# Effects of ozonation process on lignin-derived compounds in pulp and paper mill effluents

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## Abstract

The effect of ozonation process on pulp and paper mill effluents was investigated. The objectives were to: (1) identify various compounds in wastewater from a pulp and paper mill, (2) evaluate decolorization and organic removal efficiency by conventional bubble reactor and (3) evaluate the biodegradability at various progressive stages of ozonation. The qualitative GC/MS analyses were performed before and after the biological treatment and ozonation process. Two groups of compounds were observed in this wastewater: lignin-derived compounds and aliphatic compounds used in the pulp and paper production process (i.e. $n$-alkanes, fatty alcohols, fatty acid and ester). Treatment efficiency was measured by decolorization and TOC removal rates. Additionally, the utilization coefficient ($k$) and BOD/COD ratio were determined to observe the biodegradability of ozonized effluents. The results indicated that after 45 min, the ozonation of effluents yielded almost colorless effluent with over 90% decolorization efficiency and with corresponding ozone capacity rate of $20.0 \, mg \, O_3 \, L^{-1}$. This decolorization was not always accompanied by the mineralization of the organic matters therefore ozonation was not related to TOC removal rates. The BOD/COD ratio increased from 0.10 to a maximum value of 0.32 with ozone flow rate (O/F) of $4.0 \, L \, min^{-1}$. It was confirmed by the utilization coefficient as first order BOD equation, the magnitude $k$ value increased from $0.21 \, day^{-1}$ to maximum value of $0.47 \, day^{-1}$ as the ozonation time was raised to 60 min with O/F $4.0 \, L \, min^{-1}$.
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## 1. Introduction

The pulp and paper mill industry is a very water-intensive industry and ranks third in the world [1]. They are also significant contributors of pollutant discharges to the environment in the form of brown-colored effluents as a result of different operations used in processing the wood and pulp. The brownish color is mainly attributed to the complex compounds derived from polymerization between lignin-degraded products and tannin during various pulping and bleaching operations. Lignin and its derivatives are difficult to degrade naturally because of the strong linkages within their molecular structure, especially biphenyl-type carbon to carbon linkages [2,3]. Due to this

fact, even though conventional biological treatment processes are effective in decreasing organic matter in the effluents, they have little effect on decolorization of the effluents. Cristina Yaber et al. [4] reported that low BOD/COD ratio was obtained from pulp mill effluents (average 0.3) while good biodegradability value was considered in the range over 0.5 as reported by Harmsen and Voortman [4,5]. These data indicate that lignin and its derivatives in the effluents exhibit slow degradation kinetics for conventional treatment process.

There is an increasing interest in utilization of advanced oxidation processes (AOPs) for destruction of slow degrading compounds. AOPs are based on the production of hydroxyl radicals (OH$^\bullet$) as oxidizing agents to mineralize the complex chemicals in the effluents. OH$^\bullet$ is a powerful oxidizing agent with an oxidation potential of 2.33 V and exhibits a faster rate of oxidation reaction compared to that using conventional oxidants such as hydrogen peroxide or potassium permanganate [6]. OH$^\bullet$
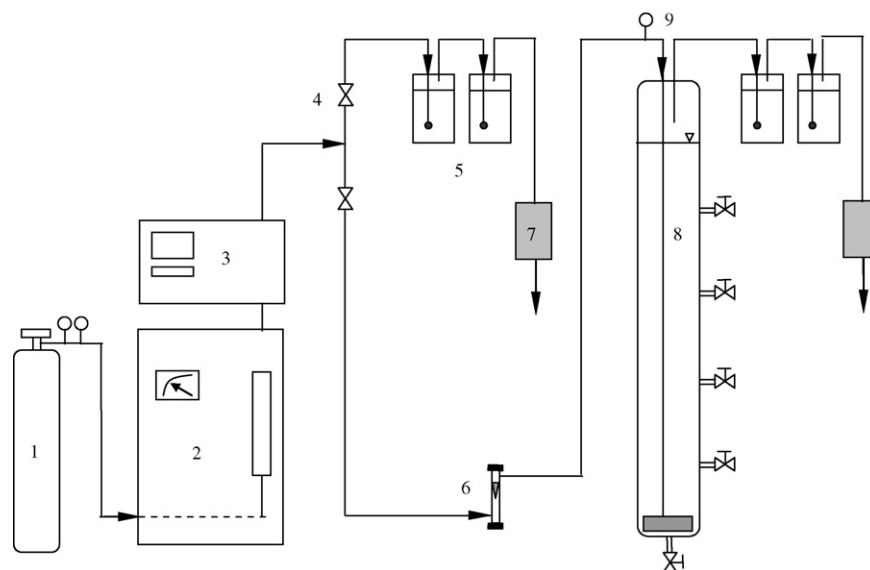
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Fig. 1. Schematic of experimental set-up for semi-batch ozonation process: (1) oxygen gas cylinder; (2) extra-dry oxygen gas generator; (3) ozone generator; (4) on/off valve; (5) ozone trap reactor; (6) air flow meter; (7) ozone gas destruction unit; (8) conventional ozone bubble reactor; (9) pressure gauge.

reacts with most organic and many inorganic solutes with high rate constants [7,8].

