



## Removal of Non-Biodegradable Organic Matters from Membrane Bioreactor Permeate By Oxidation Processes

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### ABSTRACT

This study aimed to optimize the operational parameters of oxidation processes in removing the non-biodegradable matters from the permeate of membrane bioreactor (MBR) which is used to treat dyeing and textile wastewater. The MBR was operated at the OLR of 1.3–1.7 kg COD/m<sup>3</sup>.day, HRT of 11 hours, and SRT of 60 days. The quality of MBR permeate were stable during operation period with COD and colour of 107 ±7 mg/L (96-114 mg/L) and 85 ±10 Pt-Co (70-90 Pt-Co), respectively. The insight of the advanced oxidation processes (AOPs) is to generate hydroxyl free radical (OH<sup>•</sup>) as strong oxidant to decompose the recalcitrants which cannot be oxidized by the conventional biological processes. The results show that the single ozone oxidation process removed 50% of COD and 41% of colour with the ozone generation rate of 104 mg O<sub>3</sub>/h for 25 minutes at pH 9. For the Peroxone oxidation, about 59% of COD and 53% of colour removal were achieved at the same operating conditions at pH 8.5, and molar ratio H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> of 1:2. While for the O<sub>3</sub>/UV oxidation, COD and colour reduced to 55% and 54% after 25 minutes at pH 9. The Fenton oxidation achieved removal efficiency of 90% of colour and 84% of COD at pH 3 and the mass ratio Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/COD of 1:1:1. It indicates that the three oxidation processes could removed refractory residue from MBR permeate to meet the Vietnam National Technical Regulation for dyeing and textile wastewater (level B, QCVN 13:2008/BTNMT). In general, the single ozonation shows advantages in term of simple operation, reasonable treatment cost and rational removal color and part of non-biodegradable COD among the other AOPs. During ozonation process, non-biodegradable COD in MBR permeate converted to biodegradable COD fraction which can be further mineralized by biological process.

*Keywords:* Advanced oxidation processes (AOPs); Hydroxyl free radical; Ozone; Peroxone; O<sub>3</sub>/UV; Fenton; Dyeing and textile wastewater

### 1. INTRODUCTION

Dyeing and textile industry needs a lot of water for production processes and generates large quantity of wastewater from various steps of dyeing processes, about 12-300 m<sup>3</sup>/ton of fabric. Main pollution in dyeing and textile wastewater came from dyeing and finishing processes. The wastewater contains

high amount of dyestuffs, which generally are organic compounds with complex structure, salts, heat, enzymes, surfactants, oxidizing and reducing agents. This wastewater has high COD deriving from additives, suspended solid (SS). In addition, only 47% of 87 of dyestuff are biodegradable. It is documented that residual colour is usually due to insoluble dyes which have low biodegradation as reactive blue 21, direct blue 80 and vat violet (Adel et al., 2005). Because of those, dyeing

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and textile wastewater is an important pollution source to be concerned.

COD values of dyeing and textile wastewater are high compared to other parameters. The concentration of COD varies from 150–12,000 mg/L and colour fluctuates between 50–2,500 Pt-Co. In most cases, the BOD<sub>5</sub>/COD ratio is around 0.25 that implies that the wastewater contains large amount of non-biodegradable organic matter (Adel et al., 2005). Many treatment processes were made for treating dyeing and textile wastewater such as chemical oxidation, liquid-liquid extraction, adsorption, ultra-filtration, reverse osmosis, and biological treatment. However, because of the complex structure of organic compounds and the low ratio of BOD<sub>5</sub>/COD which translates to a hardly biodegradable, the conventional treatment methods have found difficulty to mineralize dyestuffs and complex structure of organic compounds (Adel et al., 2005; Konsowa, 2003). To ease the stated problems, advanced oxidation processes (AOPs) have been developed.

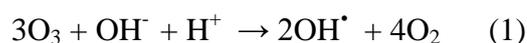
AOPs defined by Glaze et al. (1987) are involving the use of ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), UV radiation and Fenton agent to generate and use hydroxyl free radical (OH<sup>•</sup>) as a strong oxidant to destroy compound that cannot be oxidized by conventional oxidant (Adel et al., 2005). Hydroxyl radicals are extraordinarily reactive species that attack most of the organic molecules. Its oxidizing potential is quite strong more than chlorine 2.05 times (Carey, 1992).

