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THESIS

TREATMENT OF FIRE EXTINGUISHER WASTEWATER BY OZONATION

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Wastewater generated from the Emergency Response Training Center contains burnt Kerosene Oil with foam. The wastewater was found to contain varying amounts of BOD_5 (2,010 – 3,090 mg/L), and COD (4,743 – 11,410 mg/L). In all cases, these were higher than Industrial Effluent Standards for Factory Group II and III set by Thailand Pollution Control Department, and should be managed before disposal. Ozonation was found to be an appropriate and effective method for treating wastewater containing hydrocarbons.

This study examined the treatment of fire extinguisher wastewater using ozone. Wastewater was collected from the training site and treated with the ozone in one litre semi-batch reactors. BOD_5, COD and FOG were analysed. The results from the ozonation experiment of Fire Extinguisher Wastewater (FEW) showed that ozone reacted on organic contaminants. Wastewater (at pH 7) was found to be the most favourable condition for BOD, COD and FOG removal. The experiment at pH 7 with 18 hours of contact time (16,757 mgO_3/L) showed that 90% BOD could be removed. No ozone was detected in the off-gas outside the system. The highest COD and FOG reductions (86% and 67% respectively) were also achieved at this condition. However, the optimum condition of ozone treatment was found within the early stage (2 hours of treatment or 1,862 mgO_3/L). The biodegradability, as indicated by BOD_5/COD, was improved mostly at pH 7 from 0.2 to 0.6. The wastewater ozone-consumption rate was determined by the amount of ozone used in COD reduction. The ozone consumption rate at pH 7 of fire extinguisher wastewater was the highest, with a ratio change from 0.25 to 1.72 $mgO_3/mgCOD$.

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Student’s signature Thesis Advisor’s signature

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LIST OF ABBREVIATIONS

AFFF = Aqueous Film Form Foam (extinguishing agent)
AOS = Advanced Oxidation System
APHA = American Public Health Association
AWWA = American Water Works Association
BOD = Biological Oxygen Demand
BOD/COD = Ratio of Biological Oxygen Demand to Chemical Oxygen Demand
BTEX = Benzene, Toluene, Ethylbenzene, and Xylenes
COD = Chemical Oxygen Demand
CT = Contact Time
CTEP = Chevron Thailand Exploration and Production, Ltd.
DCP = Dry Chemical Powder (extinguishing agent)
ERTC = Emergency Response Training Center
FEW = Fire Extinguisher Wastewater
FOERTL = Further Offshore Emergency Response Team Leader 2 days course
FOERTM = Further Offshore Emergency Response Team Member 2 days course
FOG = Fat, Oil and Grease
HPLC = High Performance Liquid Chromatography
MSW = Municipal Wastewater
N = Normality
OERTL = Offshore Emergency Response Team Leader 4 days course
OERTM = Offshore Emergency Response Team Member 5 days course
OHETM = Offshore Helideck Emergency Team Member 1 day course

LIST OF ABBREVIATIONS (Continued)

OHETM = Offshore Helideck Emergency Team Member 1 day course

PAH Polycyclic Aromatic Hydrocarbon

PCB Polychlorinated Biphenyl

PCC = Pollution Control Committee

PCD = Pollution Control Department

SOM = Soil Organic Matter

SS = Suspended Solids

TBOSIET = Tropical Basic Offshore Safety Induction and Emergency Training 3 days course

TDS = Total Dissolved Solids

T-FOET = Tropical Further Offshore Emergency Training 2 days course

TKN = Total Kjedahl Nitrogen

THMs = Trihalomethanes

TOC = Total Organic Carbon

TS = Total Solids

UV = Ultraviolet

WW = Wastewater

TREATMENT OF FIRE EXTINGUISHER WASTEWATER BY OZONATION

INTRODUCTION

The Emergency Response Training Center (ERTC), a fire training school of Chevron Thailand Exploration and Production Co., Ltd. (CTEP) located in Songkhla Province, provides firefighting training programs throughout the year, which produces fire extinguisher wastewater (FEW) daily. The wastewater consists of groundwater, burnt Kerosene oil (C12-C15 hydrocarbon), fire extinguisher foam and dry chemical solution. In other words, the wastewater's main compositions are Polycyclic Aromatic Hydrocarbon (PAH), burnt oil, and foam that come from firefighting activities. Hydrocarbon contaminants in wastewater are the products of incomplete combustion. A variety of chemicals used in theses training programs affect the characteristics of the wastewater. The chemical structures of the contaminants differ in number and placement of hydrocarbon chains due to variation in combustion conditions each day.

There are many activities and training courses conducted at the ERTC, at different times of the day. The ERTC is responsible for all the firefighting courses for the company. These training courses can be catalogued into the following classes:

1.1 T-BOSIET, Tropical Basic Offshore Safety Induction and Emergency Training, a basic training for firefighting in small scales such as kitchen fires, and fire from carbon based sources. All workforces need to complete this course before starting work. The length of this course is 3 days.

1.2 T-FOET, Tropical Further Offshore Emergency Training, a refresher course of T-BOSIET that all offshore workforce need to attend every 2 calendar years. The length of this course is 2 days.

1.3 OERTM, Offshore Emergency Response Team, is an advanced firefighting course that requires 5 days to complete. Selected personnel who have special firefighting skill will be nominated to attend this course. The types of fires evaluated include: large scale kitchen fire, temperature induced hot oil fire from machines, fire from chemical substances, fire in confined spaces, etc. The attendants will be able to fight larger scale fires at offshore remote platforms.

1.4 FOERTM, Further Offshore Emergency Response Team Member, a refresher course of OERTM that nominated personnel need to attend every 2 calendar years. The length of this course is 2 days.

1.5 OERTL, Offshore Emergency Response Leader, an advanced firefighting course that requires 4 days to complete. This course is provided to personnel who have passed the OERTM course to learn more about firefighting and to be able to lead the firefighting response.

1.6 FOERTL, Further Offshore Emergency Response Team Leader, a refresher course of OERTL that selected personnel need to attend every 2 calendar years. The length of this course is 2 days.

1.7 OHETM, Offshore Helideck Emergency Team Member, a firefighting course for fire incident related to helicopter activities. Radio Operators and Flight Dispatchers are required to attend this training course. The length of this course is 1 day.

Normally, the extinguisher wastewater produced in these classes is diluted with municipal wastewater to reduce concentration of organic contaminants such as BOD, COD, TOC and FOG before being discharged (characteristic of ERTC wastewater can be found in literature review section). The most difficult constituents to be treated in the wastewater from the training are the oily components from foam extinguishers. Highly concerned about Thailand’s environmental regulations, the company has tried to find an optimum alternative for wastewater treatment.

The company has evaluated many approaches to treat the wastewater for 8 years trying to find the best alternative but the decision is still deferred. Because the company has a plan to move the ERTC to a new location within 5 years, the company has to find a new method to treat wastewater. The desirable treatment alternatives for this new methodology should meet the following criteria:

1. High Efficiency to treat the wastewater
2. Does not create a new highly toxic waste from the process
3. Low capital cost
4. Low maintenance and operating cost
5. Mobile or can be moved to another location
6. Easy to operate

From the constraints listed above, Activated Sludge was proposed and studied. However, after cost calculations, it shows that costs are extremely high as many chemical substances are needed. Also, the Activated Sludge tank must be permanently fixed at the particular location restricting the mobility issue. Moreover, Activated Sludge needs well-trained personnel to maintain the tank. All of these inconveniences require that a new proposed approach. One alternative treatment is ozonation.

Research on the treatment of different types of organic compounds by ozonation has already been conducted. Several researchers found ozonation an appropriate and effective way for treating wastewater containing hydrocarbons (Majumdar, 1973). However, the different types of wastewater containing various chemical compounds react differently under diverse conditions. In general, ozone could be applied to wastewater at different stages of treatment with variation in the required dosages (Langlais *et al*., 1992).

Wastewater treatment by ozonation is widely used; however, information on the efficiency of the ozonation for eliminating certain specific pollutants present in wastewater was necessary to determine. In this study, fire extinguisher wastewater was treated by ozonation with the main objectives to determine the effects of ozone dosage and pH condition (acid – pH 3, neutral – pH 7 and base – pH 13) on the changes in organic contaminants.

According to the Pollution Control Department (PCD) wastewater discharge standard, BOD_5 of Industrial Effluent Standards discharged must not exceed 20 mg/l, COD must not exceed 120 mg/l and FOG must not exceed 5.0 mg/l. (Appendix F: Standard for discharge wastewater from industrial plant and industrial estate set by Thailand Pollution Control Department).

OBJECTIVES

The main objectives of this research study are as follows:

1. To determine effect of ozone dosage on the ozonation of wastewater from ERTC, parameters of interest were BOD, COD, TOC and FOG.

2. To find the optimum condition for ozonation of wastewater in a batch reactor.

Scope of study

The scope of the study is listed below:

1. Wastewater from Emergency Response Training Center (ERTC), Chevron Thailand Exploration and Production, Ltd. was used in the study.

2. Semi batch treatment was conducted in laboratory scales.

3. Ozone generator used atmospheric air as oxygen supply.

4. Ozonation treatment was performed at Songkhla Laboratory using the 1 litre reactor.

5. Ozo-MAC, CW 300 L Ozone generator with production capacity 300 mg/hour ozone generation was used in the study.

LITERATURE REVIEW

1. ERTC wastewater characteristics

At the Chevron Thailand Exploration and Production Co., Ltd. (CTEP) training school (ERTC), a variety of chemicals are used in the training programs. Table 1 shows the chemicals and quantities used at the training center for each training course.

Table 1 Chemical used at fire training school at various training days

Training Courses	Day 1		Day 2		Day 3		Day 4	
	Chemical	Amount	Chemical	Amount	Chemical	Amount	Chemical	Amount
TBOSIET	-	-	-	-	Jet Fuel AFFF 3% DCP	100 Litres 1 Litre 40 Kg.	-	-
TFOET	-	-	Jet Fuel AFFF 3% DCP	100 Litres 1 Litre 40 Kg.	-	-	-	-
OERTM	Jet Fuel AFFF 3% DCP	100 Litres 20 Litres 50 Kg.	Jet Fuel	10 Litres	Jet Fuel AFFF 3%	600 Litres 150 Litres	Jet Fuel	200 Litres
FOERTM	Jet Fuel AFFF 3%	10 Litres 50 Litres	Jet Fuel AFFF 3%	800 Litres 150 Litres	-	-	-	-
OERTL	-	-	Jet Fuel	310 Litres	Jet Fuel AFFF 3%	300 Litres 150 Litres	Jet Fuel AFFF 3%	50 Litres 1 Litre
FOERTL	Jet Fuel AFFF 3%	700 Litres 100 Litres	Jet Fuel AFFF 3%	60 Litres 1 Litre	-	-	-	-

Table 1 (Continued)

Training Courses	Day 1		Day 2		Day 3		Day 4	
	Chemical	Amount	Chemical	Amount	Chemical	Amount	Chemical	Amount
OHETM	Jet Fuel AFFF 3%	200 Litres 200 Litre.	-	-	-	-	-	-

Remarks: AFFF = Aqueous Film Form Foam (extinguishing agent)
DCP = Dry Chemical Powder (extinguishing agent)

Source: (Feasibility study by Envire Operation Co, Ltd., 2007).

The ERTC wastewater characteristics, studied by Envirotech Co, Ltd. were measured in 2005-2006 and varied by different activities. At the time ERTC had the highest training activities, the ERTC wastewater contained high organic contents with BOD of 2,340 mg/L and COD = 5,775 mg/L. The lowest BOD from the activities was 50 mg/L and COD was 132 mg/L.

The characteristic of wastewater in different training days and different training activities from various sample points in ERTC are shown in Table 2 (15 December 2005), Table 3 (16 February 2006) and Table 4 (17 February 2006).

Table 2 Characteristic of wastewater from ERTC (15 December 2005)

Sample Name	Characteristic of Wastewater				
	pH	BOD	COD	SS	FOG
Wastewater in Tank Storage No. 1 before firefighting activities	6.15	750	906	415	80
Wastewater in Tank Storage No. 2 before firefighting activities	5.78	900	1171	405	177
Wastewater in Tank Storage No. 1 after firefighting activities	6.04	1020	1473	1050	1975
Wastewater in Tank Storage No. 2 after firefighting activities	5.99	390	906	215	74
Raw WW after First Training (morning)	6.83	540	1010	20	493
Raw WW after Second Training (afternoon)	6.38	1128	3821	35	393
Wastewater from maintenance shop and utility wastewater	5.63	29	83	12	<0.33

From Table 2, it can be seen that the raw wastewater collected after the training course in the afternoon contained the highest BOD at 1,128 mg/L. Also, the highest COD was found from this wastewater at 3,821 mg/L. The highest suspended solid was 1,050 mg/L; found from the wastewater in the tank storage number 1 after firefighting activities. The highest FOG was also found at this station at 1,974.5 mg/L. It can be concluded that the firefighting activities changed the characteristic of wastewater by adding hydro carbonated wastewater into ERTC water storage tanks.

Table 3 shows the characteristic of wastewater from ERTC on 16 February 2006. During that day, there were two firefighting activities conducted at the center. The first activity (Activity 1) was the firefighting that had oil as fuel. The second activity (Activity 2) was the firefighting that had gas as fuel. Organic content analyses show that Activity 1 generated wastewater with a higher organic content than Activity 2, which had BOD (129 vs 50 mg/L), COD (314 vs 132 mg/L), SS (16 vs 9 mg/L) and FOG (51 mg/L vs undetected).

Table 3 Characteristic of wastewater from ERTC (16 February 2006)

Sample Name	Characteristic of wastewater				
	pH	BOD	COD	SS	FOG
Activities 1 oil firefighting	6.42	129	314	16	51
Activities 2 gas firefighting	6.90	50	132	9	Undetected

Table 4 shows the characteristic of wastewater from ERTC on 17 February 2006 (the following day). During this day, there were four firefighting activities as follows:

Activity 1 and Activity 4 were firefighting that used kerosene oil as fuel and used water to extinguish the fire.

Activity 2 was the firefighting that used oil as fuel and used dry chemical to extinguish the fire. The dry chemical reacted with oil and generated the foam-like liquid.

Activity 3 was the firefighting that used gas as fuel and used water to extinguish the fire.

Activity 2 generated wastewater with the highest BOD (2,340 mg/L), COD (5,775 mg/L), SS (110 mg/L) and FOG (120 mg/L). Due to the reaction between the oil and dry chemical, foam that contained high organic carbon content was generated. The wastewater from the maintenance shop and utilized wastewater had the lowest BOD (205 mg/L) and FOG (0.57 mg/L) because the wastewater in the maintenance shop was diluted with water before discharge.

Table 4 Characteristic of wastewater from ERTC (17 February 2006)

Sample Name	Characteristic of wastewater				
	pH	BOD	COD	SS	FOG
Activity 1: oil firefighting	5.83	108	383	24	28
Activity 2: foam firefighting	5.87	2340	5775	110	120
Activity 3: gas firefighting	5.85	371	843	37	4.6
Activity 4 oil firefighting (2 training)	5.71	206	753	27	63
Maintenance shop water and utility wastewater	6.32	205	607	26	0.57

Currently, FEW is treated by diluting with water before being discharged into the public water system. However, it could be seen from Table 4 that wastewater from the maintenance shop and utility contained high organic contents. In conclusion, wastewater characteristics from the firefighting activities in ERTC contain high organic contents which need to be treated.

The company has been looking for an effective solution to treat ERTC wastewater for 8 years. Researches on the treatment of FEW, including aerobic digestion, anaerobic digestion, chemical treatment, screening, etc., were already conducted. However, after testing many approaches, the company has not found a successful method to treat the ERTC wastewater economically and reliably. The company is still looking for the treatment procedure for FEW from ERTC.

Oller *et al*. (2011) presented a review on the advanced oxidation processes in treatments of various types of wastewater. It was found that an advanced oxidation process, such as ozonation, was a highly competitive wastewater treatment technology for the removal of recalcitrant organic pollutants. The results of this study can be the starting points for ozonation on FEW.

2. Standard for pollution industrial wastewater discharge set by Pollution Control Department (PCD)

To evaluate the effectiveness of ERTC wastewater treatment, the Pollution Control Department (PCD) standards will be used. PCD set the following standards regarding wastewater from Industrial Plants: BOD_5 must not exceed 20 mg/l, COD must not exceed 120 mg/l and FOG must not exceed 5.0 mg/l. (Appendix F: Thailand Pollution Control Department Discharge Wastewater Standard from Industrial Plant and Industrial Estate). Table 5 is the summary of the wastewater discharge standard for Industrial Plants set by Pollution Control Department (PCD) which will be the target number to compare the efficiency of ozonation.

Table 5 Standards for industrial wastewater discharge set by Pollution Control Department (PCD)

Organic Contents	TPCD Standards
BOD_5 (mg/L)	20
COD (mg/L)	120
FOG (mg/L)	5

3. Wastewater biochemical oxygen demand and chemical oxygen demand

Any oxidizable material present in a natural body of water, or in industrial wastewater, will be oxidized by biochemical (bacterial) or chemical processes. This results in a decrease of oxygen content in the water. The reaction for biochemical oxidation may be written as:

$$\begin{array}{lcl} \text{Oxidizable material + bacteria} & \rightarrow & CO_2 + H_2O + \text{oxidized inorganics} \\ + \text{ nutrient} + O_2 & & \text{such as } NO_3 \text{ or } SO_4 \end{array} \quad (1)$$

Oxygen consumption by reducing chemicals such as sulfides and nitrites is shown as follows:

$$S^{--} + 2\,O_2 \rightarrow SO_4^{--} \quad (2)$$

$$NO_2^{-} + \tfrac{1}{2}\,O_2 \rightarrow NO_3^{-} \quad (3)$$

Oxygen required for the above reactions can be measured using the form of BOD and COD. Both the BOD and COD tests are a measure of the relative oxygen-depletion effect of a waste contaminant. Both have been widely adopted as a measure of pollution effect. The BOD test measures the oxygen demand of biodegradable pollutants whereas the COD test measures the oxygen demand of biodegradable pollutants plus the oxygen demand of non-biodegradable oxidizable pollutants.

