

Treatment of Refractory Organic Compounds in Treated Latex Wastewater Using Ozonation

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Abstract: Concentrated latex rubber industry is one of the major industries in the Southern region of Thailand. Typically, factories employ pond systems in series to treat large amount of wastewater which contains high organic components. However, the effluent does not meet the Thailand's effluent standards and needs to further treating by other treatment technologies that have ability to degrade the remaining contaminants that cannot be removed by the biological means. Ozonation may be the alternative treatment methods because ozone can directly react with the organic pollutants or indirectly react by hydroxyl radicals result in converting organic pollutants to low molecular weight and ultimately innocuous products such as carbon dioxide (CO₂), water (H₂O). Laboratory-scale of ozonation was conducted for experiments. Unfiltered and filtered wastewater was used and adjusted pH to about 7 prior to feed to the chamber. The experiments was varied the applied ozone dosages of 0.5:1, 1:1, and 2:1 mg O₃/mg COD. Samples were withdrawn for analysis at the contact time of 5, 15, 30, and 60 minutes, respectively. Results of the BOD₅/COD ratio of unfiltered and filtered effluent are about 0.14 and 0.10, respectively, indicating that it has substantial amounts of refractory substances that are difficult to be biodegraded. It was found that the removal efficiencies of unfiltered wastewater due to ozonation were independent of ozone dosage. On the other hands, increasing in the ozone dosage resulting in increasing removal efficiencies of ozonation for filtered wastewater.

Keywords: recalcitrant, concentrated latex rubber, ozonation, advanced oxidation technologies

NOMENCLATURE

AOTs	Advanced Oxidation Technologies
BOD ₅	Biochemical Oxygen Demand at 5 days
COD	Chemical Oxygen Demand
H ₂ SO ₄	Sulfuric acid
NH ₃	Ammonia
NO ₃ ⁻	Nitrate
O ₃	Ozone
SCOD	Soluble Chemical Oxygen Demand
SS	Suspended Solids

1. INTRODUCTION

One of the major economic goods of Thailand is rubber product. Rubber trees are planted mainly in the southern region of Thailand. Therefore, rubber factories that produce concentrated latex and skim crepe, block rubber, and smoked or non-smoked sheet rubber, are commonly found in this area of the country. Most of them generate concentrated latex rubber because it can be used as raw material for several kinds of products. Concentrated latex rubber processes employ chemicals such as NH₃, H₂SO₄ and their wastewater contain high concentration of organic matter, nitrogen, sulfate and SS. Concentrated latex factories usually use pond systems to treat their wastewater. The systems include a rubber trap and two or more of the following ponds in series: anaerobic, facultative, aerobic, and polishing. The effluent from the systems normally does not meet the Thailand's effluent discharge

standards for BOD₅ of 20 mg/L and COD of 120 mg/L. In addition, the ratio of BOD₅ to COD of the effluent is in a range of 0.13-0.30, indicating its biorecalcitrant nature [1]. It is legal for the rubber factories to retain their effluents in non-lining ponds on premises as long as there is no direct discharge into receiving waters. However, the treated wastewater in the holding pond may leach and contaminate the groundwater under and around the pond area. Groundwater is a major source of water for areas around the factories where the water supply do not services. Villagers normally pump groundwater and use it without any treatment. Furthermore, it is common that the stored effluent is flooded, especially in rainy season, and consequently causes the deterioration of water bodies. As a consequence, this effluent storage practice poses a risk to human health and the environment. There is clearly a need to further remove the pollutants from the treated latex wastewater by other treatment technologies that have ability to degrade the remaining contaminants that cannot be removed by the biological means.

