the ozonated fraction to bioreactor, the further degradation could occur easily. The removal efficiency was very effective at the recirculation rate of 1.5 which made effluent COD reduced from 73 mg/L to 20 mg/L. The breakage of macromolecule structure was confirmed by another separate COD fraction test using a batch respirometer for the membrane permeate and ozonated permeate. The biodegradable COD fraction of MBR permeate increased from 3% to 24% after ozonation. The non-biodegradable fraction reduced from 38% to 20%. The results reveal the coupling with ozonation improved COD removal efficiency significantly because of the breakage of macromolecules (non-biodegradable structure). The recirculation rate of 1.5 was effective to provide the effluent which complies with standard limits of Viet Nam national technical regulation for dyeing and textile wastewater (level A, QCVN 13: 2008/ BTNMT).



**Figure 2** Removal efficiency of COD in MBR, MBR-RR1, MBR-RR1.5



**Figure 3** Sludge concentration and substrate utilization rate during operating period

To confirm the enhancement by ozonation process, an increase in sludge concentration in MBR was noticed. Figure 3 shows that the MLSS increased from the range of 5800-6500 mg/L to the range of 7200-9300 mg/L for MBR and MBR coupling ozonation respectively. The increase in sludge concentration was due to the increase in influent degradable organic load in

MBR. In addition, specific substrate utilization rate in control MBR, MBR-RR1 and MBR-RR1.5 was 0.219-0.268, 0.339-0.449, and 0.482-0.66 g COD/g VSS·day respectively. On day 51, there was a technical problem with the level sensor so the wash-out of sludge occurred, thus sludge concentration reduced to 7400 mg/L.

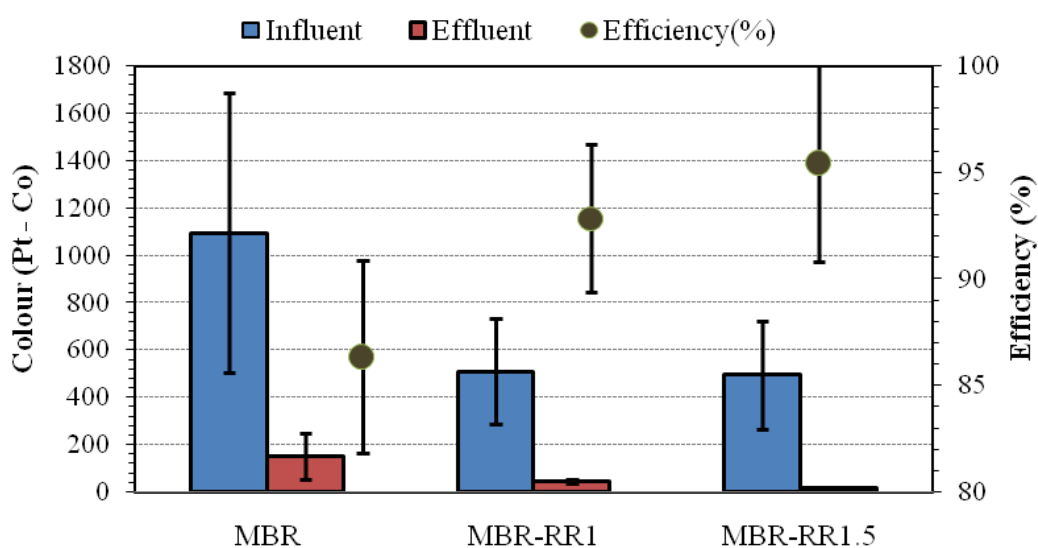
### 3.1.2 Colour removal

Figure 4 shows that the effluent colour fluctuated from 30-357 Pt-Co, 37-58 Pt-Co and 10-25 Pt-Co during operation for control MBR, MBR-RR1 and MBR-RR2 respectively. The average removal efficiency was respective  $86 \pm 5\%$ ,  $93 \pm 4\%$ , and  $95 \pm 5\%$ . This implies that the coupling with ozonation could enhance color removal. The higher recirculation rate makes the better color removal. The colour appeared due to the dyes which are often non-biodegradable. The ozonation made the structure of dyes broken into smaller molecules which does not absorb the visible light, then reducing color of wastewater (Zaisheng et al., 2009).