The so-called 5-day BOD measures the amount of oxygen consumed by biochemical oxidation of waste contaminants within a 5-day period. The total amount of oxygen consumed when the biochemical reaction is allowed to proceed to completion is called the Ultimate BOD. The Ultimate BOD is too time-consuming, so the 5-day BOD has almost universally been adopted as a measure of relative pollution effect.

There are also many different COD tests. Perhaps the most common is the 4-hour COD – specifically, the Reflux Method using a strong oxidizing agent, such as K_2CrO_7 or $KMnO_4$.

It should be emphasized that there is no generalized correlation between the 5-day BOD and the Ultimate BOD. Likewise, there is no generalized correlation between BOD and COD. It is possible to develop such correlations for a specific waste contaminant in a specific wastewater stream; however, such correlations cannot be generalized for use with any other waste contaminants or wastewater streams. (Sawyer *et al.* 2003)

4. Ozonation

4.1 Ozone Properties

Ozone (O_3) molecules consist of three oxygen atoms. It’s formation and molecular structure are shown in Figure 1. Ozone is an unstable gas produced when oxygen molecules dissociate into atomic oxygen (O) then react with an oxygen molecule (O_2). A blue gas at normal room temperatures with a distinct odor, Ozone is a powerful oxidant and readily reacts with most toxic organics. Most of the reaction products are less toxic and many are biodegradable. The aim of ozone oxidation is to break down complex compounds into simple products prior to entering biological treatment.
(http://water.me.vccs.edu/courses/ENV149/ozonation.htm)

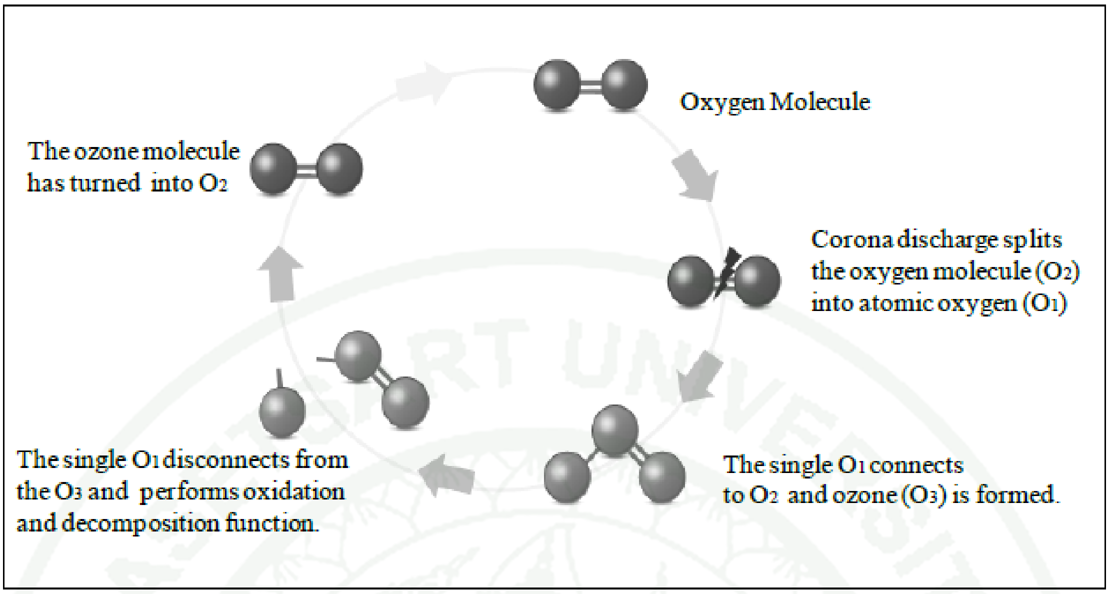


Figure 1 Ozone formation and molecular structure of ozone

The properties of ozone are summarized in Table 6.

Table 6 Properties of ozone

Properties	Unit	Values
Molecular weight	g	48.0
Boiling point	°C	-111.9
Melting point	°C	-192.5
Latent heat of vaporization at 111.9°C	kJ/kg	14.90
Liquid density at -183°C	kg/m^3	1574
Density, liquid (-112°C)	kg.m^{-3}	1358
Vapor density at 0°C and 1 atm	g/ml	2.154
Solubility in water at 20.0°C	mg/L	12.07
Vapor pressure at -183°C	kPa	11.0
Vapor density compared to dry air at 0°C and 1 atm	unit less	1.666
Specific volume of vapor at 0°C and 1 atm	m^3/kg	0.464
Surface tension (-183°C)	N.mm^{-1}	3.84x10^{-2}
Viscosity, liquid (-183°C)		
Heat capacity, liquid (-183°C to-145°C)	Pa.s	1.57x10^{-3}
Heat capacity, gas (25°C)	J.kg^{-1}.K^{-1}	818

Ozone is a strong oxidizing agent capable of participating in many chemical reactions with inorganic and organic substances. Table 7 compares the oxidation potential of ozone with other strong oxidizing agents.

Table 7 Relative oxidation potentials

Oxidizing species	Relative oxidation power
Fluorine	2.25
Hydroxyl radical*	2.05
Atomic oxygen	1.78
Ozone	1.52
Hydrogen peroxide	1.30
Perhydroxyl radical	1.25
Permanganate	1.23
Chlorine oxide	1.10
Hypochlorous acid	1.10
Chlorine	1.00
Oxygen	0.29

Remark: *formed when ozone decomposes

Source: Lin and Yeh (1993)

4.2 Solubility of ozone in water

Ozone is soluble in many substances, forming either stable or metastable solutions. It’s solubility in water follows the same rules as oxygen. Generally, an increase in pressure or decrease in temperature enhances the solubility of ozone in the aqueous phase. However, ozone is much more soluble in water than oxygen. The solubility of ozone in water is governed by Henry’s law. Typical values of Henry’s constant for ozone are shown in Table 8. Ozone solubility in water at various temperatures is shown as Table 9.

Table 8 Values of Henry's constant for ozone

Temperature °C	Henry's constant, atm/ mole fraction
0	1940
5	2180
10	2480
15	2880
20	3760
25	4570
0	5980

Source: U.S. EPA (1986)

Table 9 Ozone solubility in water at various temperatures

Ozone concentration	Ozone Solubility (mg/L)					
% w/w	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C
0.001	0.007	0.007	0.006	0.005	0.004	0.003
0.1	0.74	0.65	0.55	0.42	0.004	0.003
1	7.34	6.5	5.6	4.29	3.53	2.70
1.5	11.09	9.75	8.4	6.43	5.29	4.04
2	14.79	13.0	11.19	8.57	7.05	5.39
3	22.18	19.5	16.79	12.86	10.58	8.09

Source: U.S. EPA (1986)

Dissolved ozone in water is unstable and decomposes. When it decomposes, free radicals such as hydroxyl radical (OH˚), HO˚2, HO˚3, HO˚4, and super oxide (O-) are generated, chain reactions and occur produces fast reacting (strong) oxidizing agent. pH is also one of the main factors that influence the decomposition of ozone in water. As a general rule, pH < 7 has a slight affect on the ozone decomposition; however, at higher pH the decomposition rate increases significantly. The overall pattern of the ozone decomposition mechanism is shown in Figure 2.

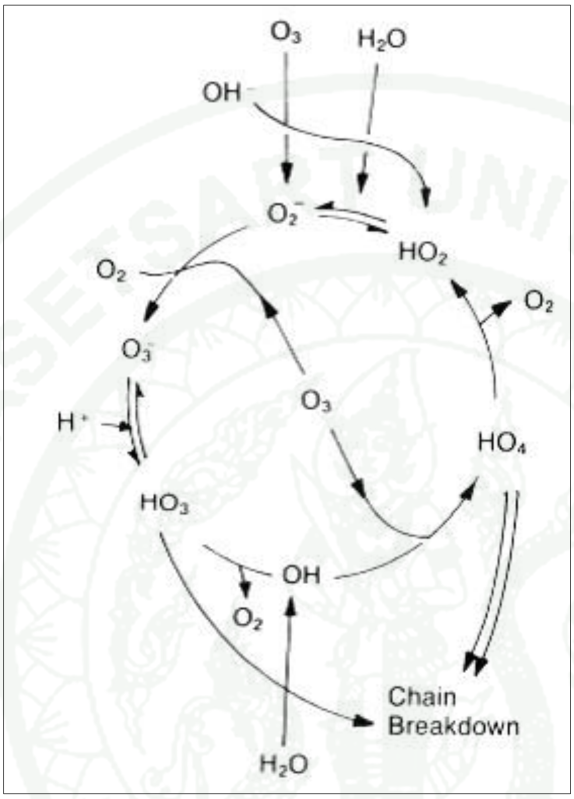


Figure 2 Ozone decomposition mechanism

Source: Langlais *et al*. (1991)

4.3 Ozone generation

Most simply, ozone can be generated by passing oxygen, or air containing oxygen, through an area having an electrical discharge, or spark. A clean smell in the air after a thunder and lightning storm is most likely caused by ozone formed from lightning bolts passing through the atmosphere.

To generate a sufficient quantity of ozone for a wastewater treatment plant, corona discharge type ozone generators are used. These ozonators have two large area metal electrodes separated by a dielectric and an air gap. An alternating electrical current is applied to the electrodes creating an electrical discharge. At the same time air or oxygen is passed through the air gap. As the air or oxygen flows through the air gap, and the electrical discharge, a portion of the oxygen is converted to ozone. The dielectric is necessary to spread the electric discharge over the entire electrode area and avoid producing an intensive single arc.

A side product from the corona discharge is the generation of a large amount of heat. The amount of air or oxygen flow in the air gap is not high enough to cool the electrodes. Since high temperatures cause ozone to very rapidly decompose to oxygen, it is necessary to provide a cooling system for the electrodes. At present, two types of cooling systems are used; they are (1) air cooled, and (2) water cooled.

The concentration of the ozone leaving the ozonator is approximately 1 to 2% by weight, which is applied to the treatable wastewater. Like chlorination, the effectiveness of treatment is dependent on the amount of ozone, thorough mixing and contact time. To satisfy the mixing and contact time requirements, three general types of contactors are usually used: (1) packed bed, (2) sparged column, and (3) sparged column with mixing. The most efficient contactor design will vary by treatment plant and may be different for wastewater with different conditions.

4.3.1 Ozone generation by corona discharge

Figure 3 shows ozone generation by Corona Discharge Procedure. Corona discharge, also known as silent electrical discharge, consists of passing an oxygen-bearing gas through two electrodes separated by a dielectric and a discharge gap. Voltage is applied to the electrodes, causing an electron flow across the discharge gap. These electrons provide the energy to dissociate the oxygen molecules, leading to the formation of ozone. Common feed gas streams are oxygen, air and recycle streams containing oxygen, nitrogen, argon, carbon dioxide and perhaps other diluents.

Although there are a number of mechanisms that may contribute to ozone formation in a corona, one particular reaction path is considered dominant. The reaction is initiated when free energetic electrons in the corona dissociate oxygen molecules.

$$e^{-1} + O_2 \longrightarrow 2O + e^{-1} \qquad (4)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (5)$$

$$O + O_3 \longrightarrow 2O_2 \qquad (6)$$

$$e^{-1} + O_3 \longrightarrow O_2 + O + e^{-1} \qquad (7)$$

In equation (5), ozone is formed by a three-body collision reaction, where M is any other molecule in the gas. At the same time, however, atomic oxygen and electrons also react with ozone to form oxygen as seen in equations (6) and (7).

The chemical equations for the formation of ozone can be written in simplified form as Equation (8) and (9).

$$O_2 + \text{energy} \longrightarrow O^\circ + O^\circ \qquad (8)$$

$$O^\circ + O_2 \longrightarrow O_3 \qquad (9)$$

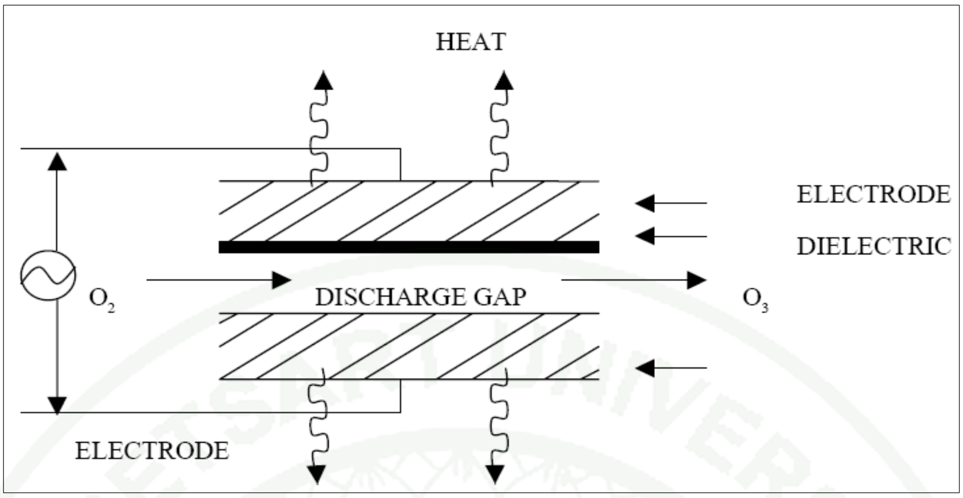


Figure 3 Ozone generation by corona discharge procedure

Source: Cheremisinoff and Cheremisinoff (1993)

4.3.2 Ozone generation by photochemical reaction

The formation of ozone from exposure of oxygen to UV light at 140-190 nm was first reported in 1900, and fully assessed by Goldstein in 1903. It was recognized that wavelengths below 200 nm are active for ozone generation. However, in present technologies, with mercury-based UV-emission lamps, the 254-nm wavelength is transmitted along with the 185-nm wavelength, and photolysis of ozone is simultaneous with its generation.

4.3.3 Ozone generation by Electrolytic reaction

Synthetic ozone was first discovered in 1840 through the electrolysis of sulfuric acid. The simplicity of the equipment required to produce synthetic ozone created a viable solution for small-scale and remote area users, providing numerous advantages. Some advantages of electrolytic generation of ozone include the use of low-voltage DC current, no feed gas preparation, reduced equipment size, possible generation of ozone at high concentrations, and generation in water, which eliminates the ozone-to-water contacting process. However, problems and drawbacks of this method include corrosion/erosion of electrodes, heat temperature variation due to anodic over-voltage and high current density, and the need for special electrolytes for water with low conductivity. Additionally, with the onsite generation process, incrustations and deposits are formed on the electrodes, and production of free chlorine is inherent to the process when chloride ions are present in the water or the electrolyte used (Langlais *et al*., 1991).

4.3.4 Ozone generation by radioactive reaction

High-energy irradiation of oxygen can promote the formation of ozone. Though the thermodynamic yield of the process is favorable, and interesting possibilities associated with waste fission isotopes exist, the cheminuclear ozone generation process has yet to become a significant application for wastewater treatment due to its complicated process requirements.

4.4 Application of ozonation

In general, ozone can be applied to wastewater at different stages of treatment. This invariably affects the dosage required. Ozonation can be applied in all branches of industry, treating almost all types of wastewaters. The operating conditions used in wastewater ozonation are dependent on the type of industry and the kind of wastewater. Generally, ozone is used for disinfection, oxidation of inorganic compounds, and oxidation of organic compounds.

Langlais *et al.* (1991) suggested the following ozone dosages for different treatment processes:

1. Treatment for primary sewage and storm water overflow – 10-100 mg/l ozone.
2. Tertiary treatment to convert secondary effluent to water of potable quality > 50-mg/l ozone.

Rosen (1971) emphasized the role of ozonation in tertiary treatment. He found that the following results could be achieved in tertiary treatment by ozonation:

1. Reduction of BOD and COD
2. Disinfection
3. Aeration to increase DO
4. Reduction of color and odor
5. Decrease of turbidity

In addition, he found that ozonation could offer the following benefits if applied to sludge treatment:

1. Oxidation of secondary sludge for partial or complete volatilization of organics.
2. Partial oxidation to make bacteria and other organics available as food recycle to activated sludge.
3. Breaking up filamentous bacterial growth and colloid structure to allow easier dewatering.

5. Previous experiments on ozonation in wastewater treatment

The large number of studies reviewed here indicates the extensive and intense research that has been carried out on ozonation oxidation capability. Some were used in the main treatment stage, and some will be added as a pre-treatment stage for industrial wastewater remediation. In recent years, many scientists have also developed alone or combined treatment systems for a diversity of industrial wastewater. Furthermore, there is growing interest in the development of different reactor configurations (batch direct reactors, activated-sludge process, membrane bioreactor, aerobic biological process, etc.) to optimize the time consuming step in the treatment line to maximize efficiency and design specific biological systems for each targeted industrial wastewater.

A systematic procedure included modeling substances prior to studying the wastewater, and evaluating toxicity and biodegradability during and after the degradation process. While the assessment of chemical parameters (such as BOD, COD and TOC) is usually implemented in these research studies, more pilot plant-scale experiments, with real industrial wastewater, must be performed.

In terms of performance, it was widely accepted that ozonation, as an AOP, has the ability to degrade. Several studies have confirmed that ozonation was one of the more effective treatments for oil, carbon, or Polycyclic Aromatic Hydrocarbon contaminated wastewater.

In addition, there have been various studies implicating that ozone can assist in the oxidization of most organic carbon. These studies proved that ozonation could oxidize organic carbon compounds, thereby treating water and wastewater. This literature review will be separated into two categories; 5.1) related study of ozonation in oil, carbon, or Polycyclic Aromatic Hydrocarbon contaminated wastewater, and 5.2) studies of ozonation of wastewater contaminated other substances.