AOTs, such as ozonation, can convert organic contaminants to low molecular weight organics and/or innocuous products, carbon dioxide and water. AOTs have been applied to treat the refractory species in water and to degrade recalcitrant wastewater [2]. O₃ comprises three atoms of oxygen. O₃ is an unstable, blue-colored gas with pungent odor at ambient condition. O₃ can dissolve in liquid. The solubility of O₃ in water is 12.5 times of O₂, thus O₃ can dissolve into water at more than 500 ppm and allow ozonated water saturated with O₂ after O₃ degradation [3]. O₃ is

highly unstable, thus, it must be generated on-site. O_3 can be artificially produced by several methods such as electrochemical, electrical discharge, and incorporate with UV radiation methods. In the aqueous phase, O_3 can react with contaminants in two different mechanisms, direct and indirect mechanisms as shown in Figure 1. Thus, it leads to produce the different oxidation products and needs to be controlled by different types of kinetics.

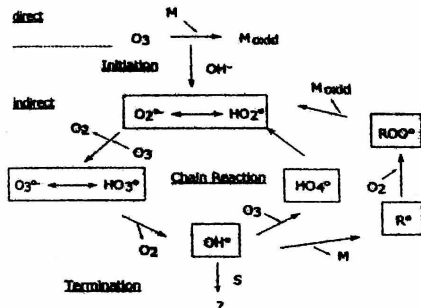


Figure 1: Mechanism of the indirect and direct ozonation, S: Scavenger, R: Reaction product, M: Micropollutants^[4]

Normally, the direct mechanism plays a major role under an acidic condition ($pH < 4$), but the indirect reaction will take place if pH is above 10. However, under normal pH ($pH \approx 7$) both reactions can occur simultaneously^[5].

2. MATERIALS AND METHODS

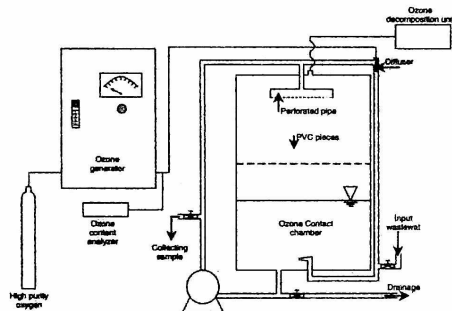


Figure 2: Schematic diagram of ozonation experimental setup

Experiments were carried out using laboratory-scale treatment systems of ozonation. Ozone gas was generated using an ozone generator (Trailgaz Inc., Model LABO-LO). High purity oxygen was used as the gas source to produce ozone gas. An ozone content analyzer (BMT MESSTECHNIK GMBH, Model BMT 964) was used for measuring the O_3 gas concentration before it was fed to the reactor. A rectangular reactor, size 37 cm $\times$ 25 cm $\times$ 68 cm

(width $\times$ depth $\times$ height), made of glass was used in this study. Diffuser, made of perforated stainless steel, was employed for distributing and mixing O_3 with wastewater. A pump was used for circulating wastewater within the reactor. Pipe inside the reactor was reduced a size as a nozzle for well mixing. A perforated pipe and PVC pieces inside the ozone contact chamber are used for distribution of O_3 and trapping the unreacted O_3 gas for efficient mixing with wastewater. The excess O_3 gas (unreacted) was collected and decomposed by an O_3 decomposition unit before emitted to ambient air. Figure 3 shows the schematic diagram of laboratory-scale of ozonation experimental setup.

3. RESULTS AND DISCUSSION

3.1 Characteristics of treated latex wastewater

The characteristics of unfiltered treated latex wastewater are shown in Table 1. The average BOD, COD, and SS concentrations of the effluent from the treatment plant are higher than the Thailand's standard for discharge (The industrial effluent standard for BOD, COD, and SS is 20, 120, and 60 mg/L, respectively). Moreover, the BOD_5/COD ratio is about 0.14 indicating that it has substantial amounts of refractory substances that are difficult to be biodegraded.