The importance of these processes is due to the high reactivity and redox potential of this free radical that reacts non-selectively with organic compounds present in water. These processes present a high degree of flexibility because they can be used individually or in combination depending on the problem to be solved. Generation of OH<sup>•</sup> is commonly accelerated by combining O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub>, UV radiation, electron-beam irradiation and

ultrasound. Of these, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/UV hold the greatest promise to oxidize dyeing and textile wastewater. Another advantage of the AOPs is that they may be applied under mild conditions (atmospheric ambient pressure and room temperature).

### 1.1 Ozone Oxidation Process

Ozone application can be generalized into two; a powerful disinfection and a strong oxidant agent for water and wastewater to remove colour, odour, eliminating trace toxic synthetic organic compounds. Once dissolved in water, ozone reacts with a great number of organic compounds in two different ways: by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidants like hydroxyl radical OH<sup>•</sup> (Baig and Liechti, 2001).



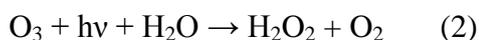
Colour removal using ozonation from dyeing and textile wastewater depends on dye concentration (Sheng and Chi, 1993; Mehmet and Hasan, 2002; Konsowa, 2003). Higher initial dye concentration of dyeing and textile wastewater causes more ozone consumption. Increasing ozone concentration enhances mass transfer that causes an increase in ozone concentration in liquid phase, which increase colour removal. The other possible explanation is that more intermediates, which consume more ozone, are generated when the initial dye concentration is high. Gianluca and Nicola (2001) reported that colour removal of biotreated dyeing and textile wastewater depended on initial COD of the wastewater. In addition, colour removal efficiency increased with increasing the temperature from 25°C to 50°C. Alkaline pH was also found as favorable condition for high removal of colour and COD.

Ozone is the basic compound for many oxidation processes included under the general term of ozonation. In these processes,

ozone may be used alone or with other agents such as hydrogen peroxide, UV radiation, catalysts, ultrasound, activated carbon, etc.

## 1.2 O<sub>3</sub>/UV Oxidation Process

According to Rein (2001), conventional ozonation of organic compounds does not completely oxidize organics to CO<sub>2</sub> and H<sub>2</sub>O in many cases. Hung-Yee and Ching-Rong (1995) documented O<sub>3</sub>/UV as the most effective method for decolorizing of dyes comparing with oxidation by UV or ozonation alone. The O<sub>3</sub>/UV system is also an effective method for the destruction of organic compounds in water. It makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals. UV lamp must have a maximum radiation output 254 nm for an efficient ozone photolysis. The photodecomposition of ozone leads to two hydroxyl radicals.



Even though ozone can be photodecomposed into hydroxyl radicals to improve the degradation of organics, UV light is highly absorbed by dyes and very limited amount of free radical (OH<sup>•</sup>) can be produced to decompose dyes. In normal cases, ozone itself will absorb UV light, competing with organic compounds for UV energy. However, O<sub>3</sub>/UV treatment is recorded to be more effective compared to ozone alone, in terms of COD and colour removals. Azbar et al. (2004) stated that using O<sub>3</sub>/UV process high COD and colour removals would be achieved under basic conditions.

## 1.3 O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> Oxidation Process

The addition of both hydrogen peroxide and ozone to wastewater accelerates the decomposition of ozone and enhances production of the hydroxyl radical. Hydrogen peroxide in

aqueous solution is partially dissociated in the hydroperoxide anion (HO<sub>2</sub><sup>-</sup>), which reacts with ozone, decomposing this and giving rise to a series of chain reactions with the participation of hydroxyl radicals. In the global reaction two ozone molecules produce two hydroxyl radicals (Glaze and Kang, 1989).

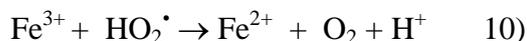
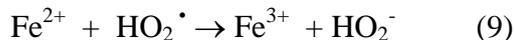
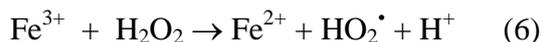
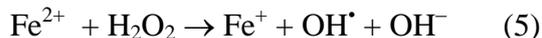