5.1 Related study of effect of ozonation in oil, carbon, or Polycyclic Aromatic Hydrocarbon contaminated wastewater

Ozonation on oil, carbon or Polycyclic Aromatic Hydrocarbon has been carried out for more than 5 decades. Within the first stage (between 1963 – 2003), several studies have been carried out to treat wastes containing alkylbenzene sulfonate (ABS) by ozonation. Buescher and Rychman (1961) and Evans and Ryckman (1963) discovered that ozonation of raw sewage and treatment plant effluent reduced the concentration of anionic ABS. Ozone concentration of 100 mg/l at 83% utilization efficiency removed 5.9 mg/l ABS (95% of the initial concentration). Also 15.6 mg/l ABS (95% of the initial concentration) was removed by 75 mg/l of ozone at 92% ozone transfer efficiency. Ozonation of settled raw sewage and treatment plant sewage effluent resulted in the added benefits of removal of color and odor, producing a crystal clear and nearly odorless byproduct. Ozonation results in BOD and COD reductions as well as a substantial decrease in suspended solids.

Kornmüller *et al.* (1998) studied the ozonation of three to five condensed ring polycyclic aromatic hydrocarbons (PAH) in synthetic oil/ water-emulsions in batch experiments. PAH can be oxidized selectively in the presence of high concentrations of dodecane as an aliphatic solvent. No oxidation of dodecane, as a representative of mineral oil, could be observed during experimentation (pH ~ 11). From acidic to neutral pH levels, were achieved due to a direct reaction with ozone resulted in high PAH oxidation rates. Temperature was also observed. Between 20°C to 40°C, no influence of temperature on the ozonation of benzo(k)fluoranthene could be found. In comparison, ozonation reactions of five PAH were completed sequentially -- acenaphthene, pyrene, benzo(e)pyrene, benzo(k)fluoranthene and phenanthrene. This experiment showed an O3 preference to aromatic ring hydrocarbons than towards straight chain hydrocarbons.

Marhaba *et al.* (2000) conducted a study on the isolation and fractionation of natural organic matter (NOM) by resin adsorption at two surface drinking water treatment plants treating the same source of surface water. The first treatment plant used conventional treatment (coagulation, sedimentation, and filtration) with chlorination. The second plant used conventional treatment with pre and intermediate ozonation, and multi-media granular activated carbon filtration. Chemical fluorescence of the NOM was used to monitor the removal/reactivity of each fraction. Several different sampling locations within each plant were selected for NOM isolation and fractionation into six fractions (hydrophobic acid, neutral and base, and hydrophilic acid, neutral, and base).

Hydrophobic base represented a mass fraction in the range of 0-6% of DOC (6% in the raw water). The effect of ozonation on the hydrophobic base fraction was significant. Examining the overall removal at the outlet of the sedimentation basin, this fraction was noticeably reduced (95%).

Hydrophobic acid fraction had a comparatively smaller slope in the mass-reduction curve than that of the hydrophobic base through the pre-ozonation process.

Hydrophobic neutral was the most abundant fraction of the hydrophobic substances ranging from 13-22% in all locations (18% in the raw water). This range fell within the raw water range of 0-25%. Hydrophobic neutral is a humic substance in nature, containing a mixture of hydrocarbon and carbonyl compounds. Because of these characteristics, a steady but noticeable reduction of the reaction shows that ozonation changed the content of the DOC substantially in terms of the operationally defined fractions investigated.

Hydrophilic base increased due to the pre-ozonation process. The 58% increase can potentially be attributed to the transformation of mass from the hydrophobic base fraction, the breakup of mass into smaller molecular sizes, and the transformation from non-biodegradable to biodegradable materials (by the oxidation process). The increase of the hydrophilic base was comparable to the decrease from coagulation/sedimentation.

Zeng *et al.* (2000) performed ozone treatment to PAH (benzo[a]pyrene) and conducted BOD (after 5, 10 and 15 days of incubation), COD, E. Coli toxicity test reaction. After the treatment, a very successful removal of E. Coli toxicity was found. Additionally, the final BOD/COD was 0.43 which indicated a high biodegradation number.

Kornmüller and Wiesmann (2002) conducted a study on the effect of ozonation on highly condensed PAH in oil/water-emulsions, which are comparable to poor water-soluble PAH in industrial wastewaters and at contaminated sites. Due to the lack of knowledge concerning the ozonation in oil/water-emulsions, the ozone mass transfer was studied first. It was then optimized from the gas to water phase and from the water to oil phase. The ratio of mass transfer to oxidation reaction was determined by the Hatta-number revealing a slow, quasi-homogeneous reaction of ozone with PAH inside the oil droplets. Because the ozone gas concentration had no influence under the optimized conditions, the selective PAH-ozonation could be described micro-kinetically by a direct ozone reaction of pseudo-first order regarding PAH-concentrations. The determined PAH mean reaction rate constants of 1.02

min−1 in oil/ water-emulsions were in the upper range for PAH dissolved in water. These results provide further insight into ozonation within the three-phase systems and into the treatment of highly condensed, hardly biodegradable PAH.

Balcioglu and Ötker (2002), effects of pH, initial COD value and the addition of hydrogen peroxide on the ozonation process. TOC, COD, BOD, and aromatic content (UV_{254}) were the parameters for evaluating the performance of the ozonation process. Comparison of the biodegradability of selected wastewaters containing different antibiotics confirmed that the variation of biodegradability was associated with the target compound. While BOD_5/COD ratio of veterinary antibiotic formulation wastewater was increased from 0.077 to 0.38 with an applied ozone dosage of 2.96 g/l, this ratio for human antibiotic I and human antibiotic II was increased from 0 to 0.1 and 0.27, respectively. Moreover the results of this investigation showed that the ozonation process is capable of achieving high levels of COD. Aromaticity was removed at about their natural pH values.

Sangave *et al.* (2006) conducted laboratory experiments in order to investigate the affect of ozone as pre-aerobic and post-aerobic treatments of distillery wastewater. The degradation of the pollutants in distillery wastewater was carried out through ozonation and the aerobic biological degradation processes. Combining these two processes provided insight into the synergies between the two modes of wastewater treatment. Pollutant removal efficiency was determined by parameters directly related to the concentration of organic compounds in those effluents. This included chemical oxygen demand (COD) and the color removal efficiency in terms of sample absorption (254 nm). COD was effectively reduced to 27% by pre-ozonation. In the combined process, pre-treatment of the effluent led to enhanced rates of biological oxidation. A 250% increase in the initial oxidation rate was observed. Post-aerobic treatment with ozone led to further removal of COD along with complete effluent discoloration. The integrated process (ozone–aerobic oxidation–ozone) achieved approximately 79% COD reduction with discoloration of the effluent sample. Comparatively, there was a 34.9% COD reduction for non-ozonated sample over a similar treatment period.

5.2 Various Studies of ozonation of wastewater contaminated with other substances.

Like ozonation in oil or carbonated wastewater, ozonation treatment on other kinds of wastewater have also been studied for more than 60 years. Research data on treatment of wastewater by ozonation from 1969 until 1972 is shown in Table 10.

Table 10 Some previous researches on treatment of wastewater by ozonation from year 1969 to 1972

References	Wastewater Treated	Concluding Remarks
Kwie (1969)	Wastewater from a polymer plant	Reduced 32% of COD
Niegowski (1956)	Composite waste	Reduced 21 % of BOD, the higher ozone dose, the higher reduction
Gardiner and Montgomery (1968)	Sewage	5 mg/l of suspended solid were reduced from initial concentration ranging from 14 to 55 mg/l by 20 mg/l of ozone
Majumdar (1973)	Primary and Secondary wastewater	• Primary wastewater reduced SS for 43% and reduced COD for 45% • Secondary reduced SS for 33% and reduced COD for 54% • Slightly increase pH on both wastewater.

Kwie (1969) found that COD of wastewater from a polymer plant was reduced significantly (32%) when the oxidizable organics present in the waste consisted of unsaturated compound that could be attacked readily by ozone.

Niegowski (1956) found that 33 ppm of ozone resulted in 21 percent of BOD reduction of a composite waste having 151 ppm of BOD. The reduction was higher when the concentration of ozone was higher.

Gardiner and Montgomery (1968) found that an ozone dosage of 0.19 g/l/h in sewage reduced COD in proportion to the weight of ozone absorbed. Further observations found that approximately 5 mg/l of suspended solid were reduced from initial concentrations ranging from 14 to 55 mg/l by 20 mg/l of ozone. This reduction increased to 14 mg/l when the amount of ozone absorbed was 40 mg/l.

Majumdar (1973) reviewed several papers on the affect of ozonation on the characteristics of primary and secondary wastewater. The primary wastewater was the discharged from municipal, when the secondary wastewater came from storage in the municipal wastewater treatment tanks. The results have been reproduced in Table 11. For primary wastewater, suspended solids were reduced by 43% and COD were reduced by 45%. This resulted in a residual ozone concentration of 2.17 mg/l. In the secondary wastewater, suspended solids were reduced by 34% and COD were reduced by 54%. This resulted in 2.42 mg/l of residual ozone. These reductions were dependent on the amount of ozone absorbed in the liquid. In both cases, pH slightly increased.

Table 11 Sanitary characteristics of primary and secondary wastewater before and after ozonation

	Ozone Concentration (mg/l)	**pH**	**Suspended Solids**	**COD**
Primary Wastewater				
Before ozonation		6.55	47	267
After ozonation	2.17	7.65	27	147
% Change or Removal		+16.8%	42.6%	44.9%
Secondary Wastewater				
Before ozonation		7.38	109	130
After ozonation	2.42	8.29	72	60
% Change or Removal		+12.2%	33.9%	53.9%

Remarks: there was no appreciable change in dissolved solids content.

Source: Majumdar (1973)

Table 12 shows the brief summary and results of ozonation in wastewater contaminated with other substances. Several research articles listed in Table 12 show that ozonation effectively treats various forms of wastewater – some treated better than others. The ozone treatment processes vary by wastewater type. Certain wastewater can be treated by ozonation alone. Combining treatment processes, however, can better treat other types of wastewater.

Table 12 Various studies of ozonation of wastewater contaminated with other substances

References	Target Wastewater (pollutant degraded)	Treatment Processes	Main Results
Lee *et al.* (2009)	Reverse osmosis brine from water reclamation facilities	Biological activated carbon system and ozonation	Combined system (Biological activated carbon system and ozonation) achieved 3 times higher TOC removal compared to using biological activated carbon process alone.
Yan *et al.* (2010)	Trihalomethanes (THMs) precursor	Biological granular activated carbon filtration and ozonation	Integration process (Biological granular activated carbon filtration and ozonation) is superior to granular activated carbon system to THMs precursor removal.
Bijan and Mohseni (2005)	Paper Mill wastewater (pulp mill alkaline bleach plant effluent)	Ozonation as pre-treatment, and batch aerobic biological system as treatment	20% organic compounds such COD and BOD_5) removed in ozonation pre-treatment. 30% TOC removal during biological process.

Table 12 (Continued)

References	Target Wastewater (pollutant degraded)	Treatment Processes	Main Results
Balcioglu *et al.* (2006)	Paper Mill wastewater (bleached Kraft pulp mill effluents)	Ozonation sequential batch reactor	BOD_5/COD ratio increase from 0.16 to 0.32. 87% AOX removal rate.
Bijan and Mohseni (2008)	Paper Mill wastewater (Kraft pulp mills)	Ozonation as pre-treatment, and activated-sludge bio-treatment as treatment	The biodegradability of the wastewater during the ozone oxidation increased significantly from 0.10 to 0.53.
Di laconi *et al.* (2002)	Tannery Wastewater	Sequencing batch ozonation	COD, ammonium and total suspended solids average removals were 97%, 98% and 99.9%, respectively.
Benitez *et al.* (2003a.b)	Cork processing industry wastewater)	Activated-sludge process as treatment, ozonation as post treatment.	Ozonation-aerobic degradation sequence increased substrate removal efficiencies
Dogruel *et al.* (2006)	Tannery Wastewater	Activated-sludge process as treatment, ozonation as post treatment.	With post-ozonation, the highest inert COD removal efficiencies together with an efficient quality meeting the discharge standards were obtained

Table 12 (Continued)

References	Target Wastewater (pollutant degraded)	Treatment Processes	Main Results
Garcia-Montaño *et al.* (2008b)	Dye wastewater (Cibacron Red FN-R reactive azo dye)	Anaerobic digestion as treatment, ozonation as post treatment.	Ozonation as post-treatment at pH 10.5 allowed achieving a global 83% mineralization.
Assalin *et al.* (2009)	Paper industry wastewater (Kraft E_1 effluent)	Activated-sludge process as treatment, ozonation as post treatment.	Ozonation as post-treatment at pH8.3 achieved COD, DOC, colour and total phenols removal of 75.5%, 59.1%, 77% and 52.3% respectively.
Mänttäri *et al.* (2008)	Paper Industry wastewater (discharge water from an activated-sludge process)	Activated-sludge process as treatment, ozonation as post treatment.	Ozone significantly decreased colour, UV absorbing materials (lignin) and turbidity of the NF concentrate. COD also decreased and simultaneously increased biodegradability.
Artanto *et al.* (2009)	Non-evaporative removal of water from low-rank coals prior to combustion by mechanical thermal expression	Anaerobic digestion as treatment, ozonation as post treatment.	Aliphatic and aromatic hydrocarbons were reduced by approximately 95% by anaerobic treatment. Overall COD removal of 97%

Table 12 (Continued)

References	Target Wastewater (pollutant degraded)	Treatment Processes	Main Results
Schaar *et al.* (2009)	Pharmaceutical wastewater (bisphenol-A 17α-ethinylestradiol, erythromycin and roxithromycin)	Aerobic digestion treatment as pre-treatment, and ozonation as treatment.	Ozonation application increased the removal of most of the micropollutants, especially for the compounds not degraded in the previous biological process.
Mascolo *et al.* (2010)	Pharmaceutical wastewater (resulting from the product of acyclovir, an anti-viral drug)	Membrane bioreactor and ozonation	MBR efficiency was improved from 20% to 60% as soon as ozonation was placed in the recirculation stream.
Reungot *et al.* (2010)	Pharmaceutical wastewater	Biological denitrification and ozonation	Overall concentration reductions were typically higher than 90%and most of the compound were removed to levels lower than 0.01 mg/L.
Rosal *et al.* (2010)	Emerging contaminants (25 compounds detected in µg/L range)	Activated-sludge process as treatment, ozonation as post treatment.	Ozonation as post-treatment allowed the removal of many individual pollutants including some of those refractory to biological treatment.

Table 12 (Continued)

References	**Target Wastewater (pollutant degraded)**	**Treatment Processes**	**Main Results**
Treguer *et al.* (2009)	Drinking water (improvement of the conventional process)	Membrane bioreactor and ozonation	Residual DOC after membrane bioreactor was the major part of the non-biodegradable fraction. Ozonation treatment increased the treatment efficiency, and the biodegradable was increased from 0.32 to 0.74.

Several more studies regarding ozonation on wastewater were found as shown below.

Singer (1974) investigated the affect of ozone on ammonia in municipal wastewater describing the application of ozone for advanced waste treatment. Ammonia oxidizes to a nitrate state, eliminating the nitrogenous oxygen demand of the waste. In buffered solutions of ammonium chloride, the reaction is first-order with respect to the concentration of ammonia. The reaction rate and pH (from 7 – 9) increased proportionally as ozone partial pressure increased. The effective removal of ammonia occurs only if the pH of the wastewater maintains alkalinity because the reaction is pH sensitive. Due to the elevated pH required for effective ammonia oxidation, ozonation is more effective lime clarification and phosphate precipitation. Application of ozone for disinfection requires recognition of the ozone demand exerted by ammonia.

Welsbach Corporation (1962) and Niegowski (1956) from Ozone Process Division found that ozonation of wastes containing phenol resulted in the formation of products. This had none of the objectionable characteristics of the phenolic compounds themselves. Unpleasant characteristics like taste, odor and toxicity were greatly reduced, if not completely eliminated. Phenolic waste liquors absorbed and reacted with ozone very rapidly. Furthermore, phenol can be oxidized by ozone at any pH value. Niegowski (1956) found that 96 percent of 5.4 ppm solution of phenol was destroyed by treatment of the composite waste with 33 ppm of ozone. Eisenhauer (1968) observed that the degree of treatment of phenolic wastes depended on the rate of absorption of ozone in wastewater.

Considerable work was carried out on the oxidation of phenolic substances by ozone. It was clearly proven by Atkinson and Palin (1972) that at the required ozone levels for elimination of bacteria and viruses, phenols and similar materials are readily broken down.

Jones *et al*. (1985) evaluated ozonation and UV radiation, which mineralize the organic solutes within processed bio-oxidized oil shale wastewater. This affects structural modification of the remaining bio-refractory organic solutes sufficiently to promote secondary bio-oxidation. Sequential application of primary biooxidation, followed by 6 hours of combined UV/ozonation, and secondary biooxidation removed only 59% of the dissolved organic carbon; total reduction of 87% was achieved by using a culture in the secondary biooxidation step that was specially adapted to this oxidized water. Each time-course sample was analyzed for the distribution of polar and nonpolar organic solutes. In general, ozonation and combined UV/ozonation mineralized carbon from the non-polar fraction; biooxidation of formerly refractory carbon was promoted by oxidation of non-polar carbon to yield more polar or lower-molecular weight species.

Gulyas *et al*, (1995) investigated treatment with ozone and ozone/hydrogen peroxide in a laboratory scale reactor for removal of organics from three different industrial wastewater sources: wastewater from paper-mill, biotechnical pharmaceutical process, and from soil remediation by supercritical water extraction. Additionally, an aqueous solution of triethyleneglycoldimethylether and humic acid, which represent the model for a biologically treated oil reclaiming wastewater, was also oxidized. Pharmaceutical wastewater was oxidized in order to remove the preservative 1.1.1-trichloro-2-methyl-2-propanol (TCMP). Although TCMP could easily be removed from pure aqueous solutions by treatment with ozone/hydrogen peroxide, the oxidation of the wastewater failed to be effective in TCMP degradation because of competitive ozonation of other organic solutes in the wastewater. The ozonation of the paper-mill wastewater and of the soil remediation process waters decreased COD and TOC to some extent. The presence of organic solutes which contain C-C double bonds (ligninsulfonic acid in the treated paper-mill effluent and humic acid in the oil reclaiming model wastewater) were shown to yield hydrogen peroxide by the reaction with ozone. Therefore, ozonation of these wastewaters are efficient even without addition of hydrogen peroxide. Chemical Oxidation of paper-mill wastewater and of wastewaters resulting from soil remediation did not improve biological degradability of organic wastewater constituents.