Table 1: Characteristics of unfiltered treated latex wastewater. (All units are mg/L, except for UV_{254} and soluble UV_{254} are cm^{-1})

Parameter	Concentration	
	Range	Average
COD	236-483	343 $\pm$ 108.7
SCOD	145- 261	165 $\pm$ 18.3
SS	38 -435	205 $\pm$ 138.9
BOD_5	21- 63	48 $\pm$ 16.9
UV_{254}	1.3121-2.1376	1.4629 $\pm$ 0.33104
Soluble UV_{254}	0.6685 - 0.9004	0.7244 $\pm$ 0.07361

It was observed that high variability for SS probably due to algae suspended in the final holding ponds. Therefore, treated latex wastewater was filtered through GF/C. Table 2 shows the characteristics of filtered treated latex wastewater. It was found that BOD_5/COD ratio is about 0.10 suggesting that the dissolved organic species are more biorecalcitrant than the non-dissolved organic species.

Table 2: Characteristics of filtrated treated latex wastewater. (All units are mg/L)

Parameter	Concentration	
	Range	Average
COD	140 -152	145 $\pm$ 5.8
BOD_5	10.5 - 22	15 $\pm$ 5.7
NO_3^-	145 - 157	151 $\pm$ 5.1

Due to the fluctuate of the initial concentration of the influent, therefore to investigate performances of AOTs, all parameter values were normalized using the equation of

$$\text{Normalized value} = \frac{\text{Concentration at time } t (C_t)}{\text{Initial concentration } (C_i)}$$

A statistical software named SPSS (Statistical Package for Social Science) for windows version 11.5 was used for analyzing data. A confidence interval at 95% (or significant level at 0.05) was used.

3.2 Performances of ozonation

3.2.1 Unfiltered wastewater

Figure 3 shows normalized SS of unfiltered wastewater.

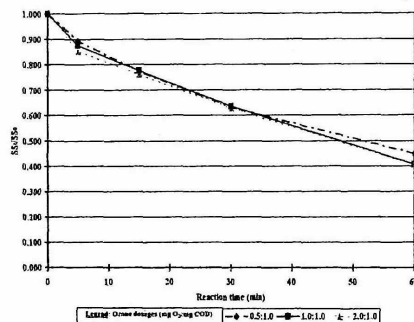


Figure 3: Normalized SS of unfiltered wastewater at the ozone dosages and reaction times tested. (Initial concentration of SS is 205 mg/L)

It appears that SS decreased rapidly with increasing reaction time. Removal efficiencies (1-normalized SS) of each ozone dosage are not significantly different ($P > 0.05$) indicating the SS removal was independent of ozone dosage. Ozone is used as preozonation ahead of particle removal units in water work, however, the applications of particles removal in wastewater were not found in literatures. Mechanisms involved in preozonation are quite complicated however; some mechanism can be used to explain. Ozonation can decrease the molecular weight and increases in hydrophilicity lead to solubilize to dissolved parts^[6]. Therefore, decreasing of SS can be resulting from changes of particle properties which lead to more hydrophilic and when it was dissolved either ozone or intermediate oxidants can play a role to oxidize it. The products of the degradation were probably both CO_2 and low molecular weight dissolved organics.

The normalized COD of unfiltered wastewater at the ozone dosages and reaction times tested is shown in Figure 4.

At the reaction time of 60 minutes, the COD removal efficiencies of the dosage of 0.5:1.0, 1.0:1.0, and 2.0:1.0 mg O_3 :mg COD are 27.8, 27.8, and 28.1%, respectively. Statistical test shows that the COD removal efficiencies of all three dosages are not different significantly ($P > 0.05$). Similar to the normalized SS result, COD removal increases with reaction time and was not dramatically affected by the ozone dose. When ozone applied to water, ozone can react with substrates directly or indirectly by radical intermediates which form when ozone decomposes in

water. Gottschalk^[4] stated that the direct mechanism plays a major role under an acidic condition ($\text{pH} < 4$), but the indirect reaction will take place if pH is above 10, however under normal pH ($\text{pH} \approx 7$) both reactions can occur simultaneously. Thus, both direct oxidation by ozone or indirect oxidation by intermediated oxidants can simultaneously play their role in order to remove organic refractory compounds in wastewater.