Arslan et al. (2002) documented that O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment of synthetic dye-house wastewater highly depended on the pH of the effluent. At acidic pH, H<sub>2</sub>O<sub>2</sub> reacts only very slowly with O<sub>3</sub> whereas at pH values above 5 a strong acceleration of O<sub>3</sub> decomposition by H<sub>2</sub>O<sub>2</sub> has been observed. At higher pH, even very small concentration of H<sub>2</sub>O<sub>2</sub> will be dissociated into HO<sub>2</sub><sup>-</sup> ions that can initiate the ozone decomposition more effectively than OH<sup>-</sup> ion (Staehlin and Hoigne, 1982; Glaze and Kang, 1989). As a result, the ozone decomposition rate will increase with increasing pH. However, hydrogen peroxide in alkaline medium reacts with sodium hydroxide. As a result, lower concentrations of hydrogen peroxide are available for the formation of hydroxyl radicals. The inhibitory performance of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process on microbial growth depended on the H<sub>2</sub>O<sub>2</sub> to O<sub>3</sub> mass ratio. This ratio ranged from 0.3 to 0.6 for different type of dyes (Rein, 2001).

## 1.4 Fenton Oxidation Process

The term of Fenton reagent refers to aqueous mixtures of Fe(II) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The Fenton reaction was discovered by Fenton (1894). Forty years later, the Haber-Weiss (1934) mechanism was postulated, which revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical (OH<sup>•</sup>). Although the Fenton reagent has been known for more than a century and shown to be a powerful oxidant, the mechanism of the Fenton reaction is still under intense and controversial discussion. Genera-

tion of  $\text{OH}\cdot$  radicals by the reaction of  $\text{H}_2\text{O}_2$  with ferrous salt has been the subject of numerous studies during the last decade (Arnold et al., 1995). Additional important reactions occurring in aqueous mixtures of iron and hydrogen peroxide under acidic conditions include the following:



Several studies have demonstrated that the best oxidation efficiency is achieved when neither  $\text{H}_2\text{O}_2$  nor  $\text{Fe}^{2+}$  is overdosed, so that the maximum amount of  $\text{OH}\cdot$  radicals are available for the oxidation of organics. Many authors suggested  $\text{Fe}^{2+}$  to  $\text{H}_2\text{O}_2$  mass ratio to be optimal at 1 to 10, but it must be optimized for particular wastewater.

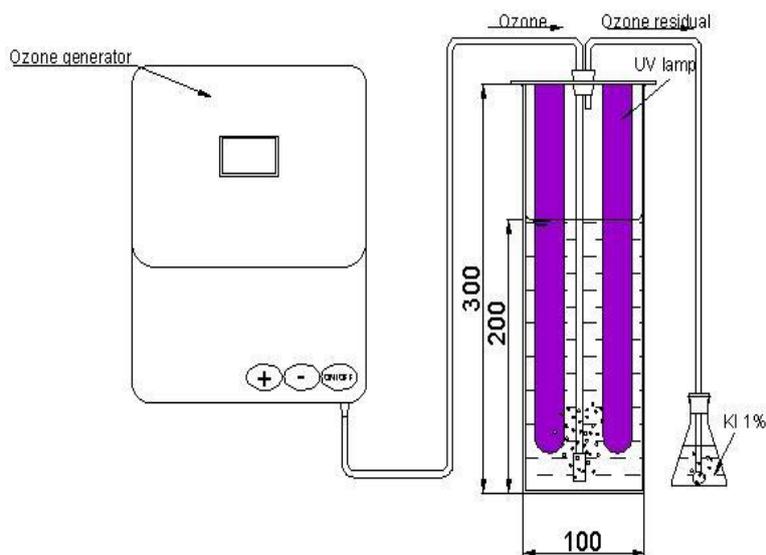
## 2. MATERIALS AND METHODS

Raw wastewater was collected from a dyeing factory in Ho Chi Minh City. The wastewater was treated biologically from a submerged

membrane bioreactor (MBR) which was operated at OLR of 1.3–1.7 kg COD/m<sup>3</sup>.day, HRT of 11 hours and SRT of 60 days. The membrane permeate which contains the COD of  $107 \pm 7$  mg/L (96–114 mg/L) and  $85 \pm 10$  Pt-Co (70–90 Pt-Co) was used for different oxidation processes.

For Ozone oxidation, 1.6 L of wastewater was placed in the reactor (Figure 1 without UV lamps) and then ozone was supplied by ozone generator with capacity of 104 mg O<sub>3</sub>/h. The duration of ozone supplied was varied from 5, 10, 15, 20, 25, 30, 35 and 40 minutes. The pH values changed from 7 to 10 to study the effect of this factor on the degradation efficiency. At the end of the reaction time, each sample was taken and analyzed for the concentrations of COD and colour in order to assure the mineralization of the wastewater.