Klasson *et al.* (2002) conducted extensive research to improve the applicability of ozonation and to help address the petroleum-industry problem of soluble organic containing effluent produce from treatment process. The combination of ozone and hydrogen peroxide did not improve the oxidation of organics to CO_2. This was true over a pH range of 3-11 in studies conducted with surrogate produced water. The effect of ultraviolet irradiation alone or in combination with ozone was studied with synthetic water. Based on the results of these experiments, it was concluded that UV light had a slightly effect on ozonation of the extractable organics present in complex waters. UV light, however, when used in combination with ozone, improved the destruction of BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes). The lower molecular-weight organic acids present in the plant produced waters were not attacked and destroyed by ozone under normal operating conditions and were thus not considered ozone scavengers. The ozone scavenging effects of organic acids were pronounced at higher pH in experiments with model compounds. Organic acids do not contribute to water-soluble organics in the measurement technique used. Experiments showed that the rate of disappearance of extractables was first-order with respect to the ozone and extractable concentrations. Rate data also suggested that there are several competing reactions demanding ozone and some of these reactions proceed at a faster rate. The extractable organics degradation rates and ozone demands were significantly better at higher operating temperatures. The products of ozonation proved to be an array of chemicals, many of which could not be verified precisely using gas chromatography mass spectroscopy. The partial identification suggested that several of the compounds were halogenated indicating activation of organic compounds by ozone-generated radials and the combination of these activated organics with salt-water components (chloride and bromide, etc).

Contreras *et al.* (2003) investigated the contribution of the ozonation, pre-treatment to the biodegradation of aqueous solution of 2,4-dichlorophenol. BOD at 5, 10 and 21 days, BOD/COD and BOD/TOC ratios and the average oxidation state are presented. Biodegradability measured as BOD_5/COD ratio was increased from 0 in the original solution to 0.25 at the moment of removing all the initial compound (corresponding to an ozone dose of 0.12 g L^{-1}, 0.48 for BOD_{21}/COD ratio). To test the effect of this pre-treatment, the biological oxidation of these pre-ozonated solutions was performed in two semi-continuous stirred tank reactors, one with non-acclimated sludge and one with acclimated-to-phenol sludge. The study showed that the TOC content of the pre-treated solution could be removed up to 68% by an aerobic biological treatment as well as co-digested with municipal wastewater (TOC removal up to 82%), with similar operating retention times to a municipal wastewater plant (12–24 h Pseudo-first-order kinetic constants were found to be in the range of 0.5–0.8 L g $TVSS^{-1}$ h^{-1} when kinetic studies based on the Monod model were carried out.

Dong *et al.* (2009) used ozone and $Mn(NO_3)2$ as raw materials. A simple hydrothermal process synthesized β-MnO2 nanowires with diameters of about 6-12 nm, lengths of 2-5 μm and surface area of 73.54 m^2g^{-1}. The influences of synthesis conditions (hydrothermal temperature, reaction time and ozone) were investigated, and the growth process of β-MnO_2 nanowires was discussed. The catalytic properties of β-MnO_2 nanowires for degradation of phenol were evaluated. They showed good separability and remarkable catalysis for the degradation of phenol.

Javorska *et al*. (2008) investigated the effectiveness of ozone treatment on degradation of polychlorinated biphenyl (PCB) contaminated soils to observe the subsequent changes in soil physico-chemical properties. Furthermore, the ability of plants to grow in ozone-treated soils was evaluated. Soils with different physico-chemical characteristics spiked with seven PCB congeners in two different time periods were used. Ozonation was more efficient for PCB degradation in freshly spiked soils and the removal efficiency increased as ozonation time elapsed. The highest decrease was found in the soil with a lower soil organic matter (SOM) content and a coarser soil structure. This indicated the substantial affect of soil characteristics on the efficiency of ozonation. The composition of individual PCB congeners changed in all treatments in terms of a higher accumulation rate of highly chlorinated biphenyls with a higher ozonation time. Increased mobility of several elements, changes in SOM content and in soil pH were detected after ozonation. No inhibition in growth during any treatment and predominantly higher concentration of PCB in non-ozonated treatments were observed. Results suggest that this method would be a promising environmentally friendly remediation for PCB contaminated soils.

MATERIALS AND METHODS

Materials

1. The equipment used for conducting the experiment and reactor design and configuration

1.1 Ozo-MAC, CW 300 L Ozone generator, the specification as follows:

Ozone Output: 300 mg/L
Corona discharge type
Ozone Concentration at 1CFH: 600 ppm. Ozone Purity: 99.9% Hydroxyl Free, 100% Free of Nitrous Compounds.
EMI Suppression and Transient Protected: Up to 2,000VAC.
Case: High Impact Polymer. System Life: 20,000 hours (nominal).
Operating Temperature: +25°F. to +140°F.
Weight: 14 ounces. Size: 6 Wide x 6 x 2½ inches.
Standard System: 220VAC, 60hz; .35 amps and Molded Spa Ozone Plug.

1.2 Reactor design and configuration

A corona discharge type ozone generator (Ozo-MAC, CW 300L) was used in this study. Ozone production rate was approximately 900 mgO_3/hr. The semi-batch experiments were carried out in the reactor (Figure 4) consisting of 2x1 litre filtering flasks sequentially connected with silicone tubes. Ozone from the generator was fed through a diffuser into the first flask containing wastewater sample. Then Ozone off gas passed through silicone tube to the second flasks containing 2% KI solution used for ozone trapping.

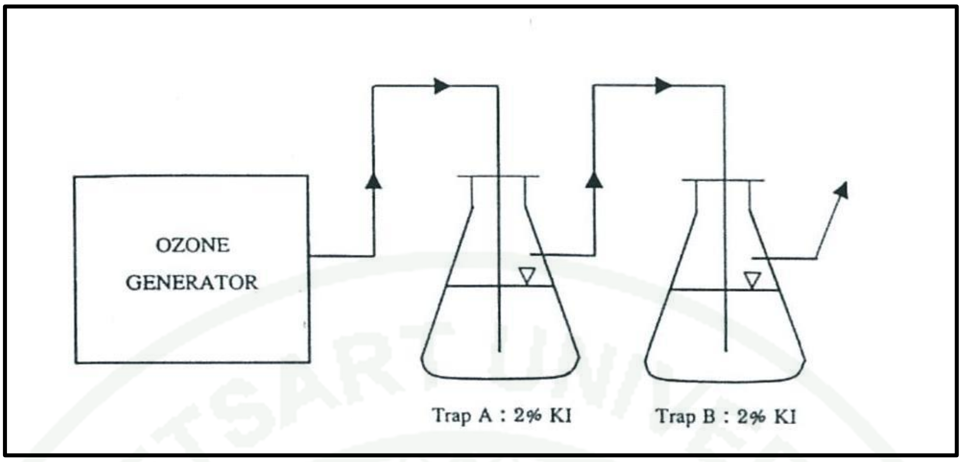


Figure 4 Experimental diagram set up of ozonation laboratory

Figure 5 Figure of laboratory setup

1.3 Materials and equipment used in the laboratory are listed below:

1.3.1 For Ozonation process

a) Ozone Generator
b) Ozone Trap
c) 2 of 1 litres Reactor
d) Diffuser
e) Water Sample Collector

1.3.2 For BOD, COD, TOC and FOG analysis

Reagent for analysis of Ozone, BOD, COD, TOC and FOG were prepared according to Standard Method for the examination of water and wastewater

a) Wastewater Sample
b) Incubation bottle (BOD bottle 300 ml)
c) Volumetric flask
d) Cylinder
e) Burette
f) Blender
g) Reflux apparatus
h) Digestion vessel (20*150 mm.)
i) Air incubator or water bath controlled at 20 ^{O}C
j) Manganese sulfate solution
k) Alkaline Iodide Azide
l) Sulfuric acid concentrated
m) Starch solution (as indicator)
n) Sodium thiosulfate solution 0.025 N
o) Standard potassium dichromate solution, 0.25 N
p) Silver Sulfate
q) Sulfuric acid concentrate
r) Ferroin indicator
s) Standard phosphorus ammonium sulfate (FAS) 0.25 N
t) Mercuric sulfate
u) Standard potassium hydrogen phthalate (KHP)

2. Wastewater collection and preparation

2.1 Wastewater collection

FEW samples were collected from an ERTC (Emergency Response Training Center), responsible for fire extinguishing training. After collection, wastewater was maintained at 4 degree Celsius during transportation to the laboratory (approximate travelling time was 45 minutes). Lab analysis and experiments were conducted at Environmental Engineering Lab#2 in Kasetsart University and at Chevron Laboratory in Songkhla Province.

2.2 Wastewater pH Adjustment

2.2.1 Original condition – raw wastewater

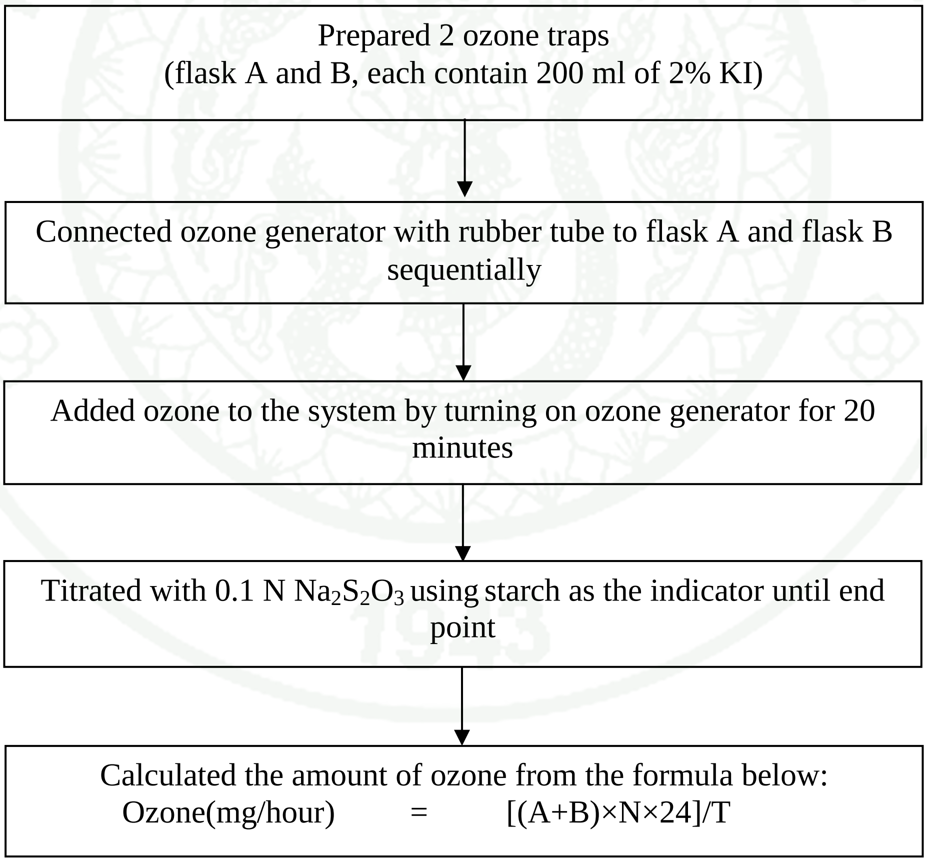
2.2.2 Acid condition – Use H_2PO_4 solution and measure the pH with pH indicator

2.2.3 Base condition – Use NaOH solution and measure the pH with pH indicator

Methods

1. Determination of ozone generating capacity

In this study, the Wet Chemistry Potassium Iodide Method was used to determine the amount of ozone produced from the generator. The method is based on the reaction between ozone and an iodide ion Potassium Iodide solution. Determination of ozone dosage can be done by a volumetric analysis, titration of liberated iodine with sodium thiosulfate solution ($Na_2S_2O_3$), using starch as an indicator. Figure 6 shows the flow diagram of Determination of ozone generating capacity.



Prepared 2 ozone traps
(flask A and B, each contain 200 ml of 2% KI)

Connected ozone generator with rubber tube to flask A and flask B sequentially

Added ozone to the system by turning on ozone generator for 20 minutes

Titrated with 0.1 N $Na_2S_2O_3$ using starch as the indicator until end point

Calculated the amount of ozone from the formula below:

$$\text{Ozone(mg/hour)} = [(A+B)\times N\times 24]/T$$

Figure 6 Determination of ozone dosage by ozone generator

The reaction between ozone and iodide is shown in the chemical reaction as follows:

$$O_3+KI+H_2O \rightarrow I_2+O_2+KOH \qquad (10)$$

From the reaction, it can be seen that liberated iodine, I_2 occur in the same proportion with ozone introduced into the system.

The thiosulfate anion reacts stoichiometrically with iodine, reducing it to iodide as it is oxidized to tetrathionate as shown in the chemical equation:

$2\ S_2O_3{}^{2}{}_{-(aq)} + I_{2(aq)} \rightarrow S_4O_6{}^{2-}{}_{(aq)} + 2\ I^{-}{}_{(aq)}$

Ozone production is then calculated from amount of thiosulfate ($S_2O_3{}^{-2}$) below:

$$\text{Ozone(mg/hour)} = [(A+B)\times N\times 24]/T \qquad (11)$$

A = sodium thiosulfate used in titration in Trap A (ml)
B = sodium thiosulfate used in titration in Trap B (ml)
N = Normality of sodium thiosulfate
T = Time (hours)

2. Determination of optimum condition of Ozonation of wastewater sample

2.2 The experiment on ozonation of the FEW samples were conducted in three conditions, (1) actual condition of raw wastewater, pH 7 (2) acid condition, pH 3 adjusted with H_2PO_4, and (3) basic condition, pH 13 adjusted with NaOH. After treated with ozone, treated samples were collected at different time intervals (0, 0.5, 1, 2, 3, 4, 6, 12, 18 hours) and analyzed for COD, BOD, TOC and FOG.

2.3 Analytical methods employed were the AWWA (American Water Works Association) standard methods (Standard Method of the Examination of Water and Wastewater 18th Edition, 1992). Parameter and analytical methods are summarized in Table 13.

Table 13 Parameters and analytic methods

Parameter	APHA Number	Method
Ozone Dosage	2350 E	Wet Chemistry Potassium Iodide
BOD	5210 B	5-Day BOD Test
COD	5220 D	Closed Reflux, Colorimetric
TOC	5310 D	Wet-Oxidation
FOG	5520 B	Partition-Gravimetric

Experiments can be shown in Figure 7.

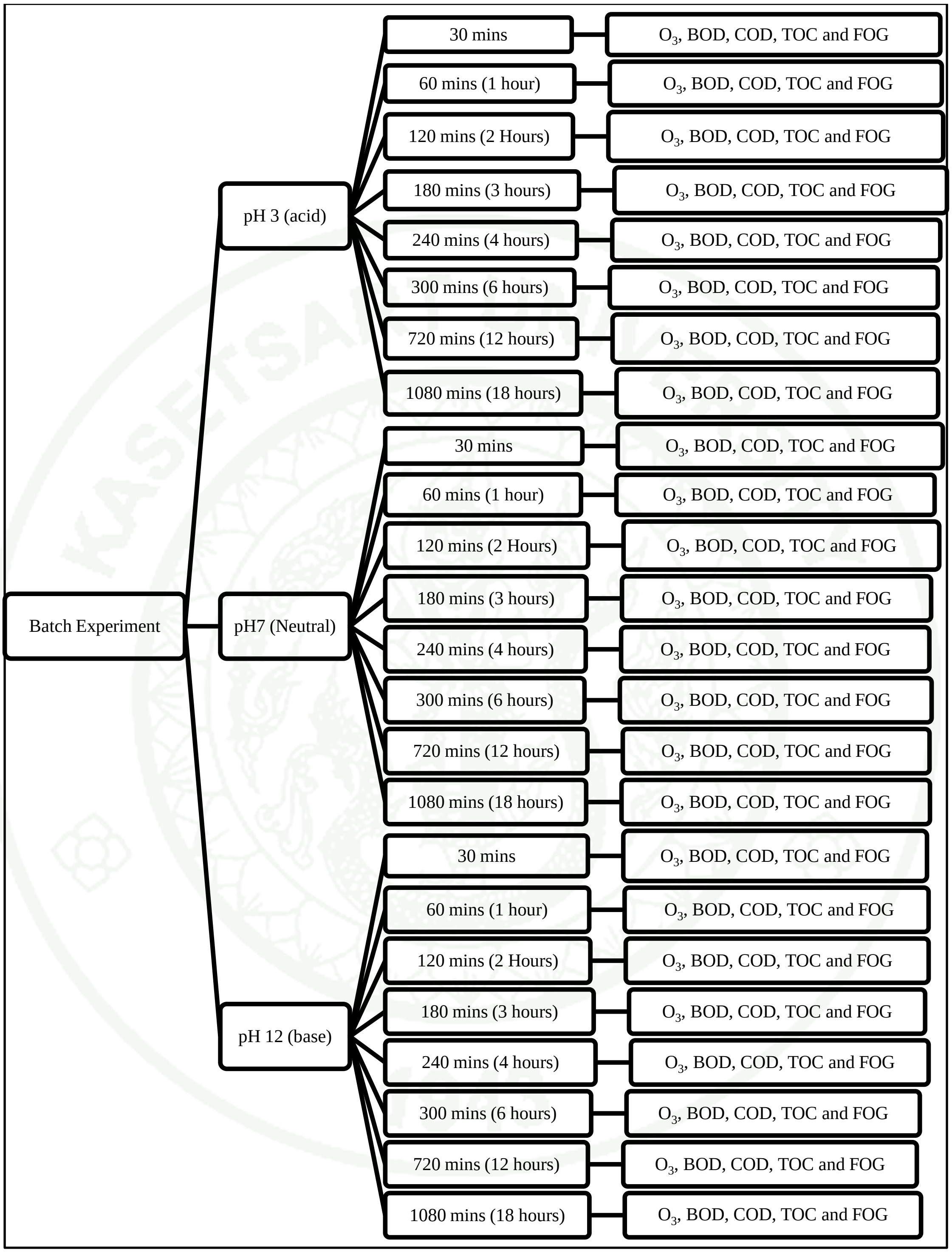


Figure 7 Tree Diagram for 3 experimental programs on the effect of ozonation on FEW

RESULTS AND DISCUSSION

1. Characteristics of Fire Extinguisher Wastewater

Fire Extinguisher Wastewater (FEW) from ERTC was collected and analyzed four times, used in four experiments from 30 July 2009 to 27 October 2011. The organic contents found in the FEW samples varied; however, all tests contained high amounts of organic contents. As shown in Table 14, the COD was found in the range from 4,743 – 11,410 mgCOD/L. BOD_5 was found from 2,010 – 3,090 mgBOD/L. FOG was found in the range from 120 – 176 mgFOG/L. The organic contents from FEW were higher than the limit set by Thailand's Pollution Control Department (PCD). The values set within the Industrial Effluent Standards for Factory Group II and III are 20 mgBOD/L, 120 mgCOD/L and 5 mgFOG/L (appendix Table D). Due to the BOD_5:COD ratio (0.360 on average) within the FEW organic contaminants, biodegradability cannot be readily assumed. An alternative treatment to the biological process was preferred.