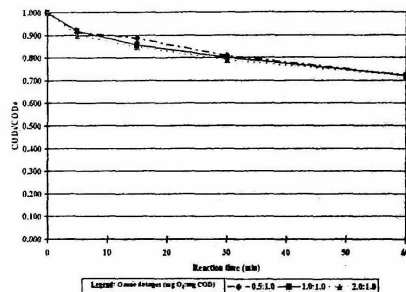


Figure 4: Normalized COD of unfiltered wastewater at the ozone dosages and reaction times tested. (Initial concentration of COD is 343 mg/L)

As shown in Figure 5, which a plot of soluble COD and reaction time. SCOD decreased about 10% during the first 5 minutes of the reaction time, same trend as COD. However, it increased about 30% proportionally between 5 and 60 minutes resulting in 20% net enhancement at 60 minutes. Removal efficiencies of SCOD were compared to not significantly different. Algae in wastewater may also solubilized by ozone. However, the algae cells are not destroyed at the low dosages required^[4]. Therefore, increasing in SCOD concentration after the first 5 minutes of the reaction time resulted from degradation of SS.

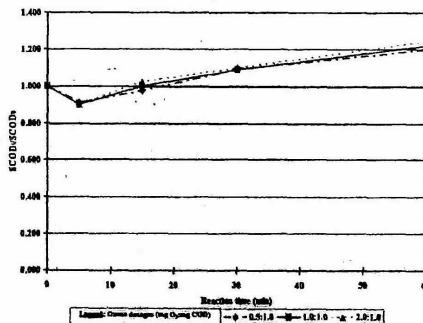


Figure 5: Normalized SCOD of unfiltered wastewater at the ozone dosages and reaction times tested. (Initial concentration of SCOD is 165 mg/L)

Figure 6 illustrates the normalized BOD_5 of unfiltered wastewater at the ozone dosages and reaction times tested. About 60% of BOD_5 was

enhanced during the first 5 minutes of the reaction time but it decreased after that to about net 3 to 13% removal at the reaction times of 30 and 60 minutes where the removal was not significantly different ($P > 0.05$). The partial oxidation of refractory organic compounds by direct or indirect oxidation results in increasing the BOD₅ values during the first 5 minutes of the reaction time. Direct oxidation by ozone is a selective mechanism and slow rate compared with indirect oxidation by hydroxyl radicals. Reaction between hydroxide ions and ozone leads to the formation of superoxide anion radical ($O_2^{\cdot -}$) and hydroperoxyl radical ($HO_2^{\cdot}$) which can be further decomposes immediately into $OH^{\cdot}$ radical. $OH^{\cdot}$ radical acts as a promoter to promote the chain reaction which can oxidize organic molecules. The intermediate species of organic molecules can also act as promoters and further react with other molecules^[4]. Therefore, these mechanisms can lead to decrease in BOD₅ concentration after the first 5 minutes of the reaction time. However, the BOD₅ removal efficiencies of all three dosages remained constant after the reaction was take place about 30 minutes. It was maybe due to some intermediate species react with $OH^{\cdot}$ and form secondary radicals which do not produce $HO_2^{\cdot}/O_2^{\cdot -}$. These inhibitors (or scavengers) generally terminate the chain reaction and inhibit ozone decay. $OH^{\cdot}$ itself can also react with $HO_2^{\cdot}$ to form oxygen and water which is terminated the chain reaction^[4].

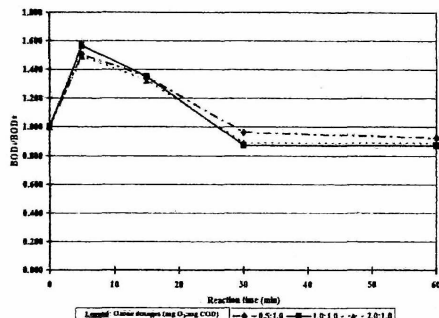


Figure 6: Normalized BOD₅ of unfiltered wastewater at the ozone dosages and reaction times tested. (Initial concentration of BOD₅ is 48 mg/L)

The normalized UV₂₅₄ of unfiltered wastewater at the ozone dosages and reaction times tested is presented in Figure 7. UV light is known to be preferentially adsorbed by unsaturated chemical bonds. UV absorbance at 254 nm provides some molecular information about the structure of the organic matter. Gradual reduction of UV₂₅₄ with reaction time was observed indicating that ozone and/or $OH^{\cdot}$ broke down UV absorbing compounds, unsaturated and aromatics organics, to non UV absorbing compounds, less refractory saturated molecules. Like the other results presented above,

increasing the ozone dose had no apparent benefit on the removal due to there are no statistically significant.