Ozone is one of the existing AOPs and can be used for treatment of effluents from various industries [9,10]. A major limitation of the ozonation process is the relatively high cost of ozone generation coupled with the very short half-life period of ozone. Thus, ozone always needs to be generated at site. Moreover, the process efficiency is highly dependent on efficient gas liquid mass transfer, which is quite difficult to achieve due to the low solubility of ozone in the aqueous solutions.

A number of studies have focused on ozonation application for improvement of wastewater quality both preliminary and tertiary treatment (before and after the conventional biological treatment process) depending on the application purposes [11,12]. Furthermore, Pokhrel and Viraraghavan [13] also reviewed several experiments, indicating that the ozonation was highly efficient for decolorization (95–97%) and total organic carbon removal (12%) of pulp and paper mill effluents when high dosage of ozone (100–300 mg L$^{-1}$) were used [13]. Advantages of ozone application in preliminary treatment concern improvement of wastewater biodegradability before subjected to the treatment resulting in improvement of the efficiency of treatment [14,15]. For the application after biological treatment, apart from the biodegradability of effluents are improved, the reuse of treated effluents are also possible.

This research focuses on application of ozone technologies (operating at ambient conditions) as a post-treatment stage after the conventional biological process for pulp and paper mill wastewater treatment. Furthermore, this work has been extended to identify some compounds and ozonized products from pulp and paper mill effluents by GC/MS analysis. This phase of identification can be of interest for the pulp and paper mill industries.

## 2. Experimental

### 2.1. Apparatuses

In this research, the actual pulp and paper mill effluents were obtained from the pulp and paper mill located in Kanchanaburi, Thailand. Fig. 1 shows the flow diagram of the experimental apparatus. The ozonation system included extra-dry oxygen gas generator, ozone generator, conventional ozone bubble reactor and two ozone trap reactors. OZONAIR 3.0 was used for production of pure oxygen and ozone, this initially provided ozone at flow rates ranging from 1.0 to 4.0 L min$^{-1}$ and then converted it into ozone production rate ranged from 20.0 to 150.0 mg O$_3$ min$^{-1}$. The laboratory-scale ozone bubble reactor was a cylindrical type reactor with 18.0 L hold-up volume and 15.0 L operating capacity (internal diameter of 0.11 m, height of 1.25 m), made from a polycarbonate vessel. The bottom of the reactor was equipped with gas diffusers to produce fine ozone bubbles. The outlet ozone gas concentrations were measured with ozone trap reactors. Each of them contained 2.50 L of acidified 2.0% potassium iodide solution for determination of unreacted ozone. The average characteristics of actual effluents are shown in Table 1.

Table 1
The average characteristic of: (a) actual pulp and paper mill wastewater and (b) biological treated effluents

| Parameter | (a) | (b) |
|---|---|---|
| pH | 7.5 ± 0.5 | 7.4 ± 0.5 |
| BOD (mg L$^{-1}$) | 550 ± 50 | 25 ± 5 |
| COD (mg L$^{-1}$) | 2000 ± 100 | 210 ± 10 |
| TOC (mg L$^{-1}$) | 650 ± 50 | 50 ± 5 |
| ADMI value | 1100 ± 100 | 300 ± 50 |
| BOD/COD ratio | 0.27 ± 0.01 | 0.12 ± 0.02 |
| $k$ (day$^{-1}$) | – | 0.21 |

## 2.2. Methods

In each experimental run, pulp and paper mill effluents were filtered to remove all small particles before putting into the ozone bubble reactor. The pure oxygen from oxygen generator was allowed to pass into the ozone generator and then the diffuser connecting to the bottom of ozone bubble reactor created fine bubbles in order to increase ozone mass transfer efficiency. Before the ozonation process, the pH of effluents was varied at 5.0, 7.5 and 10.0 with sodium hydroxide or sulphuric acid solution to determine the optimum pH for the process. The ozone flow rates (O/F) were at 1.0, 2.0, 3.0 and 4.0 L min$^{-1}$. For these conditions, the ozone production rates were 20.0, 50.0, 100.0 and 150.0 mg O$_3$ min$^{-1}$, respectively. The reaction temperature was fixed at 25 °C during all experiments. Unreacted ozone was taken out of the bubble column reactor through the tube into 2.0% potassium iodide solution in the ozone trap reactor where potassium iodide solution reacted with excess ozone.

The resulting iodine was titrated using standard sodium thiosulphate in the presence of starch as the indicator. The values of unreacted and reacted ozone were determined. For the period of the experiment, ozonized effluents were taken from the ozone reactor at time intervals for determination of the compounds and intermediate products by GC/MS technique. Two major pollution indicators, the true color in terms American Dye Manufactures Institute value (ADMI color value) and total organic carbon (TOC) representing the intensity of effluent pollution were also determined. The biodegradability of ozonized effluents was indicated by the individual BOD/COD ratio and utilization coefficient (k value) [16–18]. The k value, relating to biodegradability of the effluents, was calculated by Thomas slope method equation [19,20]. This method involves development of a straight line equation representing the relationship of BOD$_t$ and incubation time, t.