Table 14 COD, BOD_5, FOG and BOD_5/COD from 4 experiments

Experiment Date	COD (mg/L)	BOD_5 (mg/L)	FOG (mg/L)	BOD_5/COD
30 July 2009	4,743	2,010	176	0.424
20 June 2010	5,775	2,340	120	0.405
10 May 2011	8,790	2,980	150	0.339
27 October 2011	11,410	3,090	150	0.271
Average	**7,680**	**2,605**	**149**	**0.360**

As noted in Table 15 below, due to training classes, the COD and BOD in FEW from 27 October 2011 were found to be higher than other days. As discussed in the literature review session, the frequency of training courses at ERTC directly affected the chemicals used. This directly impacted FEW quality. The more organic contents the FEW contained, the more chemicals were used during firefighting training.

However, FOG did not significantly vary at the time of the experiment. The ERTC scheduled a weekly cleanup up of sludge (oil layer).

Table 15 Training Schedule at ERTC before the experiment date

Experiment Date	**Training Classes on the previous Days**			
	1 day before	**2 days before**	**3 days before**	**4 days before**
30 July 2009	-	-	-	T-BOSIET
20 June 2010	-	-	-	-
10 May 2011	-	FOERTM	FOERTM	-
27 October 2011	T-FOET, FOERTM, FOTREL	FOERTM, FOTREL	OERTM	OERTM

2. Ozone generating capacity and ozone dosage calculation

Twenty tests, under the same conditions, were conducted to determine ozone generation using Ozo-MAC CW 300 L Ozone generator. Figure 8 shows that the ozone generation rate varied from 828.0 - 993.6 mgO_3/hr, averaging 931.0 mgO_3/hr, with a standard deviation of 48.39. The variance was acceptable and was due, in part, to the daily variations in temperature and humidity (Gottschalk, 2000). The temperature during the test run was between 28-30 °C. The relative humidity varied between 60-80%. Therefore, ozone was generated within the stable range according to commercial specifications.

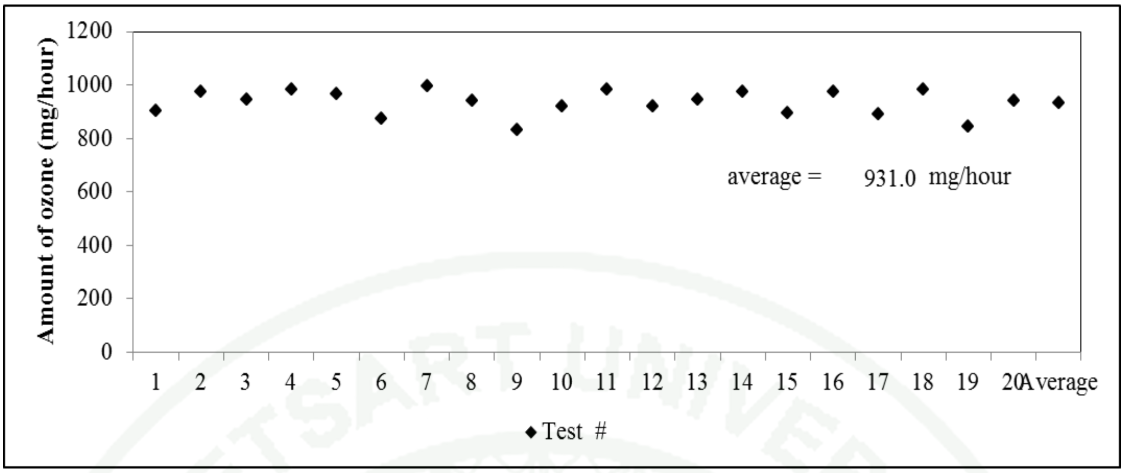


Figure 8 Ozone generating capacity by Ozo-MAC CW 300 L generator

The affect of ozonation on organic content reduction from FEW wastewater is dependent upon several variable including ozone dosage, initial wastewater contents, and pH. In addition to pH, varying ozone dosages were applied at varying times into 1 liter of wastewater (ozone dosages ranged from 0 to 16,757 mgO$_3$/L varying by time 0 to 18 hours). Table 16 shows the amount of ozone dosage at varying time.

Table 16 Ozone dosage in wastewater at various time

Time (hours)	**The amount of ozone (mgO$_3$/L)**
0	0
0.5	465
1	931
2	1,862
3	2,793
4	3,724
6	5,586
12	11,172
18	16,757

3. Effects of ozonation on organic contaminants

Wastewater samples were ozonated at three different pH conditions – pH 3, neutral pH of raw wastewater of raw wastewater, pH 13. Organic contaminants in the form of COD, BOD, TOC and FOG were identified after ozonation (at 0.5, 1, 2, 3, 4, 6, 12 and 18 hours). The wastewater used for the experiment was collected from a wastewater discharge tank, found in colloid condition. Before treatment, the organic contents from the wastewater varied due to different training activities each day. In order to normalize the results from different test conditions, the removal percentage will be used for discussion**.**

The results from the ozonation experiment of fire extinguisher wastewater showed that ozone reacted on organic contaminants. The reactions varied with pH condition and ozone dosages. Adjusting pH of FEW to acid and base conditions gave similar results. Higher removal or organic contents was achieved at pH condition of raw wastewater (pH 7**).** The reduction of organic contents in the forms of COD are shown in Figures 9 - 10, BOD_5 in Figure 11 - Figure 12 (BOD_5), FOG in Figure 13 - Figure 14 and TOC in Figure 15 - 16.

3.1 Effects of ozonation on COD Reduction

With increased ozonation time, there was a tendency toward decreased COD; although, in some cases, the values increased with ozonation time.

At different pH levels, initial COD were not equivalent. The results of removing COD are shown in Figure 9. It was apparent that pH adjustment significantly reduced initial wastewater COD. The wastewater in raw pH (pH 7) contained the highest initial COD (11,410 mgCOD/L). Adjusting to pH 3 and pH 13 (pH13), COD was lowered to 6,520 mgCOD/L and 3,605 mgCOD/L, respectively). The pH adjustment removed COD as much as 43% and 38% in pH 3 and pH 13 wastewater, respectively.

The COD was removed most effectively at the pH of raw wastewater (pH 7) as compared to pH 3 and pH 13.

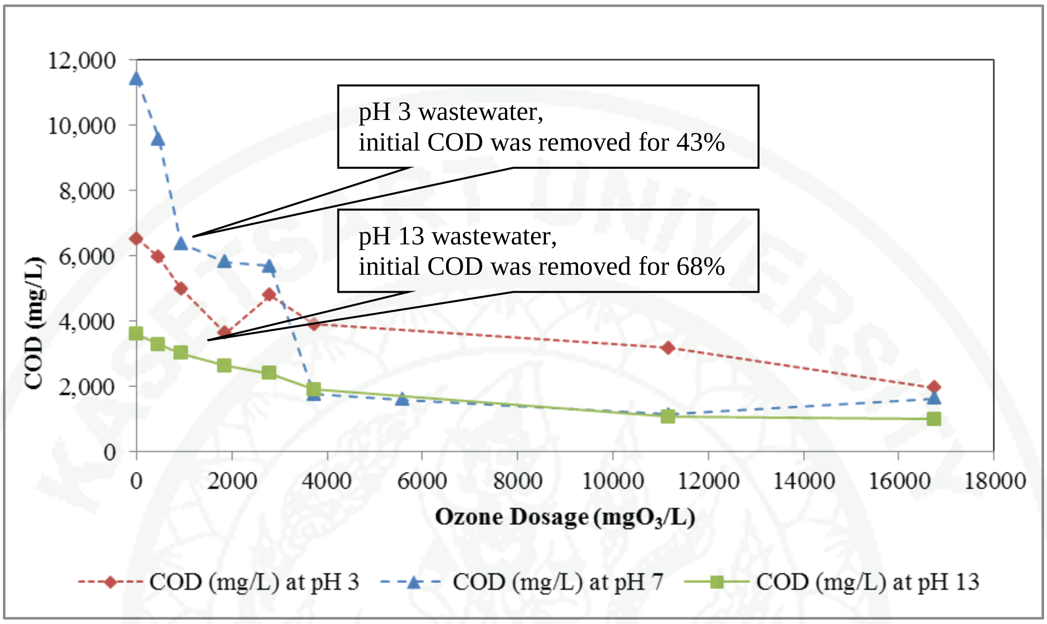


Figure 9 COD in FEW after ozonation at pH 3, pH 7 and pH 13

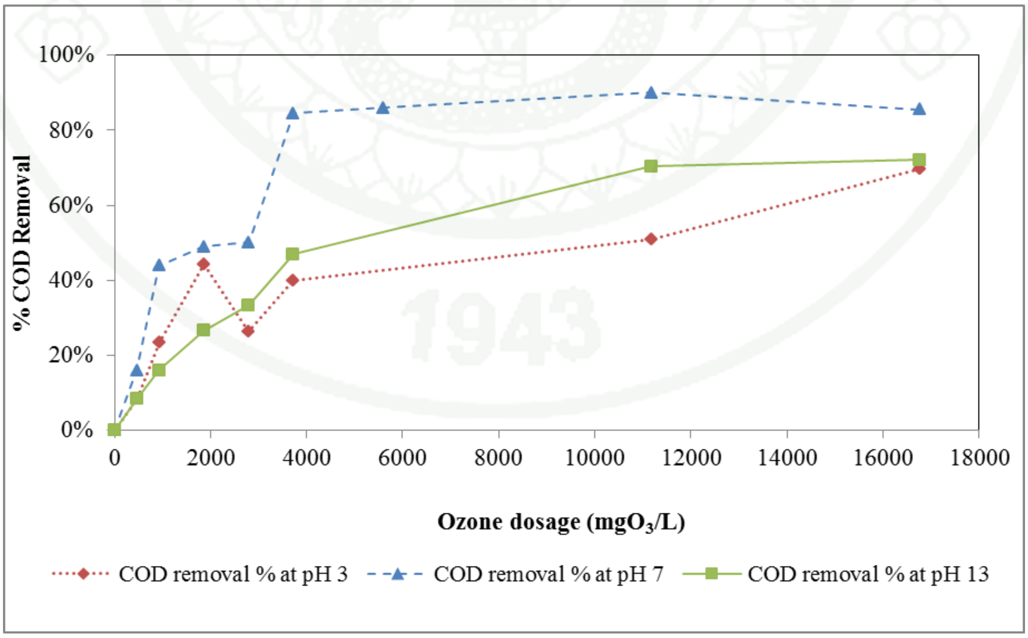


Figure 10 COD removal percentage in FEW by ozonation at pH 3, pH 7 and pH 13.

The percentage of COD removed increased significantly in the first 2 hours (1,862 mgO_3/L) of ozonation. Comparing the results at each of the three pH values, the highest removal percentage was achieved at pH 7 after 4 hours (3,724 mgO_3/L) of ozonation, followed by pH 13 and pH 3 wastewater (84%, 47% and 40%, respectively).

After 4 hours, FEW continued to be treated by ozone. The results show no further COD removal in raw wastewater. At pH 13, removal percentage slightly increased during 4-12 hours (3,724 mgO_3/L to 11,172 mgO_3/L) from 47% to 70%. It increased slightly to 72% at 18 hours treatment (16,757 mgO_3/L). While at pH 3, COD reduction continuously reduced at a slower rate reaching 69% removal after 18 hours (16,757 mgO_3/L) of ozonation.

In conclusion, COD in wastewater was removed after ozonation at all 3 pH studied. The removal percentage varied by ozone dosage and the rate was higher at the earlier treatment stage. After 2 hours (1,862 mgO_3/L), the removal efficiency decreased. Removal percentage at pH 3 and 13 increased to 60% and 69%, respectively, after 18 hours of ozonation (16,757 mgO_3/L). The increased dosage at the later stage had a slight affect at pH 7. However, combining the pH adjustment affect with COD removal, COD removal percentage reached 68% after 2 hours treatment (1,862 mgO_3/L) as compared to the raw wastewater. At pH 13, the combined pH adjustment affect and ozonation remove COD by 77% after 2 hours of treatment (1,862 mgO_3/L) as compared to the raw wastewater.

The results of this experiment regarding COD removal were consistent with a study of ozonation on polycyclic aromatic hydrocarbon wastewater conducted by Kornmüller and Weismann (2002), where pH 7 was the most favorable condition.

3.2 Effects of ozonation on BOD reduction

Biodegradability, represented by BOD_5, was observed, as the affect of pH was apparent. The results of BOD_5 removal of fire extinguisher wastewater are shown in Figure 11.

The initial wastewaters' BOD_5 at various pH levels were unequal. The raw wastewater (pH 7) had the highest initial BOD_5 (3,090 $mgBOD_5/L$). Acid (pH 3) wastewater and base (pH 13) wastewaters had lower initial BOD_5 (960 mg BOD_5/L and 630 mg BOD_5/L respectively). It was also noted that pH adjustments (at pH 3 and pH 13) significantly reduced wastewater BOD by as much as 80% and 69%, respectively.

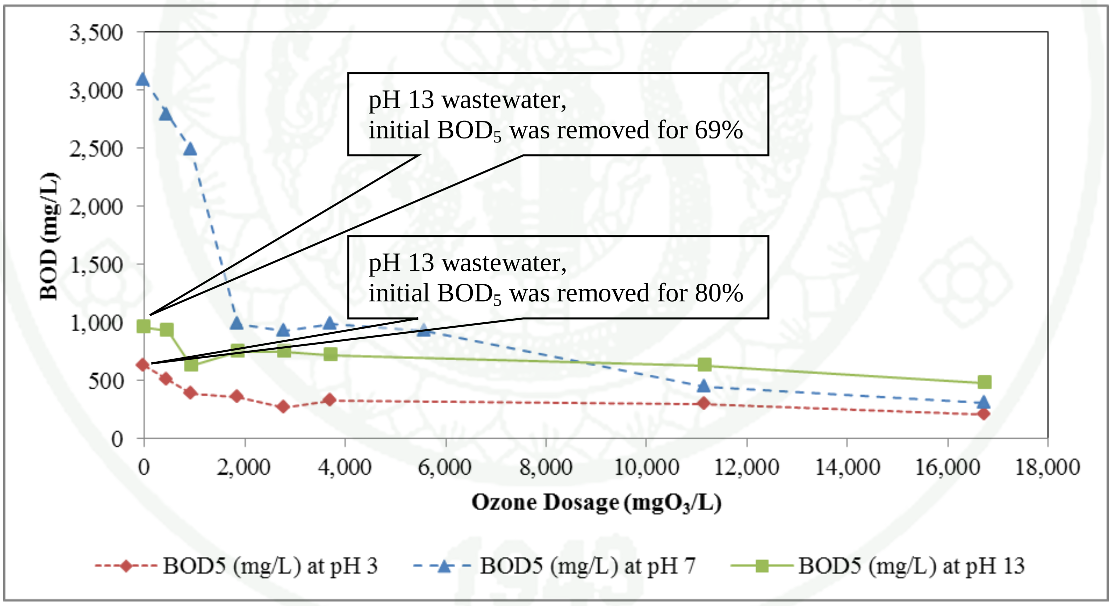


Figure 11 BOD_5 in FEW after ozonation at pH 3, pH 7 and pH 13

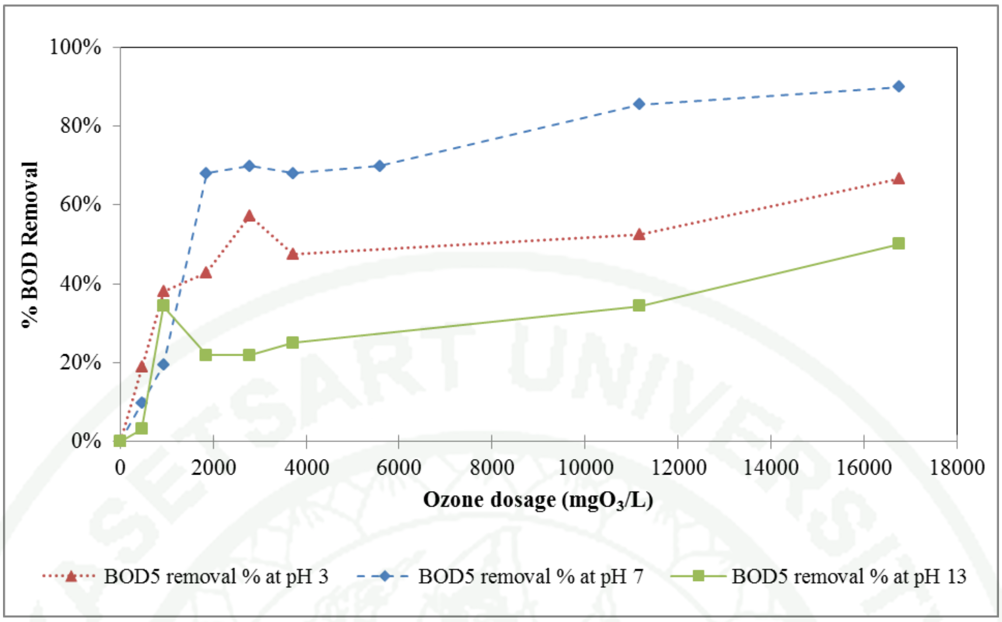


Figure 12 BOD$_5$ removal percentage in FEW by ozonation at pH 3, pH 7 and pH 13.