Figure 8 shows the normalized soluble UV₂₅₄ of unfiltered wastewater at the ozone dosages and reaction times tested.

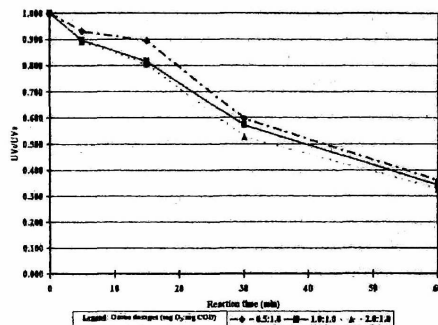


Figure 7: Normalized UV₂₅₄ of unfiltered wastewater at the ozone dosages and reaction times tested. (Initial concentration of UV₂₅₄ is 1.4629 cm⁻¹)

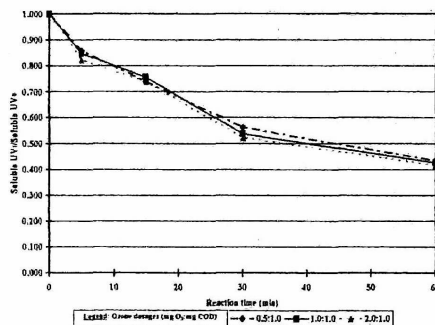


Figure 8: Normalized soluble UV₂₅₄ of unfiltered wastewater at the ozone dosages and reaction times tested. (Initial concentration of soluble UV₂₅₄ is 0.7244 cm⁻¹)

It appears that soluble UV₂₅₄ decreased quite linearly with increasing reaction time. It may indicate that soluble UV absorbing compounds, soluble unsaturated and soluble aromatics organics were broken down by ozone and/or $OH^{\cdot}$ to non UV absorbing compounds, less refractory saturated molecules. Similar to the normalized UV₂₅₄ result, soluble UV₂₅₄ removal increases with reaction time and was not dramatically affected by the ozone dose ($P > 0.05$).

3.2.2 Filtered wastewater

The graph of normalized COD of filtered wastewater at the ozone dosages and reaction times tested is shown in Figure 9.

The COD removal efficiency at the reaction time of 60 minutes of ozone dosage at 2.0:1.0 was about 55% while that at 1.0:1.0 was approximately 40%. These efficiencies were higher than the efficiencies for unfiltered wastewater at the same conditions. When there was no SS in the wastewater, ozone and/or $\text{OH}^\bullet$ were more available for the reaction with dissolved organics. The COD removal efficiency at the reaction time of 60 minutes of dosage of 2.0:1.0 shows the significant different COD removal efficiency at dosage of 1.0:1.0 ($P < 0.05$). Ozone reacts promptly with the portion of dissolved in wastewater. Lidia^[7] reported that removal of colloids and SS leads to increasing in COD removal efficiency. Therefore, it can be concluded that the ozone dose affected the COD removal efficiency; the higher dose provided more removal efficiency.