The studies for O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidations were similar to ozone oxidation. For O<sub>3</sub>/UV oxidation, two UV lamps (6 Watt) were added inside the reactor (Figure 1). And for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation, different volumes of H<sub>2</sub>O<sub>2</sub> 30% solution were investigated to determine the removal efficiency. The molar ratio of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> was varied from 0.3; 0.4; 0.5; 0.6; 0.7 and 0.8.



**Figure 1** Experimental setup of advanced oxidation processes (O<sub>3</sub>, O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>)

For Fenton oxidation, a 400 mL sample was placed into a 500 mL beaker, pH was adjusted prior to chemical oxidation experiments. The pH values were changed from 2 to 5. The  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added to attain selected mass ratio  $\text{Fe}^{2+} : \text{H}_2\text{O}_2$  (1:5, 1:4, 1:3, 1:2, 1:1 and 2:1). Finally, Fenton reaction was started with addition of  $\text{H}_2\text{O}_2$  (30%) to achieve the mass ratio (1:5, 1:4, 1:3, 1:2, 1:1 and 2:1). The aqueous solution of Fenton reagent and wastewater were stirred during the reaction period with the stirring speed of 60 rpm. At the end of the reaction time, each sample was taken and analyzed for the concentrations of COD and colour in order to determine the removal efficiencies of pollutants.

The COD fractions including biodegradable and slowly biodegradable were measured by a batch respirometer with the  $S_0/X_0$  ratios ranging from 0.01-0.03 mg COD/mg VSS. The sludge of 1500 mgVSS/L was taken from conventional activated sludge process. The

biodegradable COD and slowly biodegradable COD were quantified based on the oxygen consumption rate during the experiment. The non-biodegradable COD was estimated by the subtraction from the initial COD. This COD fraction was according to Mathieu and Etienne (2000). This experiment was triplicate for each wastewater sample before and after ozonation.

### 3. RESULTS AND DISCUSSION

#### 3.1 Ozone Oxidation

Figure 2 shows that the COD and colour removal using ozonation are dependent on pH values. The rate of oxidation increased slightly with increasing solution pH. At pH 9, 50% of COD and 41% of colour were removed for 25 minutes and ozone generating rate of 104 mg  $\text{O}_3/\text{h}$ . The results show that 0.4–0.5 g ozone would treat 1 g COD, and the efficiency of ozone usage was 70%.