## 2.3. Analyses

The GC/MS analysis was performed using an HP model 5890 gas chromatograph interfacing with an HP model 5872A mass selective detector. The analytical column connecting to the system was an HP5MS capillary column (30 m × 0.32 mm internal diameter, 0.5 μm film thickness). Helium gas was used as carrier gas with the flow rate of 1.0 mL min$^{-1}$. The column temperature program was 80 °C (1 min); 80–280 °C (7 °C min$^{-1}$, hold time: 5 min). The ozonized effluents (100 mL) were acidified to pH 2.0 by HCl (1.0 N), extracted with ethylacetate (3× 40 mL) and then dried under vacuum conditions. N,O-bis-trimethylsilyl)trifluoroacetamide 100 μL and trimethylchlorosilane 100 μL were added to the organic extract and the mixture was treated at 60 °C under vacuum conditions for 5 h. The residue was redissolved in chloroform (1 mL) and analyzed by GC/MS [21].

ADMI color value was calculated by applying the Adams–Nickerson color difference formula, which substituted transmittance data into 30 wavelengths from 400 to 700 nm every 10 nm interval [22]. The absorption spectrum was determined by a Shimadzu 200 Visible-UV spectrophotometer. The

above procedure applied in this study was described in section 2120E of Standard Methods for the examination of water and wastewater [23]. TOC value, representing the mineralization of dissolved organic compounds, of effluents and ozonized effluents was measured using the Shimadzu 5000A TOC analyzer according to section 5310B [23].

The BOD/COD ratio was chosen as biodegradability indicator of the effluents. The BOD and COD were measured according to the procedures stipulated in method section 5210B and 5220C, respectively [23]. BOD kinetic of effluents was collected by HACH BOD Trak instrument conducted at 20 °C within 20 days in controlled instrument. This measured the amount of O$_2$ consumed by bacteria in the effluents. The BOD kinetic indicated general O$_2$ uptake patterns. This allowed the operator to estimate biodegradability of effluents in terms of k value.

## 3. Results and discussions

### 3.1. Identification of compounds in pulp and paper mill effluents

Fig. 2A and B shows gas chromatograms corresponding to the compounds extracted with ethyl acetate from the acidified supernatants obtained from pulp and paper mill wastewater (before being treated by biological treatment process) and treated effluents, respectively. Fig. 2A demonstrated that two groups of compounds were observed in wastewater: (1) the lignin-derived compounds and (2) aliphatic compounds used in the pulp and paper production process (i.e. n-alkanes, fatty alcohols, fatty acid and ester). Fig. 2B shows the chromatogram obtained from treated effluents indicating that several compounds previously observed in Fig. 2A were not detected in treated effluents.

Table 2 lists identities and relative abundances of the lignin-derived compounds and other compounds upon GC/MS analysis of pulp and paper mill wastewater and treated effluents. The identification labels (2), (4), (6), (7), (11), (12), (13), (15), (16), (17), (19), (25) and (26) had been oriented mainly towards the lignin-derived compounds according to their moieties standard (p-hydroxyphenyl units, guaiacyl units, and syringyl units) usually found in lignin structure [24]. Other prominent peaks (labeled (5), (8), (9), (10), (18), (22) and (27)) were n-alkanes, ester and fatty acid from aliphatic compounds. All the compounds detected in the extracts obtained from the effluent decolorized by ozone (Fig. 2C) were identified and labeled as (14), (19), (20) and (26). All these compounds decreased during the decolorization process carried out by ozone, and even compounds (8), (9), (10), (12), (24) and (25) could not be detected after ozonation time of 60 min with O/F of 4.0 L min$^{-1}$.