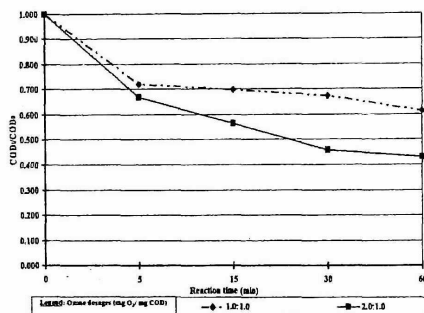


Figure 9: Normalized COD of filtered wastewater at the ozone dosages and reaction times tested. (Initial concentration of COD is 145 mg/L)

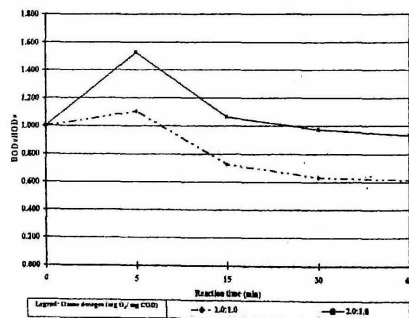


Figure 10: Normalized BOD₅ of filtered wastewater at the ozone dosages and reaction times tested. (Initial concentration of BOD₅ is 15 mg/L)

Figure 10 illustrates the normalized BOD₅ of ozonation of the filtered wastewater at the ozone dosages and reaction times tested. The normalized BOD₅ at the ozone dosage of 2.0:1.0 exhibited a similar trend as for the unfiltered wastewater. However, BOD₅ increase in the first 5 minutes was much less and higher BOD₅ removal efficiency was observed at the reaction time of 60 minutes when the dosage of 1.0:1.0 was applied (39% versus 8%). It was probably due to when refractory organic compounds were oxidized at a high dose (as compared with BOD₅ concentration) it may result in the formation of intermediates that difficult to degrade by microorganisms. This result was confirmed by the previous studies of Gilbert^[8] which reported that the ozonation of aromatic compounds can lead to formation of primary intermediates difficult to degrade biologically. Beltran^[9] also observed that a large ozone dose could lead to a decrease of the BOD because of the oxidation of biodegradable compounds results in the decrease of the biological treatment efficiency. Moreover, Scott and Ollis^[10] noted that an overdose of the chemical oxidation may result in highly oxidized products with a little metabolic value for microbes and in an excessive cost.

Figure 11 shows the graph of normalized nitrate and reaction time. Nitrate remained relatively constant throughout the ozonation at both doses. This indicates that ammonium was not oxidized to nitrate and did not compete with organics in wastewater for the oxidants. This agree with the previous studies which reported that with pH ranges between 7-8 the reactions of ammonia with ozone is so low that it may be regarded as insignificant. Only when the pH is increased to values above 9.0, ozone oxidizes ammonia at a reasonable rate^[11].

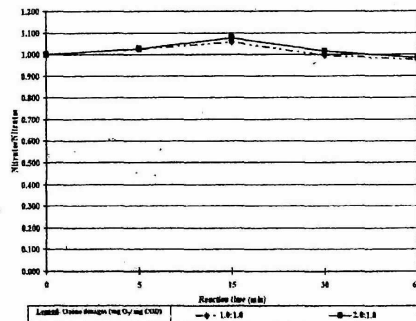


Figure 11: Normalized NO₃⁻ of filtered wastewater at the ozone dosages and reaction times tested. (Initial concentration of NO₃⁻ is 151 mg/L)

4. CONCLUSION

Removal efficiencies of unfiltered wastewater were independent of ozone dosage. Removal mechanism of SS is the changes in particle properties

lead to more solubilize. Algae may also solubilized, however, it needs high ozone dosage to break algae cell wall. Therefore, increasing in SCOD resulting from decreasing of SS in wastewater. Refractory organic compounds were degraded either direct oxidize by ozone or indirect oxidize by the intermediate oxidants. This result confirmed by the decreasing of UV₂₅₄ which indicated that absorbing compounds, soluble unsaturated and soluble aromatics organics were broken down by ozone and/or OH[•] to non UV absorbing compounds, less refractory saturated molecules. Results found that in the absence of SS, the increasing of COD removal efficiency was obtained and higher removal efficiency can achieved at high ozone dosage. However, when applied a high ozone dosage, it may resulting in the formation of intermediates that difficult to degrade by microorganisms. Ammonia in wastewater was not competing with carbonaceous organic substances to oxidize with O₃/OH[•] to nitrate.

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