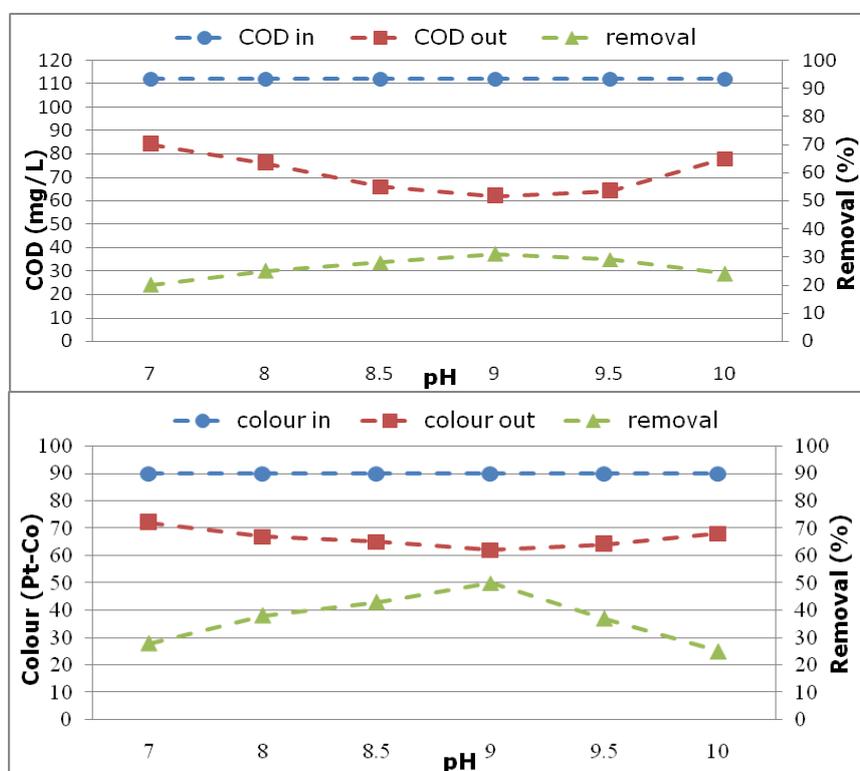


Figure 2 Removal efficiency at different pH by ozone oxidation

Higher COD and colour removal at alkaline pH could be due to enhancement of ozone decomposition by hydroxyl radical. The rate of ozone decomposition is favoured by the formation of hydroxyl radicals at higher pH values. Arslan et al. (2002) reported that high colour removal of simulated reactive dye bath effluent was achieved at pH 7 when using ozone concentration of 2,970 mg/L and remained unchanged at pH 11.

The removal of COD depends on the strength of dye waste, where COD reduction was low with the medium- and high-strength dye waste. The low COD reduction is attributable to the fact that the structured polymer dye molecules (non-biodegradable COD) are broken by ozonation to small molecules, such as acetic acid, aldehyde, ketones, etc. instead of CO<sub>2</sub> and water (Sheng and Chi, 1993).

### 3.2 O<sub>3</sub>/UV Oxidation

The trend of COD removal is similar with that

of ozone oxidation process (Figure 3). At pH 9, 55% of COD and 54% of colour were removed for 25 minutes and ozone generating rate of 104 mg O<sub>3</sub>/h. The results show that 0.3–0.4 g ozone would treat 1 g COD, and the efficiency of ozone usage was 58%.

The O<sub>3</sub>/UV process makes use of UV photons to activate ozone molecules, thereby facilitating the formation of hydroxyl radicals. So the O<sub>3</sub>/UV oxidation is more effective compared to ozone alone. For 25 minutes of reaction, the O<sub>3</sub>/UV treatment could remove 55% of COD while the single ozone oxidation reduced only 50%. Bes-Piá et al. (2003) reported that O<sub>3</sub>/UV treatment of biologically treated dyeing and textile wastewater reduced COD from 400 to 50 mg/L for 30 minutes. While using ozone oxidation alone, COD reduced to 286 mg/L in same duration for the same operating conditions. Azbar et al. (2004) documented that using O<sub>3</sub>/UV process high COD removal would be achieved under basic conditions (pH 9).

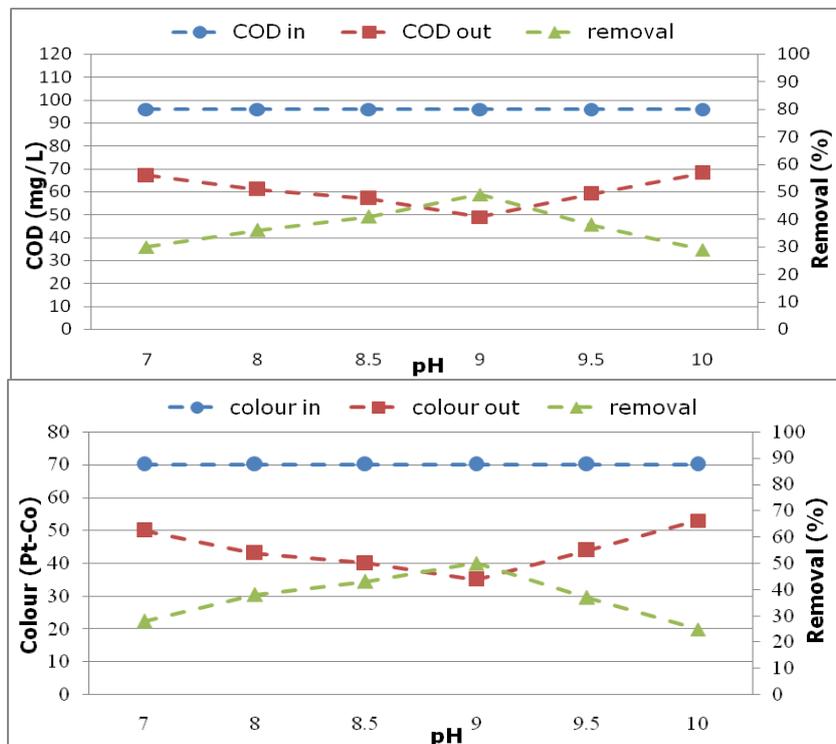
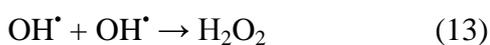