Relative peak areas were calculated for lignin-derived compounds and aliphatic compounds. The summed areas of relevant peaks were normalized to 100%. In pulp and paper mill wastewater, lignin-derived compounds represented 62.3% (range 60.7–65.6%) and aliphatic compounds represented 37.7% (range 34.0–40.1%) of the identified compounds. The lignin-derived/aliphatic compound ratio as calculated by GC/MS chromatogram was decreased from 0.62/0.38 to 0.54/0.46 when compared between pulp and paper mill
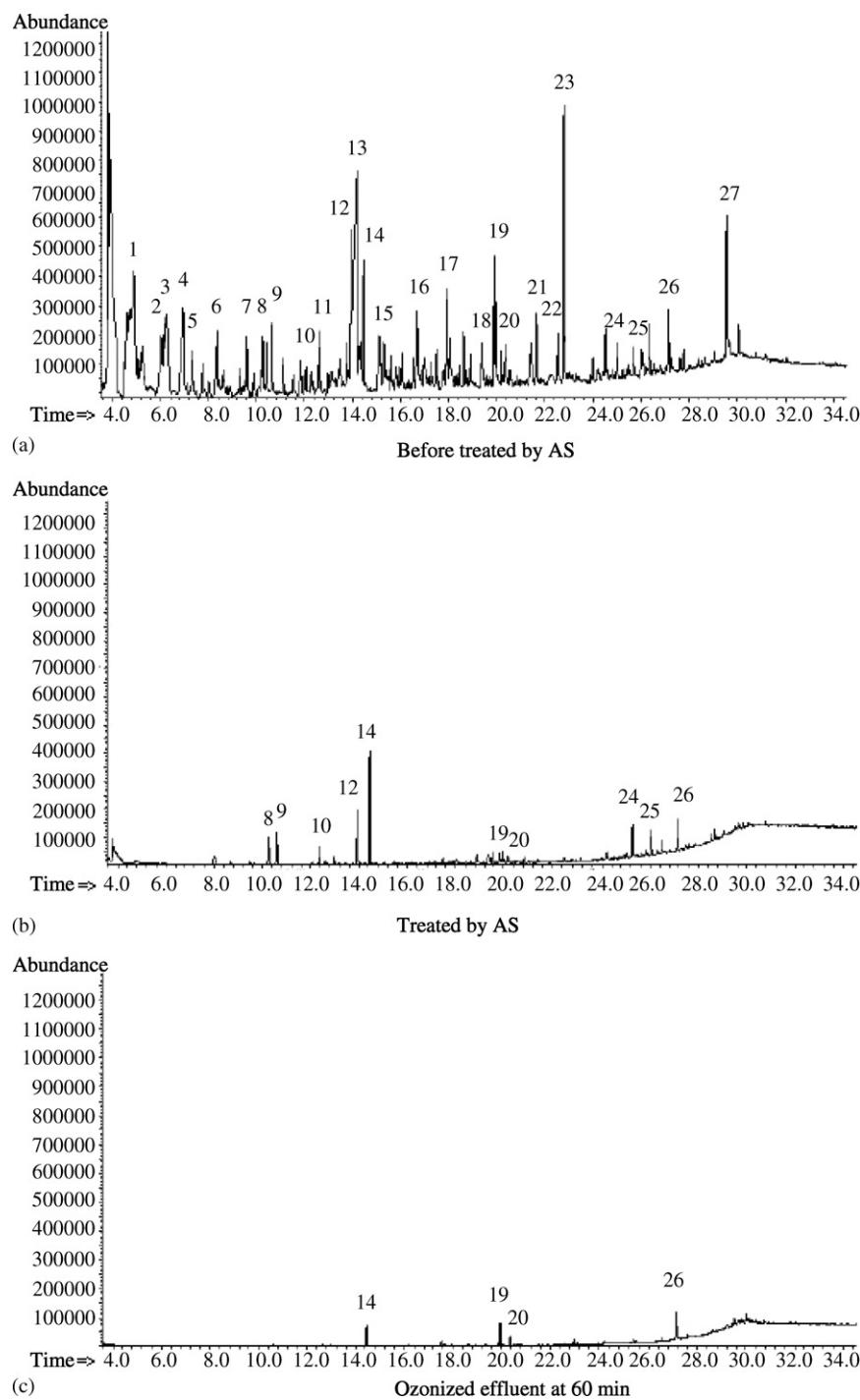
Fig. 2. GC/MS chromatogram for: (a) actual pulp and paper mill wastewater (before treated by AS), (b) pulp and paper mill effluents (treated by AS) and (c) ozonized effluents at 60 min. The correspondence between peaks and structure is shown in Table 2.

wastewater and treated effluents. The data indicated that conventional biological treatment process was able to slightly degrade lignin-derived compounds into aliphatic compounds (e.g. *n*-alkanes, fatty alcohols, fatty acid and ester). In contrast, the ozone treated effluents showed even smaller ratio between lignin-derived/aliphatic compound ratio down to only 0.28/0.72 indicating that ozone was more efficient for oxidizing lignin-derived compounds into aliphatic compounds and small degraded products resulting in decolorization of the effluents.

### 3.2. The ozone mass transfer efficiency

The effect of ozone flow rate (O/F) on ozonation process was investigated and it was clear that the ozone capacity decreased linearly with an increasing ozone concentration. The O/F affecting fluid dynamic conditions had a positive effect on the oxidation process as shown in Fig. 3. After 45 min as the initial phase, the color of 320 ADMI value (initial color concentration) was reduced by approximately 73.8%, 84.3%, 92.7% and

Table 2
The quantitative analysis of the lignin and components released upon GC/MS of pulp and paper mill wastewater and treated effluents