Figure 12 shows wastewater BOD$_5$ removal percentage at pH 3, pH 7 and pH 13. Removal of BOD was slightly different from COD. Within the first 30 minutes of ozonation (465 mgO$_3$/L), pH 13 showed better removal results. 34% BOD removal was achieved at pH 13, with 20% and 10% removal at pH 3 and pH 7, respectively.

However, after adding ozone for 1 hour (931 mgO$_3$/L), BOD$_5$ removal percentage at pH 7 became higher than pH 3 and pH 13 wastewater. At the completion of the experiment (after 18 hours, 16,757 mgO$_3$/L), 90% of BOD$_5$ was removed at pH 7. Further removal percentages showed 59% and 50% at pH 3 and pH 13, respectively.

In conclusion, BOD$_5$ in FEW was removed after ozonation at all 3 pH value. The removal percentage varied by ozone dosage. Optimal time for ozonation was determined at 2 hours (1,862 mgO$_3$/L) for BOD$_5$ removal. The removal of 49%, 44% and 27% was achieved at pH 7, pH 3 and pH 13, respectively; however, combining the pH adjustment affect with BOD removal found that pH 3 wastewater achieved the highest BOD removal. At pH 3, wastewater BOD removal percentage reached 90% after a 4-hour treatment (3,724 mgO_3/L) compared to raw wastewater. At pH 13, the pH adjustment/ozonation affect helped in a 77% BOD removal after a 4-hous treatment (3,724 mgO_3/L), as compared to the raw wastewater.

The dosage increase at the later stage (from 3 to 18 hours or 1,862 mgO_3/L to 16,757 mgO_3/L) resulted in a slight increase of BOD removal. At the end of the test period (18 hours), 16,757 mgO_3/L with wastewater at pH 7 saw BOD reduction by 90%. Reduction at pH 3 and 13 was only 67% and 50% at the end of experiment. The BOD removal results from this experiment agreed with results of an ozonation study on polycyclic aromatic hydrocarbon (benzo[a]pyrene) wastewater conducted by Zeng *et al*. (2000), where pH 7 was the most favorable condition in BOD removal of 85%.

Compared to COD, BOD was also reduced with a high rate in the early ozonation stage. The optimal condition in BOD was found at the same ozone dosage as COD removal, which was 1,862 mgO_3/L (2 hours). In terms of pH, raw wastewater (pH 7) had the highest reduction in both COD and BOD_5.

As mentioned earlier, COD and BOD_5 were reduced significantly with pH 3 and pH 13 level adjustments. Previous studies also found similar results. For example, Li *et al*. (2006) discovered that with pH 10 adjustments, applying NaOH to oily wastewater from oil fields showed similar findings. COD reduced by 23% after pH adjustment. Another study found that with *p*-chlorophenol in an aqueous solution, a pH 2.0 - 8.0 adjustment reduced COD before treatment process.

3.3 Effects of ozonation on FOG Reduction

FEW FOG reduction by ozonation at various pH levels can be found in Figure 13. Initial concentrations of FOG at all three pH values were not significantly different. Raw wastewater pH (pH 7) had the highest initial FOG (150 mgFOG/L). Base pH 13 and pH 3 wastewaters have lower initial FOG at 140 mgFOG.

FOG Removal percentages of FEW are shown in Figure 14. Within the early ozonation stage (from 0 to 2 hours), FOG removal percentage at pH 3 was the highest (64%) among tested pH wastewater. Removal of FOG at pH 7 increased slightly (from 7% to 20%) at 0.5 hour (465 mgO_3/L) and 1 hour (931 mgO_3/L). After 2 hours (1,862 mgO_3/L) of treatment, the efficiency of FOG removal increased significantly -- up to 47% at 4 hours of treatment (3,754 mgO_3/L).

After 18 hours of ozonation (15,757 mgO_3/L), pH 7 wastewater achieved the highest removal efficiency at 66% when FOG wastewater treatment in pH 3 and pH 13 efficiency were both 57%.

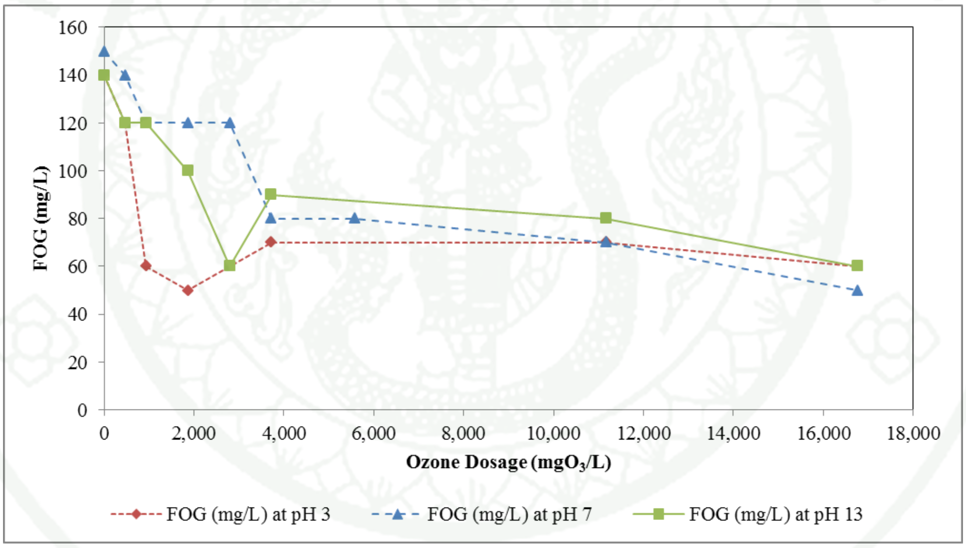


Figure 13 FOG in FEW after ozonation at pH 3, pH 7 and pH 13

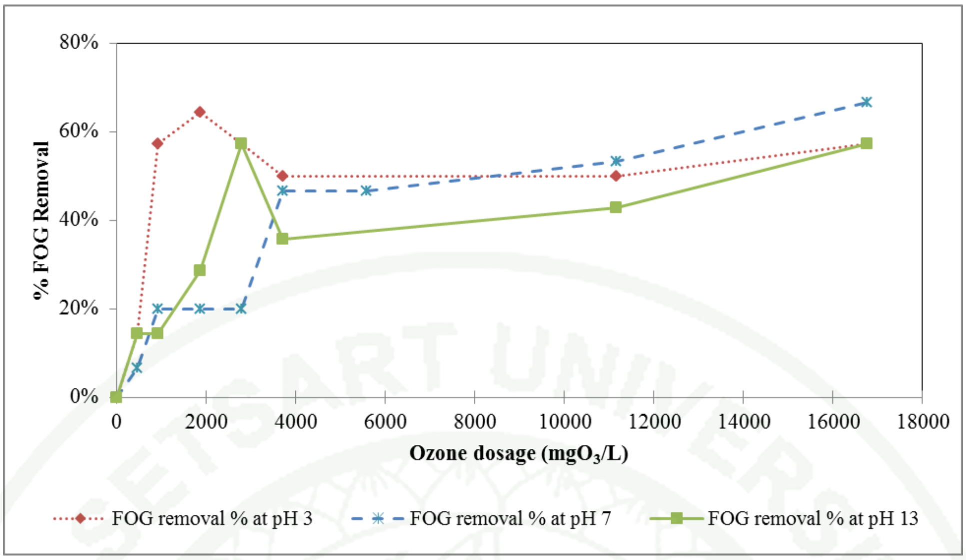


Figure 14 FOG removal percentage in FEW by ozonation at pH 3, pH 7 and pH 13

In conclusion, similar to COD and BOD, FOG was also removed by ozonation. FOG could be slowly removed while a significant portion remained after ozonation. Effect of pH on FOG removal was not as clear as those on COD and BOD_5. Great portions of FOG were removed at 4 hour ozonation time with 50%, 47% and 36% removal at pH 3, 7 and 13, respectively. By the end of test period with dosage of 16,757 mgO_3/L, removal increased to 57%, 67% and 57% at pH 3, 7 and 13, respectively. It should be noted that the 4 hours ozonation (3,724 mgO_3/L) was the most efficient for organic contaminant removal; further increase in dosage had only slight effect on the removal of FOG.

3.4 Effects of ozonation on TOC

The result of TOC removal of FEW is shown in Figure 15. Ozonation had some treatment affect on TOC in wastewater – the removal percentage is shown in Figure 16. After 18 hours (16,757 mgO_3/L) of ozone treatment, the highest TOC removal percentage was observed at pH 3 (46%), followed by pH 13 at 27% and raw wastewater (pH 7) at 18%.

At all 3 pH values, the most significant amounts of TOC were removed within the first 4 hours of ozone treatment (3,724 mgO_3/L). After 4 hours, no noticeable increase in treatment removal could be observed. TOC, unlike other organic contents, was not significantly reduced from wastewater ozonation. Considering only the removal of the TOC, there is no advantage in adding ozone to the process. However, when observing the overall time of TOC removal, there was some apparent affect from ozonation.

BOD was removed rapidly in the early stage (within 2 hours) of ozonation to account for the different results of TOC to BOD_5 removal efficiency. Rapid mineralization occurred forming ozonated byproducts during this period of the process, most of which were organic acids that were difficult to oxidize. Therefore, TOC in FEW was not effectively removed by ozonation like BOD_5. Similar observations were reported in the Chang (2008) study during the ozonation experiment with coke-oven wastewater.

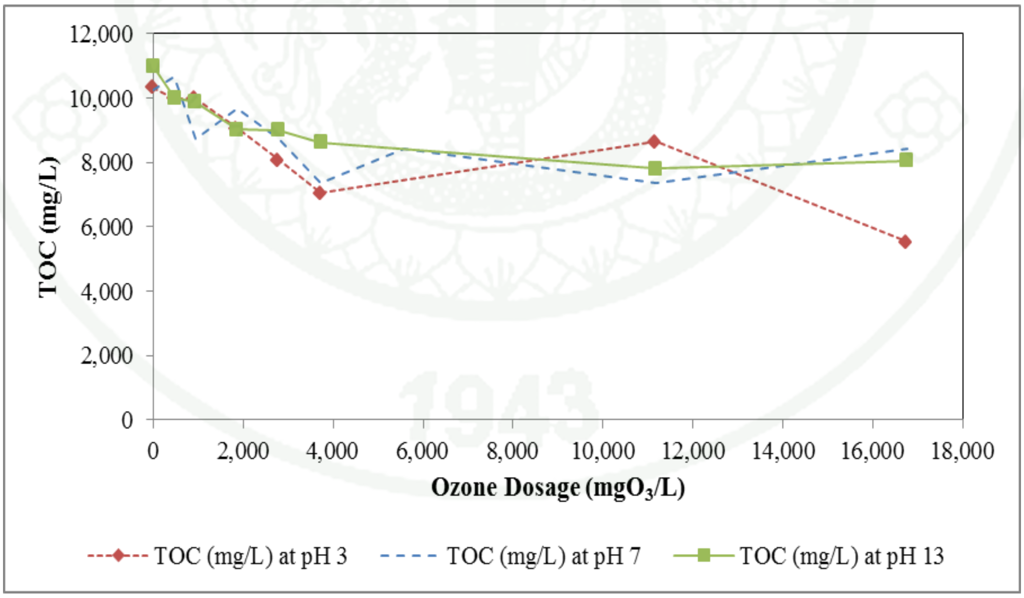


Figure 15 TOC in FEW after ozonation at pH 3, pH 7 and pH 13

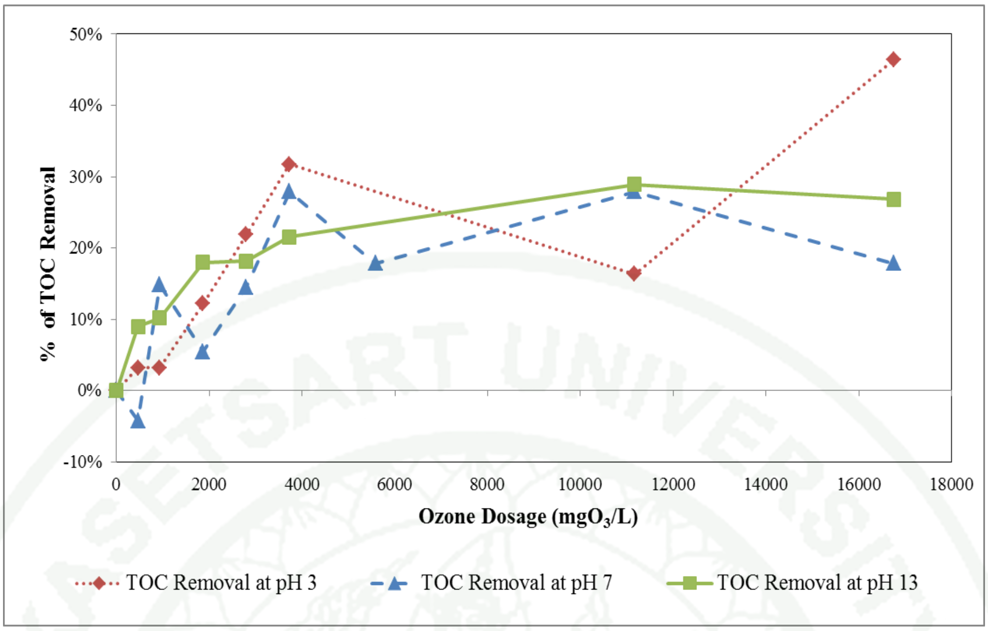


Figure 16 TOC removal percentage in FEW by ozonation at pH 3, pH 7 and pH 13

3.5 Comparison of ozonated wastewater with TPCD standard for the industrial effluent

Table 17 shows the comparison of organic contents treated for 18 hours (end of experiment, equivalent to ozone dosage at 16,757 mgO$_3$/L) with the Standards for Industrial Effluent for Factory Group II and III set by Thailand Pollution Control Department (TPCD). COD, BOD$_5$, FOG and TOC of the samples were relatively high. After ozonation treatment for 18 hours (16,757 mgO$_3$/L), none of the organic contents measured in this experiment (BOD$_5$, COD, TOC, and FOG) met the standard.

Table 17 COD, BOD$_5$, FOG and TOC reduction by ozonation after 16,757 mgO$_3$/L (18 hours of treatment)

Organic Contents		pH 3	pH 7	pH 13	TPCD Standard
COD	Before	6,520	11,410	3,605	120
(mg/L)	After	1,975	1,640	1,005	
	Removal Percentage	70%	86%	72%	
BOD$_5$	Before	630	3,090	960	20
(mg/L)	After	210	310	480	
	Removal Percentage	67%	90%	50%	
TOC	Before	10,330	10,240	11,000	-
(mg/L)	After	5,540	8,410	8,050	
	Removal Percentage	46%	18%	27%	
FOG	Before	140	150	140	5
(mg/L)	After	60	50	60	
	Removal Percentage	57%	67%	57%	

Table 18 shows the comparison of organic contents treated for 4 hours (end of experiment, equivalent to ozone dosage at 3,724 mgO$_3$/L) with the Standards for Industrial Effluent for Factory Group II and III set by Thailand Pollution Control Department (TPCD). It was found that the removal percentage of COD and BOD$_5$ at this stage has removal percentages as high has 85% and 68% at pH 7. It can be observed that further treatment did not have significant impact on organic content removal. Thus, a 4-

hour treatment (3,724 mgO_3/L) confirmed the optimal condition -- FEW treatment by ozonation.

Table 18 COD, BOD_5, FOG and TOC reduction by ozonation after 3,724 mgO_3/L (4 hours of treatment)

Organic Contents		**pH 3**	**pH 7**	**pH 13**	**TPCD Standard**
COD (mg/L)	Before	6,520	11,410	3,605	120
	After	3,915	7,380	1,910	
	Removal Percentage	40%	85%	47%	
BOD_5 (mg/L)	Before	630	3,090	960	20
	After	330	990	720	
	Removal Percentage	48%	68%	25%	
TOC (mg/L)	Before	10,330	10,240	11,000	-
	After	7,050	7,380	8,630	
	Removal Percentage	32%	28%	22%	
FOG (mg/L)	Before	140	150	140	5
	After	70	80	90	
	Removal Percentage	50%	47%	36%	

4. Affect of ozonation on biodegradability (BOD_5 per COD ratio)

The BOD_5/COD ratio reflects biodegradability of the sample. A BOD_5/COD ratio of 0.4 is generally considered the lower threshold of biodegradability. Domestic wastewater typically has a BOD_5/COD ratio between 0.4 and 0.8 (Tchobanoglous *et al*., 1985). The results of ozonation on BOD_5/COD in Figure 17 show an affect on FEW biodegradability, dependent upon pH condition and ozone dosage. Because the ratio was similar to dosages over 2,793 mgO_3/L, dosage remains only a partial affect to the overall result. At pH 7, where the removal percentage was the highest, biodegradability was also improved with a ratio change from 0.2 to 0.6. At pH 13, the FEW ratio increased slightly from 0.2 to 0.6; however, no marked change in the ratio was observed at pH 3. The increase in BOD/COD ratio over time thus showed that proper ozonation could improve FEW biodegradability.

Gilbert, E. (1987) performed an ozonation treatment on substituted aromatic substances and Contreras, S. *et al*. (2003) performed an ozonation treatment on aqueous solutions of 2,4-dichlorophenol. Both found biodegradability improvement. Therefore, this study was agreeable with the results of previous studies by Gilbert, E. (1987) and Contreras, S. *et al*. (2003).