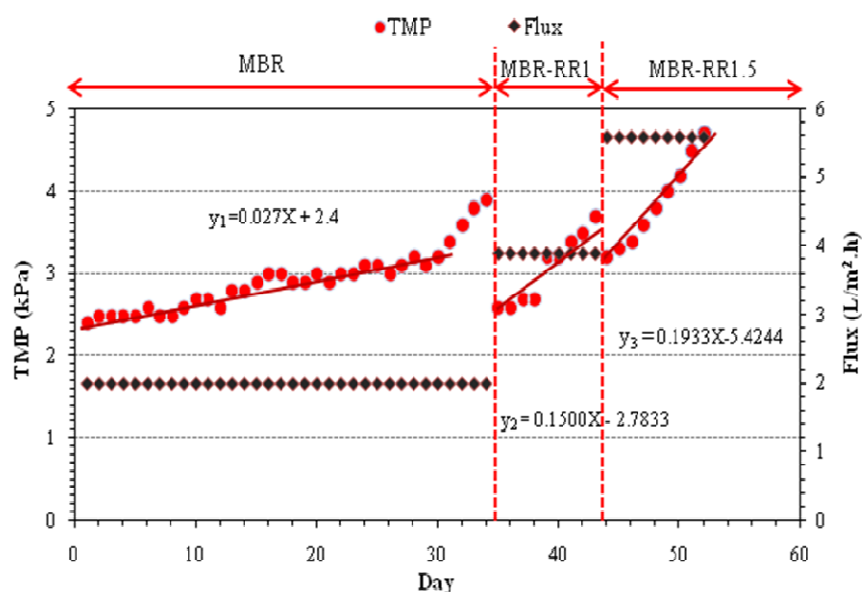
The color of effluent with ozonation process met the standard limits of Viet Nam national technical regulation QCVN 13:2008/BTNMT (level B). However it was not able to meet the level A which is effluent standards for wastewater discharging into drinking water resource. Less than 50% of effluent samples could reach this standard limits. The treated wastewater could be reused for washing and/or staining of dark cloths.

### 3.2 Membrane fouling

Figure 5 describes the change of flux and trans-membrane pressure (TMP) of MBR system with time. The value of the flux was maintained constant during each operation period. The flux was 2.0, 3.9 and 5.6 L/m<sup>2</sup>·h for control MBR, MBR-RR1 and MBR-RR1.5 which was increased due to the recirculation flow from ozonation reactor to MBR. At the flux of 2 L/m<sup>2</sup>·h, the TMP increased at very slow rate, only 1.5 kPa, from 2.4 to 3.9 kPa for 34 days of operation. This equals to the fouling rate of 0.027 kPa/day. While at the flux 3.9 and 5.6 L/m<sup>2</sup>·h the TMP increased much faster 1.1 kPa and 1.5 kPa for 3.9 and 5.6 L/m<sup>2</sup>·h during 9 days of operation. The fouling rate was 0.027, 0.150, 0.193 kPa/day for the fluxes of 2.0, 3.9 and 5.6 L/m<sup>2</sup>·h respectively. In general, the slower fouling rate is observed at lower flux (Thanh et al., 2013). As a result, the high recirculation rate provides better treated effluent but faster fouling rate. The fouling rate increased approximately 1.9 and 7.2 times when the membrane flux was double and triple, respectively.



**Figure 4** Colour removal in MBR, MBR-RR1 and MBR-RR1.5



**Figure 5** Flux, TMP in MBR stage, two different circulation rates

## CONCLUSIONS

From the research results, some of conclusions could be withdrawn as follows:

The combination of MBR and ozonation process could treat the dyeing and textile wastewater effectively. The ozonation broke down the macromolecules into smaller biodegradable fractions which can be decomposed in the recycled flow into MBR. The removal efficiencies of COD and color were 87-96% and 86-95%, respectively.

The higher recirculation rate provides better treated effluent. The fouling rate was faster at the higher recirculation rate. It increased approximately 1.9 and 7.2 times when the membrane flux was double and triple.

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