| Labeled number | RT (min) | Compound | Relative percentages of areas | |
| --- | --- | --- | --- | --- |
| | | | Influent | Treated by AS |
| (1) | 4.62 | Unidentified compound | 7.20 | 0.00 |
| (2) | 5.26 | 2-Furancarboxylic acid | 2.61 | 0.00 |
| (3) | 6.16 | Unidentified compound | 5.18 | 0.00 |
| (4) | 6.96 | Benzoic acid | 8.56 | 0.00 |
| (5) | 7.30 | 1-(2-Butoxyethoxy)ethanol | 2.42 | 0.00 |
| (6) | 8.36 | Phenylacetic acid | 3.25 | 5.71 |
| (7) | 9.59 | Phthalic anhydride | 2.59 | 0.00 |
| (8) | 10.26 | Isobutyl isobutyrate | 2.39 | 8.91 |
| (9) | 10.62 | Butyl butyrate | 3.47 | 9.52 |
| (10) | 12.35 | Propanoic acid | 1.03 | 4.78 |
| (11) | 12.65 | Ethanone | 2.51 | 1.88 |
| (12) | 13.91 | Isovanillic acid | 5.90 | 15.77 |
| (13) | 14.17 | Vanillic acid | 5.90 | 0.00 |
| (14) | 14.46 | Unidentified compound | 4.44 | 26.20 |
| (15) | 15.31 | Homovanillic acid | 2.69 | 0.00 |
| (16) | 16.67 | 3′,5′-Dimethoxy-4′-hydroxyacetophenone | 4.50 | 0.00 |
| (17) | 17.94 | 4-Hydroxy-3,5-dimethoxybenzoic acid | 5.18 | 0.00 |
| (18) | 19.87 | Palmitic acid | 3.98 | 3.10 |
| (19) | 19.96 | Dibutyl phthalate | 2.97 | 2.89 |
| (20) | 20.35 | Icosane | 2.26 | 2.43 |
| (21) | 21.64 | Unidentified compound | 2.23 | 0.00 |
| (22) | 22.52 | Stearic acid | 1.90 | 0.00 |
| (23) | 22.77 | *n*-Docosane | 8.69 | 0.00 |
| (24) | 25.27 | Bis(trimethylsiloxy)methylsilane | 1.39 | 8.98 |
| (25) | 25.84 | Hexamethylcyclotrisiloxane | 1.13 | 1.76 |
| (26) | 27.14 | Dioctyl phthalate | 1.69 | 8.08 |
| (27) | 29.55 | Erucamide | 3.97 | 0.00 |

96.6% for the O/F of 1.0, 2.0, 3.0 and 4.0 L min$^{-1}$, respectively.

This result was consistent with the theory of mass transfer. According to this theory, as the ozone concentration increases in the air bubbles (carrier of ozone), the driving force for transfer of ozone to the pulp and paper mill effluents increases resulting in increase of oxidation rate. The gas-phase resistance of mass transfer is negligible since ozone is slightly soluble in water. In this study, liquid side ozone volumetric mass transfer coefficient

($k_L a$) was calculated by the following Eq. (1):

$$\frac{dC_L}{dt} = k_L a(C_L^* - C_L) - k_d C_L \tag{1}$$

where $C_L^*$ is the saturated concentration of ozone in liquid phase (mg O$_3$ L$^{-1}$), $C_L$ the concentration of ozone in liquid phase at time $t$ (mg O$_3$ L$^{-1}$), $k_L a$ the volumetric mass transfer coefficient (min$^{-1}$), $k_d$ self-decomposition rate constant of ozone (min$^{-1}$), and $t$ is the ozonation time (min).
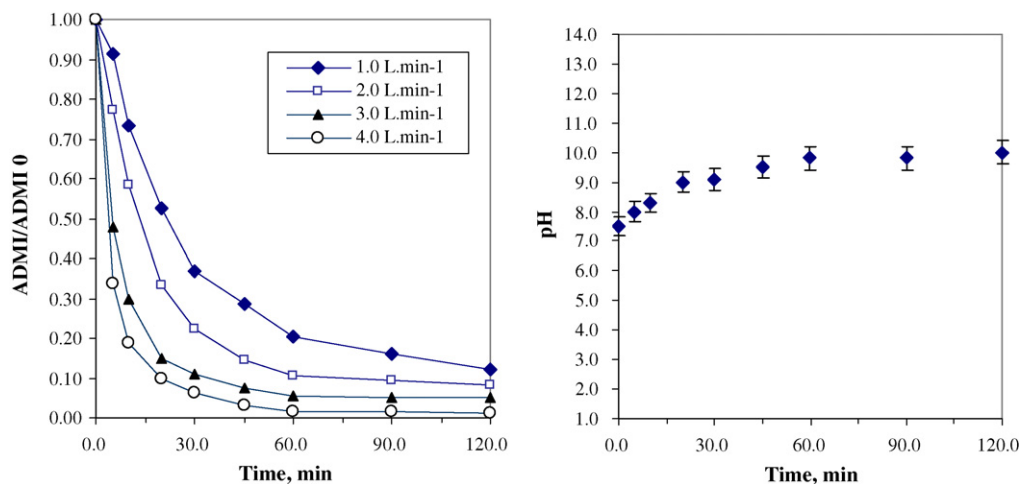


Fig. 3. Effect of ozone flow rates on the decolorization time. (Initial condition; ADMI$_0$ = 320.0 ADMI unit, pH$_{initial}$ 7.0, $T$ = 25 °C and $V$ = 15.0 L.)
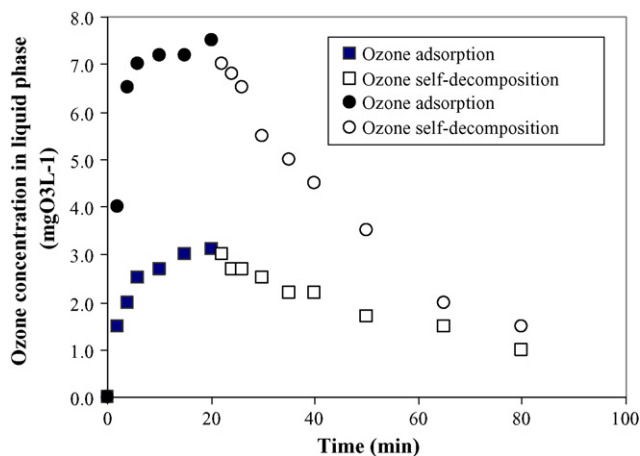
Fig. 4. Time course of ozone absorption and self-decomposition with (□) O/F = 1.0 L min⁻¹ and (○) O/F = 4.0 L min⁻¹.