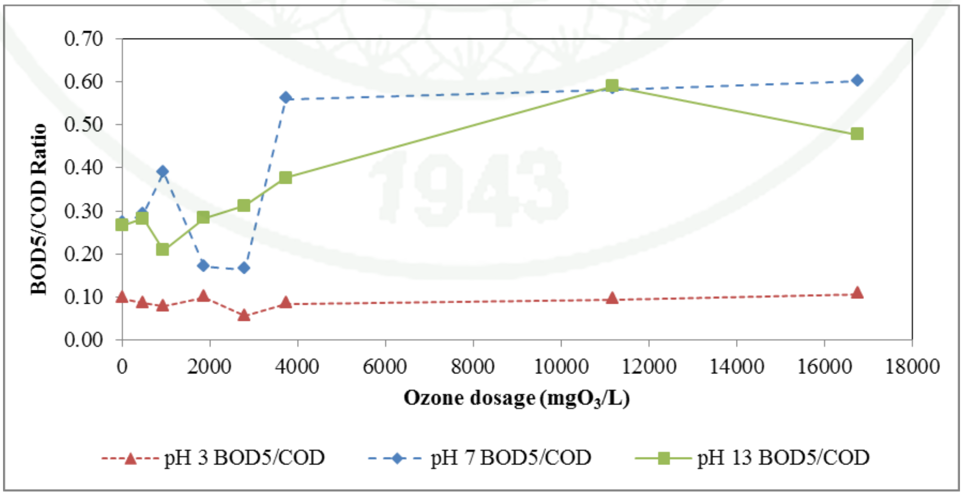


Figure 17 Changes in BOD_5/COD during ozonation of FEW at pH 3, pH 7 and pH 13

5. Ozone consumption on FEW treatment

To evaluate the affect of ozone in FEW treatment, the amount of ozone used per COD removed ($mgO_3/mgCOD$) was analysed. Figure 18 illustrates the efficiency of ozone on oxidizing organic compounds. This shows that ozonation, at the earlier stage, with less ozone dosage, removed the same amount of mgCOD. An increase in ozone dosage resulted in a less efficient removal.

Considering the affect of pH, pH 7 gave the lowest consumption rate (ranging from 0.25 – 1.72 $mgO_3/mgCOD$). At pH 3, a higher consumption rate of 0.84 – 3.69 $mgO_3/mgCOD$ was encountered. At pH 13, consumption was the least with a rate ranging between 1.33 - 3.45 $mgO_3/mgCOD$.

The ratio of ozone consumed to COD eliminated (mgO_3 per mgCOD) was an important parameter in evaluating the feasibility of the ozonation process. The optimal condition of this experiment was identified at the early stage. In the first 4 hours of treatment (3,724 mgO_3/L), ozone was used effectively to remove COD. An increase in ozone dosage resulted in a less efficient removal, afterwards. The optimal time of ozonation on FEW, therefore, was at the earlier stage (4 hours of treatment or 3,724 mgO_3/L).

Wu., D. *et al*. (2012) performed ozonation on bamboo industrial wastewater (at pH 7). They found the ratio to be higher than this study at 2.8 to 3.9 $mgO_3/mgCOD$.

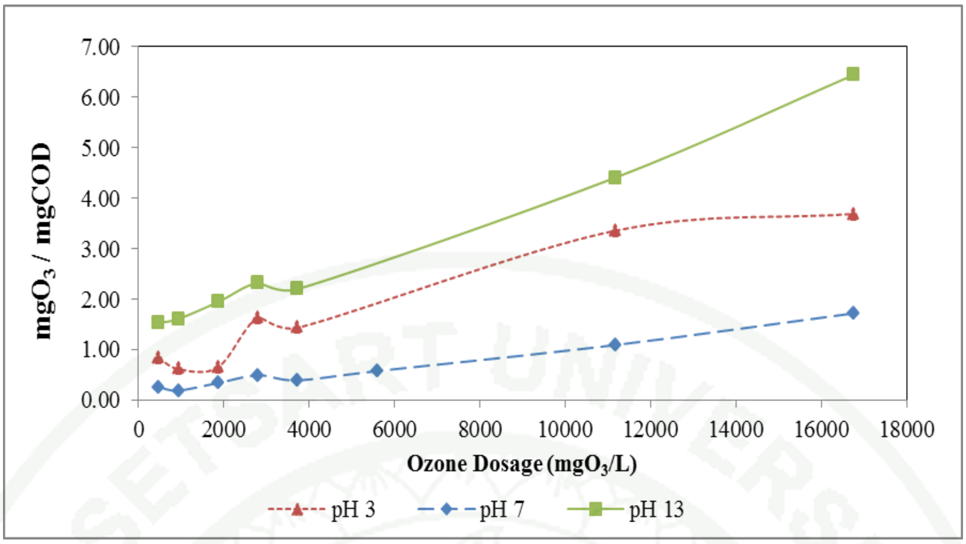


Figure 18 Ozone consumption on COD removal ($mgO_3/mgCOD$) in ozonation of fire extinguisher wastewater

6. Affect of ozonation on pH

Figure 19 indicates that the ozonation did not significantly affect the pH of wastewater during treatment (at pH 7 or 13). However, wastewater (at pH 3), which had direct oxidation reactions with ozone, presented a slight decrease of pH after introducing ozone into the reaction system. Lucus, M. (2009) found that winery wastewater decreased marginally in pH through ozonation (from pH 4 to pH 3.5). The reduction in pH is attributed to the formation of dicarboxylic acids, small molecule organic acids, CO_2 and carbonic acid from total mineralization.

The reaction of ozone with hydroxyl anions and degraded oxidized hydroxyl radical (usually carboxylic acids) byproducts resulted in pH decrease (pH 3). This was more evident in the initial phase of the process due to greater ozone consumption. (Ulson de Souza. *et al*. (2010)).

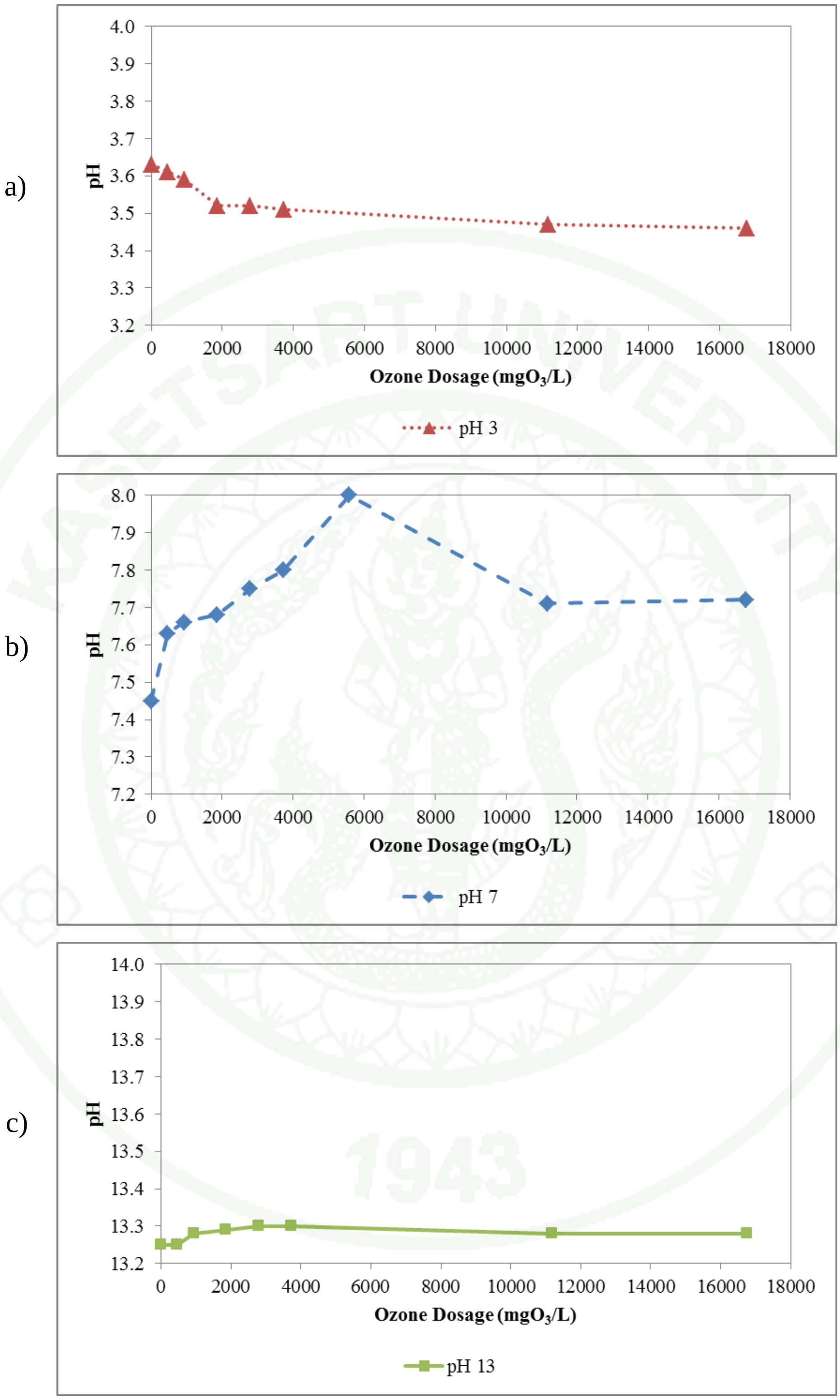


Figure 19 pH values during ozonation at various conditions, a) pH 3, b) pH 7 and c) pH 13

7. Affect of ozonation in color removal

The wastewater sample, presenting an oil colloid, was initially black in color exuding a burnt oil aroma. The change in sample color observed during the experiment is shown in Appendix Figure C1. While a color test was not performed, wastewater de-colorization was noticeable at each pH level.

A previous study on dye concentration, by Konsowa *et al*. (2009), found that where ozone concentration increased over time from 9.61 - 17.02 g/m^3 (ppm), the de-colorization time (of 300 ppm) reduced by approximately 41.07%. Additionally, Wu *et al.* (2012) found that bamboo wastewater color was reduced by 95% after treatment with 3.15 gO_3/h over 25 minutes.

CONCLUSION AND RECOMMENDATION

Based on the analysis of the Results and Discussion, the following set of conclusions and recommendations were derived.

Conclusions

The fire extinguisher wastewater (FEW) was treated under different pH values (pH 3, pH 7 and pH 13) during varying time periods ranging from 0 to 18 hours (0 to 16,757 mgO_3/L). Results have proven that ozonation, under proper conditions and by different organic content tests (BOD, COD, TOC and FOG), can treat FEW ERTC at all three pH conditions. BOD_5 achieved the highest removal, with COD and FOG following. Removal levels for TOC were inconclusive during this experiment. Additionally, color removal was observed.

The removal percentages associated with various parameters identify the optimum condition for ozone treatment. A neutral pH of raw FEW (pH7) was found to give the best treatment results. As much as 86% COD removal could be achieved at pH of 7 with 16,757 mgO_3/L (18 hours of treatment). Although, COD of treated FEW (1,640 mgCOD/L) was still higher than the PCD established limit. BOD was reduced by 90% at the same condition. The BOD_5:COD ratio change, from 0.27 to 0.60 at pH 7, suggests that it is a significant improvement on biodegradability of ozonated treated FEW.

The highest ozone consumption of FEW was at pH 7 with a ratio ranging from 0.25 to 1.72 $mgO_3/mgCOD$. The earlier stage of treatment (4 hours = 3,724 mgO_3/L) achieved more efficient COD removal. For this reason, it can be determined that the optimum condition for the ozonation treatment of wastewater was at pH 7. Its optimum treatment efficiency occurred at 4 hours of treatment.

Recommendations

1. Ozonation is an effective and economically viable treatment of fire extinguisher wastewater (FEW). Pre-treatments are recommended for ozonation in order to achieve PCD standards, such as Dissolved Air Flotation, chemical treatment, trickling filter and activated sludge. Post-treatment recommendations include filtration, UV, and chemical treatment (Chlorine).

2. The combination of ozone and various types of oxidants should be considered. Further studies of ozonation with various types of catalysts should also be pursued.

3. Increasing the ozone production rate reduces experimental time (via an ozone generator).

4. Prior to production-scale implementation, pilot-scale experiments should be pursued with various initial COD.

5. Analysis of organic compounds, products of ozonation, should be investigated to determine ozone efficiency and to confirm non-toxic products generation. These can additionally be applied to industrial wastewater treatment.

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APPENDICES

Appendix A

Ozone production (mg/L) with OZO-MAC determination by Wet Chemistry

Potassium Iodide method, titrated with 0.1 N $Na_2S_2O_3$

Appendix Table A1 Ozone Dosage Determination from the Ozo-MAC CW 300 L Ozone Generator

Test #	Normality of sodium Thiosulfate	Sodium Thiosulfate in Trap A	Sodium Thiosulfate in Trap B	Time (min)	Ozone mg/hour
1	0.1	120.0	5	20	900
2	0.1	132.0	3	20	972
3	0.1	129.0	2	20	943.2
4	0.1	131.0	5	20	979.2
5	0.1	134.0	0	20	964.8
6	0.1	116.0	5	20	871.2
7	0.1	133.0	5	20	993.6
8	0.1	126.0	4	20	936
9	0.1	115.0	0	20	828
10	0.1	127.0	0	20	914.4
11	0.1	135.0	1	20	979.2
12	0.1	124.0	3	20	914.4
13	0.1	131.0	0	20	943.2
14	0.1	131.0	4	20	972
15	0.1	120.0	4	20	892.8
16	0.1	130.0	5	20	972
17	0.1	123.0	0	20	885.6
18	0.1	135.0	1	20	979.2
19	0.1	115.0	2	20	842.4
20	0.1	130.0	0	20	936
Average		**126.9**	**2.5**	**20.0**	**931.0**

Appendix B

Analytical parameter of ozonation treatment in pH 3 (acid),
pH 7 (neutral) and pH 13 (base) wastewater.

Appendix Table B1 Effect of Ozone Treatment in pH 3

Treatment (hr)	**pH**	**BOD$_5$ (mg/L)**	**COD (mg/L)**	**TOC (mg/L)**	**FOG (mg/L)**
Method	**Meter**	**Azide Modification Method**	**Photometric Method**	**Photometric Method**	**Partition-Gravimetric Method**
No Treatment	3.63	630	6,520	10,330	140
0.5	3.61	510	5,965	10,000	120
1	3.59	390	4,995	10,000	60
2	3.52	360	3,635	9,070	50
3	3.52	270	4,805	8,070	60
4	3.51	330	3,915	7,050	70
12	3.47	300	3,190	8,640	70
18	3.46	210	1,975	5,540	60

Appendix Table B2 Effect of Ozone Treatment in pH 7

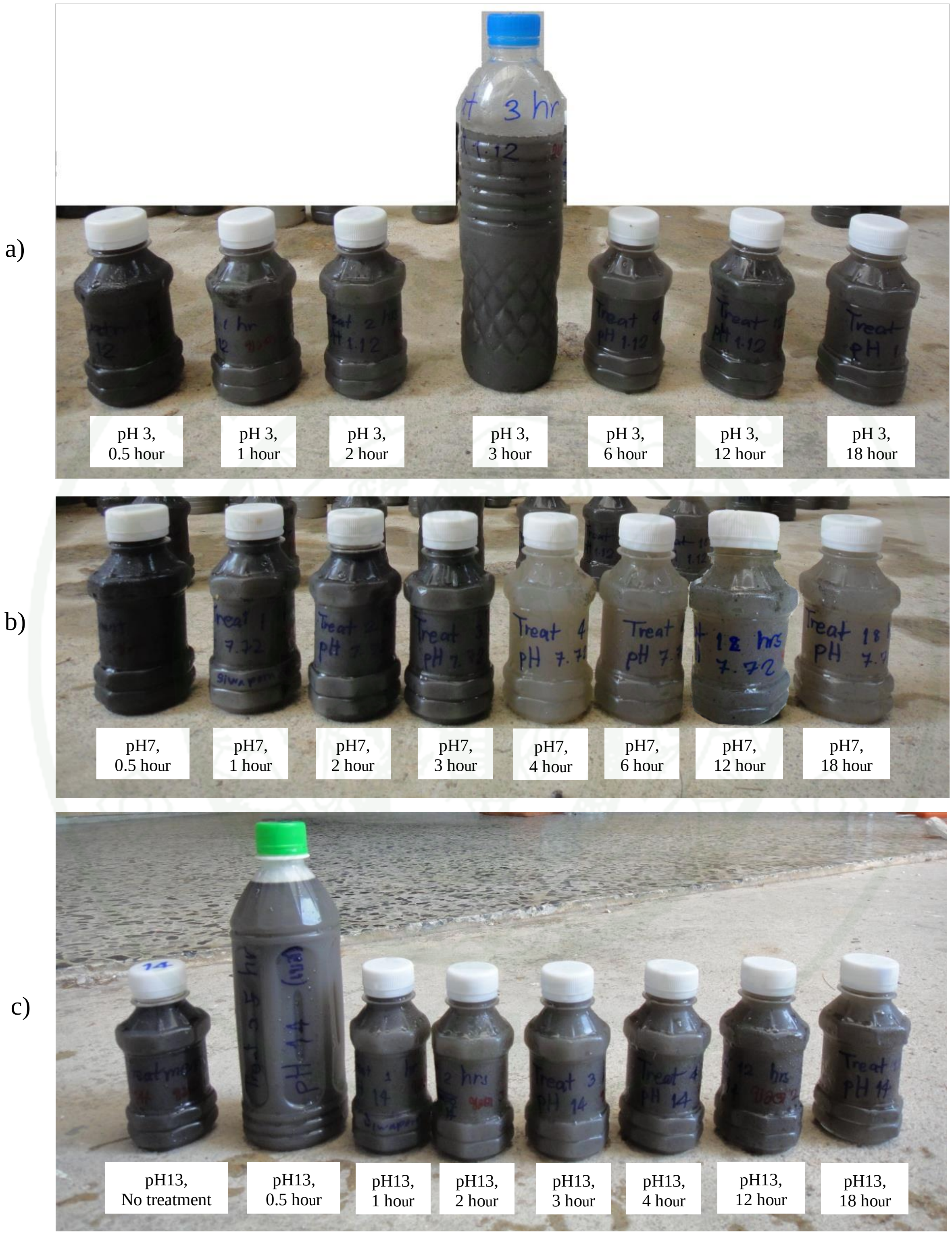
Treatment (hr)	**pH**	**BOD_5 (mg/L)**	**COD (mg/L)**	**TOC (mg/L)**	**FOG (mg/L)**
Method	**Meter**	**Azide Modification Method**	**Photometric Method**	**Photometric Method**	**Partition-Gravimetric Method**
No Treatment	7.45	3,090	11,410	10,240	150
0.5	7.63	2,790	9,570	10,670	140
1	7.66	2,490	6,390	8,720	120
2	7.68	990	5,820	9,680	120
3	7.75	930	5,690	8,750	120
4	7.80	990	1,770	7,380	80
6	8.00	930	1,600	8,410	80
12	7.71	450	1,141	7,380	70
18	7.72	310	1,640	8,410	50

Appendix Table B3 Effect of Ozone Treatment in pH 13

Treatment (hr) Method	**pH Meter**	**BOD$_5$ (mg/L) Azide Modification Method**	**COD (mg/L) Photometric Method**	**TOC (mg/L) Photometric Method**	**FOG (mg/L) Partition-Gravimetric Method**
No Treatment	13.25	960	3,605	11,000	140
0.5	13.25	930	3,300	10,010	120
1	13.28	630	3,025	9,880	120
2	13.29	750	2,645	9,020	100
3	13.30	750	2,400	9,000	60
4	13.30	720	1,910	8,630	90
12	13.28	630	1,070	7,820	80
18	13.28	480	1,005	8,050	60

Appendix C

Wastewater after ozonation treatment by pH



Appendix Figure C1 Color of wastewater in each acidity condition, a) pH 3 wastewater, b) pH7 wastewater and c) pH 13, found after ozonation with different time

Appendix D

Organic content reduction by ozonation in different pH

Ozonation experiments were carried out on raw wastewater with initial pH states (pHs = 3,7 and 13) to investigate the transformative affect of BOD, COD, TOC and FOG removal. The degradation of organic matter within wastewater may occur by direct reaction with molecular ozone at pH 3. Ozone decomposition of highly reactive radical species also takes place at pH 7 and 13 (Hoigne and Bader 1976).