Figure 3 Removal efficiency at different pH by O<sub>3</sub>/UV oxidation

### 3.3 O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> Oxidation

Similar to ozone oxidation, at alkaline pH of 7-8.5, the efficiency of COD and colour removal is higher (Figure 4). At pH 8.5 about 59% of COD and 53% of colour removal were achieved for 25 minutes and ozone generating rate of 104 mg O<sub>3</sub>/h. The results indicate that 0.24–0.40 g ozone would treat 1 g COD, and the efficiency of ozone usage was 59%.

The decolorization efficiency increases with increasing hydrogen peroxide dose up to a point where it reaches a maximum and then starts to decrease. This is due to the fact that hydrogen peroxide is a scavenger for hydroxyl radicals according to the reaction given in the following equation (Dionysiou et al., 2004):



When enough hydrogen peroxide is present

in the solution, it starts to compete with the dye for reaction with hydroxyl radicals since HO<sub>2</sub><sup>•</sup> is less reactive than the OH<sup>•</sup> radical. An increased level of hydrogen peroxide has a diminishing effect on the reaction rate (Aleboye et al., 2003). Therefore, it is important to optimize the applied dose of hydrogen peroxide. The molar ratio H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> of 1:2 was determined by many experiments in this study. Many researchers (Glaze, 1989; Singer and Reckhow, 1999 and Rein, 2001) stated that the molar ratio H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> ranged from 0.3-0.6 for different types of dyes.

### 3.4 Fenton Oxidation

In this study, Fenton treatment could achieve removal efficiency of 90% of colour and 84% of COD at pH 3 with the mass ratio COD/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> 1:1:1. The reaction of Fe (II) and hydrogen peroxide occurs under acidic condition. This result shows the removal of COD and colour was highest at pH 3 which is similar to other researchers.

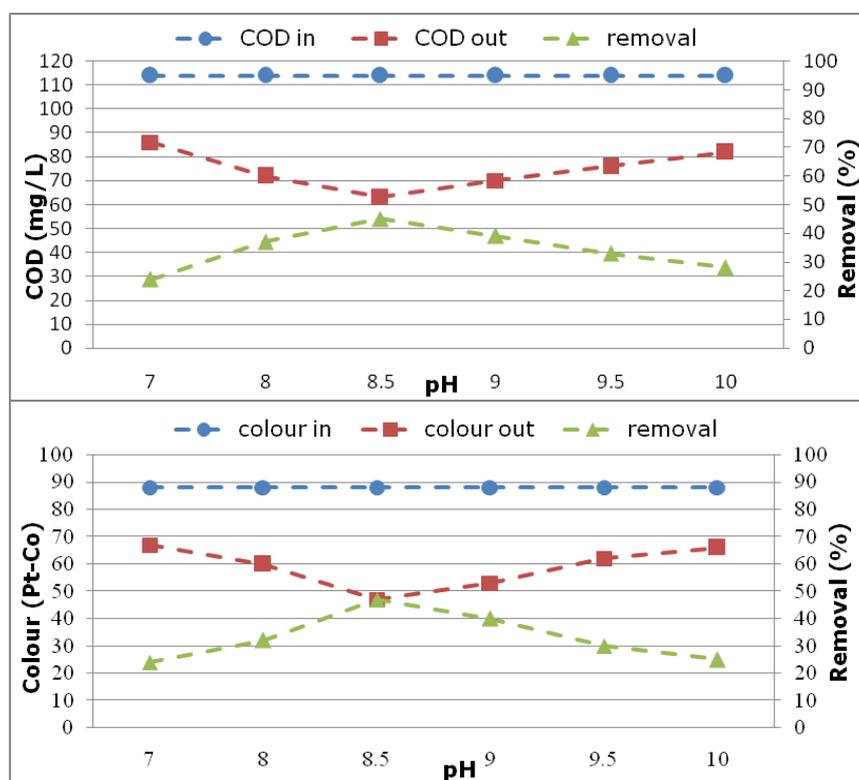


Figure 4 Removal efficiency at different pH by O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation

Figure 5 shows the removal efficiency of COD and colour by Fenton oxidation at pH 3, mass ratio  $\text{H}_2\text{O}_2/\text{COD}$  1:1 and values of mass ratio  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ . The maximum amount of  $\text{OH}^\bullet$  radicals is available for the oxidation of organics, neither  $\text{H}_2\text{O}_2$  nor  $\text{Fe}^{2+}$  is overdosed. This study suggested  $\text{Fe}^{2+}$  to  $\text{H}_2\text{O}_2$  mass ratio to be optimal at 1:1. When dosage of hydrogen peroxide and Fe (II) are too high, they starts to compete with the dye and the organic carbon for reaction with hydroxyl radicals according to equations (7) and (8).