To obtain the value of $k_d$ under neutral conditions, ozone gas was bubbled into reverse osmosis (RO) treated water in the conventional bubble reactor until ozone was saturated. Then, the value of $k_d$ was calculated by the decrease of ozone concentration in water with time. As shown in Fig. 4, the decrease of ozone concentration was considered as a first-order process within 80 min and the self-decomposition constant $k_d$ could be calculated from the following Eq. (2):

$$\frac{dC_L}{dt} = -k_d C_L \qquad (2)$$

Based on Eq. (2), $k_d$ was calculated as $2.2 \times 10^{-2}$ min⁻¹, which was much lower than the $k_L a$ of ozone to be derived later. The influence of $k_d$, therefore, was not taken into account in the derivation of $k_L a$. Consequently, the $k_L a$ was derived by the following Eq. (3):

$$\frac{dC_L}{dt} = k_L a(C_L^* - C_L) \qquad (3)$$

The $k_L a$ of bubble column reactor increased from 0.22 min⁻¹ at the O/F of 1.0 L min⁻¹ to 0.32, 0.44 and 0.50 min⁻¹ at the O/F of 2.0, 3.0 and 4.0 L min⁻¹, respectively. In addition, the ozone mass transfer rate was proportion to the $k_L a$ of the bubble column reactor. The enhancement of mass transfer rate of ozone from ozone bubbles to the liquid phase is attributed to the O/F as a result of: (1) eddies generated in the wake of floating bubbles and reduced the diffusion layer thickness surrounding the bubbles, and (2) increase in the gas hold up [25]. Therefore, the decolorization of effluents increased with the oxygen flow rate increase.

### 3.3. Effects of pH on decolorization and TOC removal

Since color can be attributed to many compounds in pulp and paper mill effluents, the variation of ADMI value is one of the characteristic ozonation behaviors on decolorization. More than 70.0% of color carriers were removed with ozonation time of 45 min with respect to ADMI value. Fig. 5 shows the effects of pH on ADMI value removal efficiency. The initial ADMI value
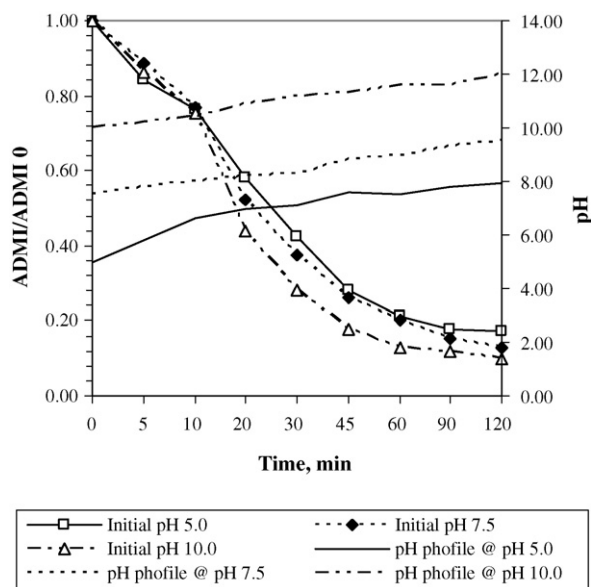
decreased from 320.0 to 55.9, 47.5 and 39.3 (O/F 1.0 L min⁻¹, ozone capacity 20.0 mg O₃ min⁻¹ in 90 min) at pH 5.0, 7.5 and 10.0, respectively. From these results, the maximum and minimum efficiencies of effluents decolorization in ADMI value were 87.7% and 82.5% at pH 10.0 and 5.0, respectively. Therefore, the pH value has a slight effect on decolorization of effluents. It is desirable to carry out the ozonation at the natural pH of effluents (range pH 7.5–8.0) therefore pH adjustment prior to ozonation is not needed. In addition, the self-purification of effluent in the water reservoir was more effective at natural pH.
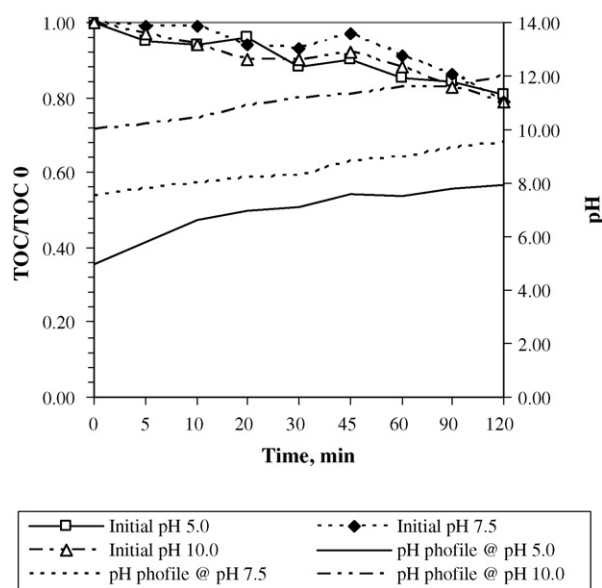


Fig. 5. Effects of pH on decolorization efficiency. (Initial condition; ADMI₀ = 320.0 ADMI unit, O/F = 1.0 L min⁻¹, Ozone capacity = 20.0 mg O₃ min⁻¹, $T$ = 25 °C and $V$ = 15.0 L.)



Fig. 6. Effects of pH on TOC removal efficiency. (Initial condition; TOC₀ = 50.0 mg TOC L⁻¹ O/F = 1.0 L min⁻¹, Ozone capacity = 20.0 mg O₃ min⁻¹, $T$ = 25 °C and $V$ = 15.0 L.)

Likewise, the pH value also slightly affected TOC removal efficiency as shown by the range of 23.33–24.6% in the value (Fig. 6). However, it was observed that both TOC and ADMI value removal efficiency increased with increasing pH due to self-decomposition of ozone into free hydroxyl radicals, which were able to oxidize the organic compounds more efficiently. As shown, the inductions of decolorization and TOC removal were in two distinct regions: (1) during the initial stage of ozonation, higher and rapid reduction efficiency occurred and (2) gradual reduction in the reduction efficiency [26,27]. For these reasons, the initial TOC removal rate was high due to high reactivity of less-complex structure compounds in the effluents towards ozone. After most less complex structure compounds were ozonized into water and carbon dioxide, the TOC removal rate became lower because the end products (i.e. oxidized compounds and $CO_2$) were released from the reaction.

The ozonation of effluents was more effective for decolorization than the TOC removal. The maximum decolorization efficiency in terms of ADMI value and TOC removal were 87.7% and 24.6%, respectively. These results were consistent with the results of El-Din et al. (2003) [28]. After the initial oxidation stage, the easily oxidizable sites became less available for further ozone oxidation. The ozone competing reaction between the remaining organic and chromophoric structures (cause of color) became more dominant. This behavior could be explained by the higher selectivity of ozone towards oxidizing the easily degradable chromophoric structures compared with the ozone selectivity towards reacting with the remaining organic structures.

## 3.4. Effects of ozonation process on biodegradability

In order to understand the biodegradability of the effluents and ozonized effluents, the experiments were conducted to determine the individual BOD/COD ratio and utilization coefficient ($k$) of effluents. The $k$ value is based on the classical first-order empirical BOD equation (Eq. (4)):

$$BOD_t = BOD_u(1 - e^{-kt}) \qquad (4)$$

where $BOD_t$ is biochemical oxygen demand at time $t$ (mg L$^{-1}$), $BOD_u$ ultimate BOD (mg L$^{-1}$), $k$ utilization coefficient (day$^{-1}$) and $t$ is the incubation time (day).

Thomas slope method involves developing a straight line equation that approximates the relationship of BOD and time
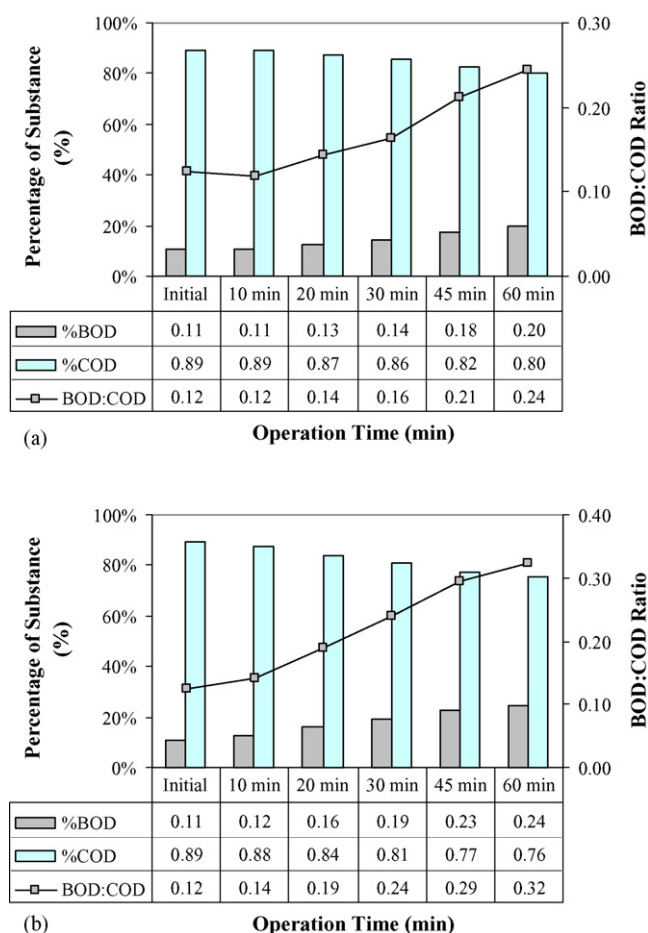


Fig. 7. The BOD/COD ratio of ozonized effluents during the ozonation time 60 min with O/F (a) 1.0 L min$^{-1}$ and (b) 4.0 L min$^{-1}$.