### 3.5 Removal efficiency of COD and color of the four oxidation processes

Figure 6 shows that Fenton oxidation was the most effective process in removing COD and colour from MBR treating dyeing and textile wastewater. The removal of COD and color was almost similar for the ozone combining processes. The Fenton process is the most effective but it is costly and complicated due to chemical usage, sludge production and tank

construction. The costs of wastewater treatment for were 0.20, 0.22, 0.35 and 0.24 USD/ $\text{m}^3$  of MBR permeate for the  $\text{O}_3$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{O}_3/\text{UV}$  and Fenton respectively. Because the removal efficiencies of other ozone based processes were almost similar, the single ozone oxidation was selected as the appropriate process in coupling with MBR because the following reason: (a) this single ozone oxidation can treat the MBR permeate reaching Vietnamese discharge limits with the lowest cost among the AOPs; (b) there is no use of chemical or UV equipment in the processes like perozone, Fenton and  $\text{O}_3/\text{UV}$ ; and (c) there is no sludge production and additional reactors like Fenton process. The sludge production from Fenton process was observed approximately  $0.1 \text{ m}^3/\text{m}^3$  of wastewater (after 30 minute of settling) which could generate a burden in sludge management of the treatment plant. In general, the single ozone oxidation process is the most suitable process coupling with MBR treating dyeing and textile wastewater.

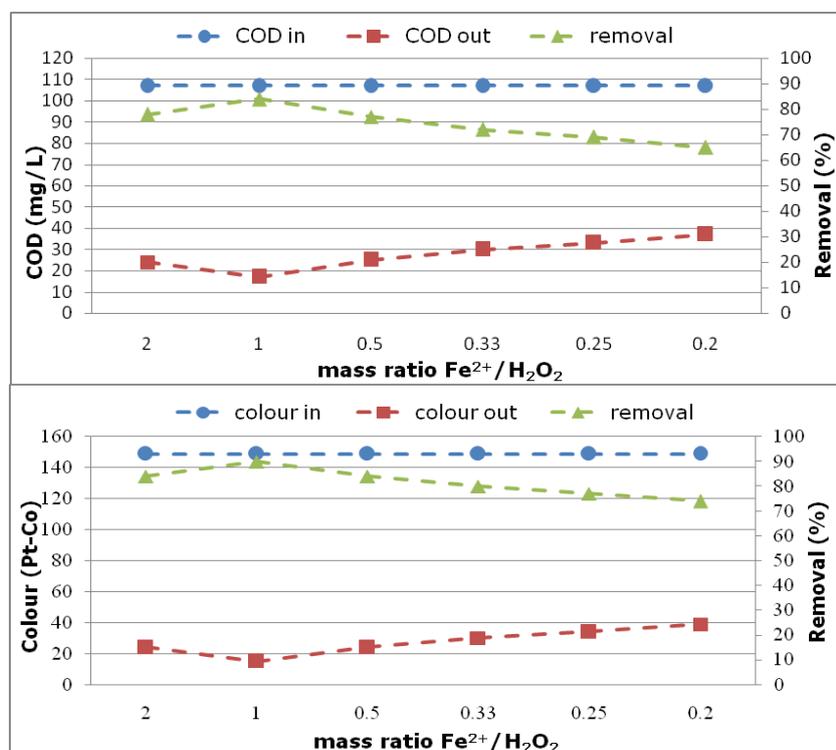
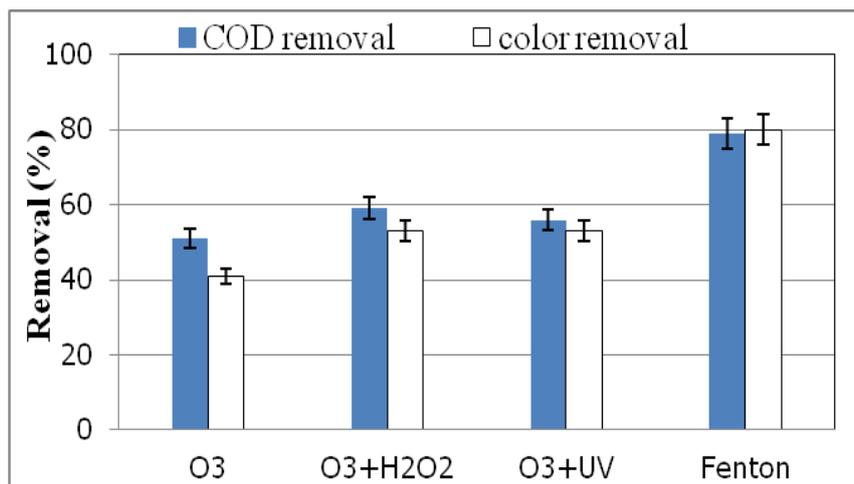
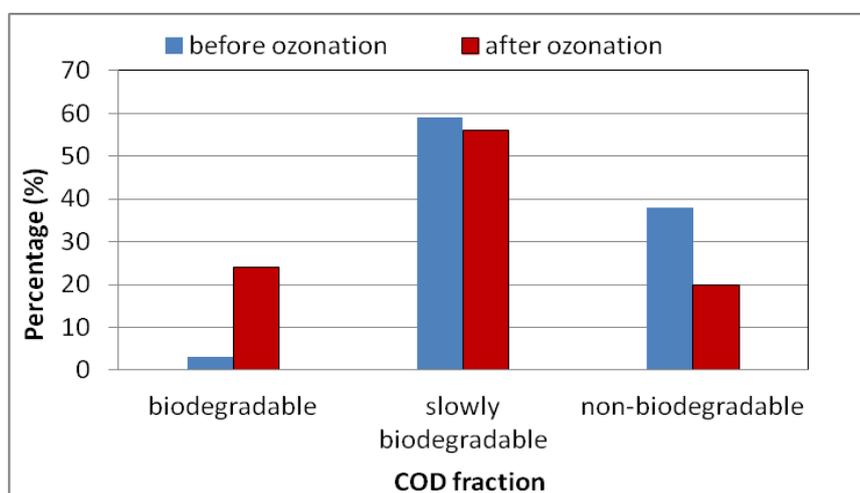


Figure 5 Removal efficiency at different  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratios by Fenton oxidation



**Figure 6** Removal efficiency of COD and colour of AOPs



**Figure 7** Fate of COD during ozone oxidation

Figure 7 shows the fate of COD in MBR permeate before and after ozone oxidation. It reveals that dye macro-molecules were broken to smaller molecules, thus a part of non-biodegradable COD transformed into biodegradable one. This result found that the oxidation process did not mineralize all organic matter completely, i.e. into carbon dioxide and water. For the ozone oxidation, organic matter was partly mineralized and partly transformed. The biodegradable COD was increased from 3% into 24% after ozone addition. Thus, the suitable operation for dyeing and textile wastewater treatment is to combine the ozone oxidation and biological

process. The ozonized flow could be recycled to biological reactor for further degradation.

## CONCLUSIONS

The AOPs process could remove COD residue and color from the MBR permeate during 25 minutes and ozone generation rate of 104 mg O<sub>3</sub>/h. The single ozone oxidation process removed 50% of COD and 41% of colour. The Peroxone oxidation eliminated about 59% of COD and 53% of colour. The O<sub>3</sub>/UV oxidation rejected 55% of COD and 54% of color. The Fenton oxidation achieved removal efficiency of 90% of colour and 84% of COD

at pH 3 and the mass ratio  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{COD}$  of 1:1:1. The single ozone oxidation was found to be appropriate operation coupling with MBR in terms of removal efficiency, treatment cost and simple operation in real practice.

The three oxidation processes could removed refractory residue from MBR permeate to meet the Vietnam National Technical Regulation for dyeing and textile wastewater (level B, QCVN 13:2008/BTNMT).

For ozone oxidation process, organic matters in MBR permeate was partly mineralized and partly transformed. Non-biodegradable organic compounds were converted to biodegradable fractions. The biodegradable COD was increased from 3% into 24 % after ozone addition.

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