[29]. And by rearranging above equation, Eq. (4) becomes

$$\left[\frac{t}{BOD_t}\right]^{1/3} = (BOD_u k)^{-1/3} + \left[\frac{k^{2/3}}{6 BOD_u^{1/3}}\right] t \qquad (5)$$

During the ozonation, the effluents were sampled at time intervals for measurement of their biodegradability. The results are shown in Table 3.

The magnitude of $k$ was related to the nature of waste. The low value of $k$ indicated poor biodegradability of effluents [30]. Reported $k$ values for pulp and paper mill effluents lie between 0.15 and 0.30 [31–33]. In this study, the magnitude of $k$ increased from 0.21 day$^{-1}$ to maximum value of 0.47 day$^{-1}$ as the ozonation time was raised to 60 min with O/F 4.0 L min$^{-1}$.

Table 3
The value of calculated $k$ and BOD$_u$ in the effluents and ozonized effluents

| Ozonation time | Rearranging of classical first-order BOD equation | $R^2$ | Calculated $k$ | Calculated BOD$_u$ |
|---|---|---|---|---|
| Initial | $y = 0.0137x + 0.3982$ | 0.93 | 0.21 | 113 |
| 10 min | $y = 0.0156x + 0.3979$ | 0.99 | 0.24 | 76 |
| 20 min | $y = 0.0262x + 0.4661$ | 0.96 | 0.34 | 26 |
| 30 min | $y = 0.0293x + 0.506$ | 0.95 | 0.35 | 24 |
| 45 min | $y = 0.0326x + 0.5214$ | 0.97 | 0.38 | 19 |
| 60 min | $y = 0.0489x + 0.6199$ | 0.88 | 0.47 | 9 |

For this condition, the calculated $BOD_u$ from the first-order reaction decreased from 113 to 76, 26, 24, 19 and $9 \, mg \, L^{-1}$ during operation times 10, 20, 30, 45 and 60 min, respectively. Higher BOD/COD ratio indicated better biodegradability of the effluents. The BOD/COD ratio that increased with increasing ozonation time was fully confirmed by the $k$ value as the first-order BOD equation. The BOD/COD ratio increased from 0.10 to maximum value of 0.32 with O/F $4.0 \, L \, min^{-1}$. This means that ozone was able to oxidize the compounds yielding more biodegradable compounds. The relation of BOD/COD ratio and ozonation time are shown in Fig. 7.

From the results of biodegradability and GC/MS analysis, it is clear that most of the aromatic compounds in wastewater were difficult to be decomposed by the microorganisms used in biological treatment process. The aliphatic compounds in ozonized effluents were dominant whereas the organic acids were more susceptible to be decomposed by the microorganisms used.

## 4. Conclusions

The following conclusions can be extracted from the present work:

(1) The characteristic compounds of pulp and paper mill effluents generated in the laboratory were the lignin-derived compounds and aliphatic compounds used in the pulp and paper production process (i.e. $n$-alkanes, fatty alcohols, fatty acid and ester). The phenolic/aliphatic compound ratio as calculated by GC/MS chromatogram was decreased from 0.62/0.38 to 0.54/0.46 when compared between pulp and paper mill wastewater and biological treated effluents.

(2) The pH value slightly affected decolorization of pulp and paper mill effluents. It is desirable to carry out the ozonation at actual pH of effluents.

(3) In this study, the volumetric mass transfer coefficient $k_L a$ of conventional bubble reactor increased from $0.22 \, min^{-1}$ at O/F $1.0 \, L \, min^{-1}$ to 0.32, 0.44 and $0.50 \, L \, min^{-1}$ at O/F 2.0, 3.0 and $4.0 \, L \, min^{-1}$, respectively. Therefore, the ozone mass transfer rate was proportion to $k_L a$.

(4) With the experimental conditions, ozonation process was efficient enough to decolor pulp and paper mill effluents. Ozonation led to more than 90.0% color removal in less than 45 min. This decolorization was not always accompanied by the mineralization of the organic matters therefore ozonation was not related to TOC removal rates.

(5) The BOD/COD ratio and utilization coefficient ($k$) were studied for evaluation of biodegradability of ozonized effluents. The biodegradability increased with increasing ozonation time (the BOD/COD value increase from 0.10 to 0.32 with O/F $4.0 \, L \, min^{-1}$) and this is confirmed by the $k$ value as first-order BOD equation, which increased from $0.21 \, day^{-1}$ to a maximum value of $0.47 \, day^{-1}$.

These results show that ozonation is a promising technique for the final treatment of colored effluents from pulp and paper mills.

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