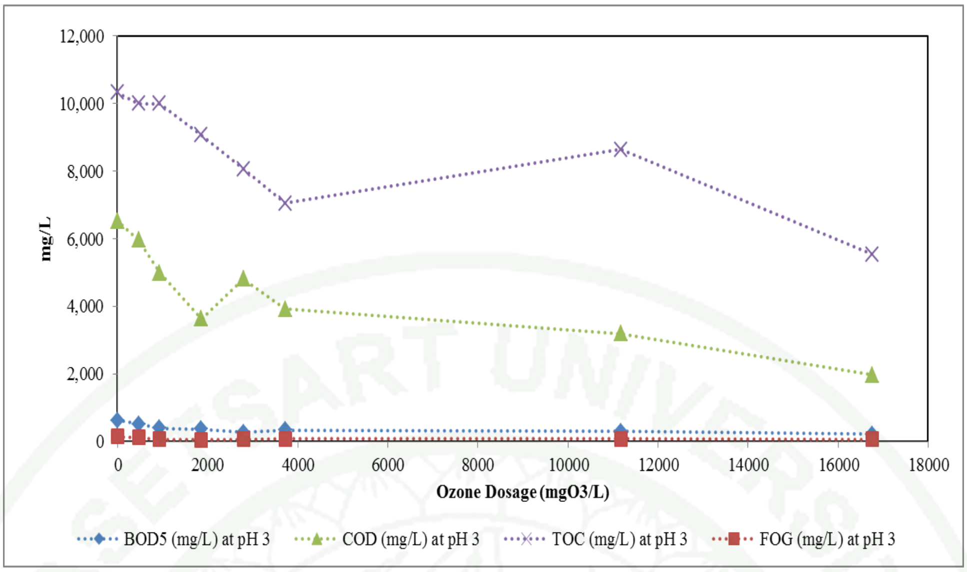
1. Organic contents reduction by ozonation in pH 3

For initial pH 3, ozonation results are shown, in Appendix Figure D1 and Appendix Figure D2, by treatment of acidic wastewater at different rates. The analysis can be separated into two periods, the early stage (0-3,724 mg$O_{3,}$ between 0-4 hours) and the later stage (3,724 – 16,757 mgO_3/L, after 4 hours).

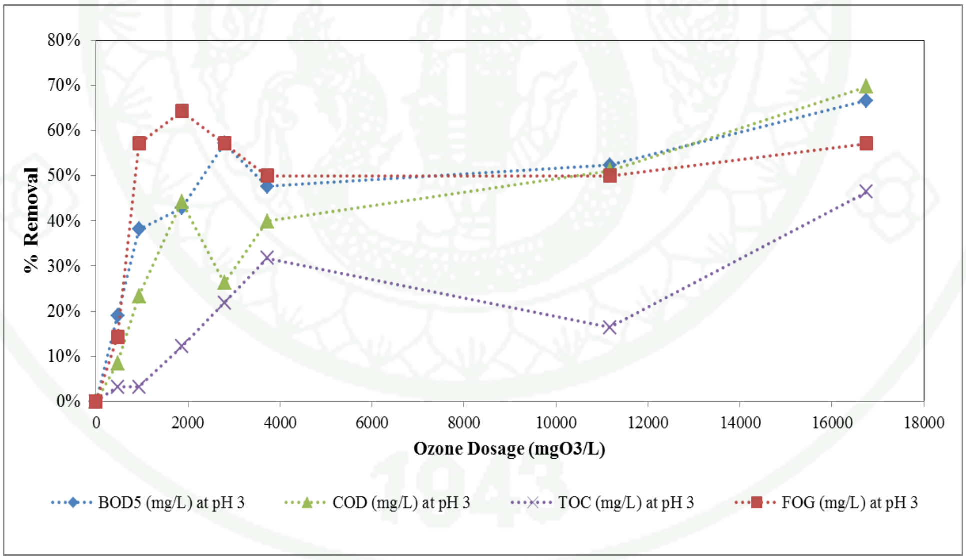
In the early stage, the BOD_5 removal capacity increased, after treatment, to 465 mgO_3, while COD removal percentages continue from 465 mgO_3, 931 mgO_3 and 1,862 mgO_3. Some transitioning of BOD_5, COD, TOC and FOG removal occurred in this stage.

After 4 hours of 3,724 mgO_3, wastewater ozonation continued. Figure 15 illustrates that the removal percentage increased as more ozone entered into the system. This implies that the removal capacity is relatively proportional to the amount of ozone entering into the experimental system. Removal percentage of BOD_5, COD, TOC and FOG are at 59%, 61%, 46% and 57%, respectively.

As a percentage of removal, COD (60%) presented the highest when compared to BOD_5 (59%), FOG (57%) and TOC (46%). Appendix Figure D2 does indicate later TOC removal beyond the 18-hour experiment window.



Appendix Figure D1 BOD$_5$, COD, TOC and FOG Removal by mg/L in pH 3 wastewater



Appendix Figure D2 BOD$_5$, COD, TOC and FOG Removal Percentage in pH 3 wastewater

2. Organic contents reduction by ozonation in pH 7

pH 7 is the raw condition of fire extinguisher wastewater. The ozone treatment result is shown in Appendix Figure D3 and the percentage of removal is shown in Appendix Figure D4.

The graph shows that removal percentage on the BOD_5 started from the beginning of treatment, when first measurement at 465 mgO_3/L, 931 mgO_3 and 1,832 mgO_3. When 1,862 mg of ozone was given to the system, removal capacity of BOD_5 increased the most (increased from 19% to 68%). The treatment ability still continued when continued on the ozonation treatment.

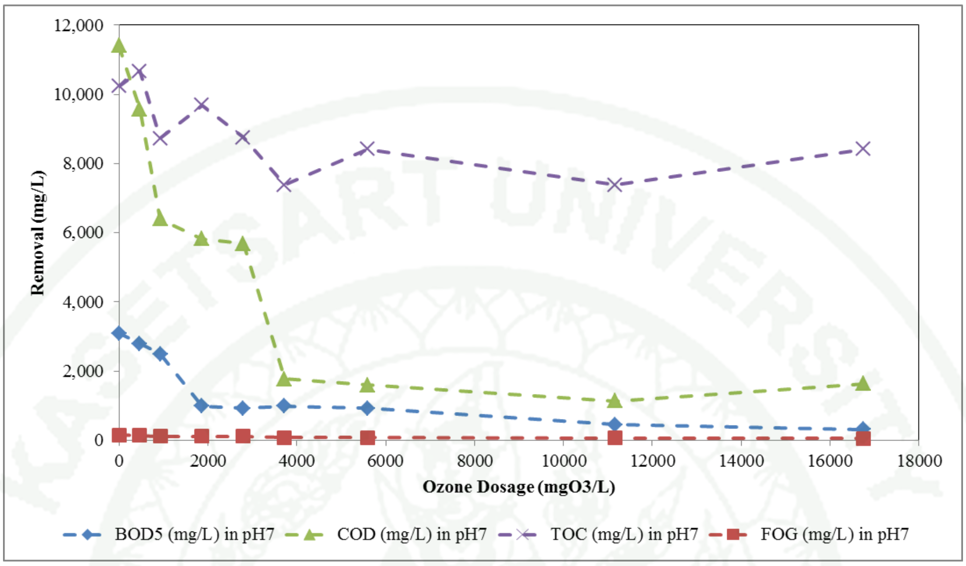
COD removal had the same removal capacity as BOD_5, the removal percentage increased since the early stage of treatment from 465 mgO_3/L, 931 mgO_3/L, 1,832 mgO_3/L, 2,793 mgO_3/L and 3,724 mgO_3/L (increasing from 16% COD removal at 465 mgO_3/L to 85% at 3,724 mgO_3/L).

Ozonation treatment to TOC in the sample wastewater result was not as high as other parameters. Some TOC increasing were found at the first 4 hours of the experiment while ozonation with 3,724 mgO_3/L (4 hours) resulted in the most optimum condition of removal capacity.

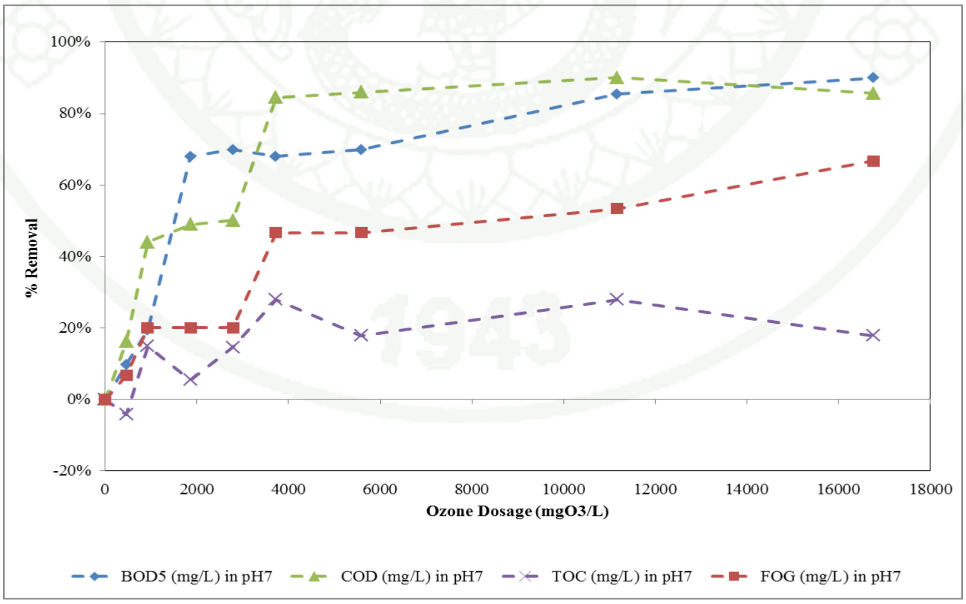
FOG removal was also measured after the wastewater was treated by ozone. The treatment capacity increased with the more amount of ozone into the treatment system. With 1,241 mgO_3/L of treatment gave the highest increasing in FOG removal.

After 18 hours of experiment and measuring of the 4 parameters, BOD_5 was removed at the highest percentage (90%) following by COD at 86% and FOG at 67% but the TOC did not remove more than 18%. The optimum treatment hour of BOD_5 was at 2 hours (1,862 mgO_3/L), when COD, TOC and FOG had the optimum treatment condition at 4 hours (3,724 mgO_3/L).

Comparing to pH 3, BOD_5, COD and FOG removal was better in pH 7. However, TOC was removed with the higher percentage in pH 3 wastewater.



Appendix Figure D3 BOD_5, COD, TOC and FOG Removal by mg/L in pH 7 wastewater



Appendix Figure D4 Effect of BOD_5, COD, TOC and FOG Removal Percentage in pH 7 (Raw Wastewater)

3. Organic contents reduction by ozonation in pH 13

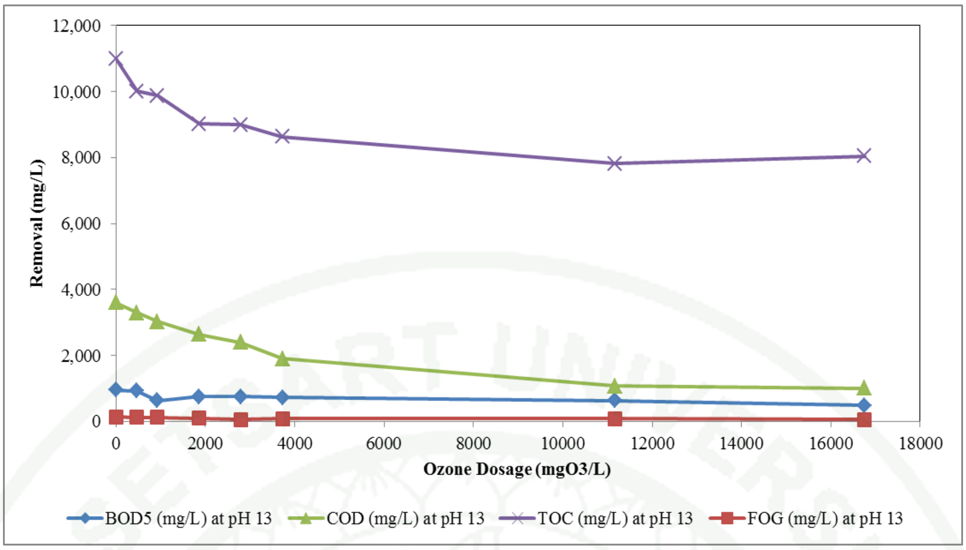
At pH 13, the fire extinguisher wastewater (FEW) ozone treatment result is shown in Appendix Figure D5. The removal percentage is shown in Appendix Figure D6. Four parameters were measured and analyzed at various ozone doses.

The BOD_5 removal percentage (34.18%) was determined at 465 mg/L (0.5 hour treatment), reduced by 3.13%, when ozone dosage was at 931 mgO_3/L (1 hours). Over time, the BOD removed gradually until the end of the experiment.

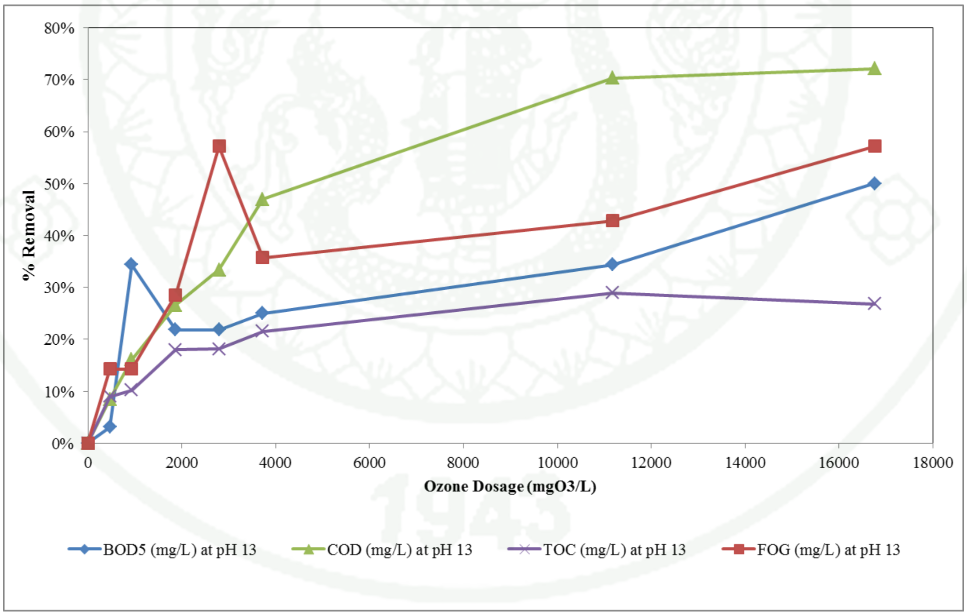
COD was removed significantly after ozone treatment from 8.33% to 69.55% with ozone dosage was increased from 465 mgO_3/L (0.5 hour) to 16,757 mgO_3/L respectively (18 hours of treatment). TOC was removed by 10.18% at the early stage of treatment with ozone dosage at 465 mgO_3/L (0.5 hour) and increased gradually when more ozone was introduced into the system.

The ozonation removed FOG by 14.29% with ozone dosage of 465 mgO_3/L (0.5 hour). The removal percentage increased significantly when provided ozone up to 1,862 mgO_3/L (28.57%). The treatment continued to significantly increased to 57.14% with the ozone dosage at 5,586 mgO_3/L. The more ozone provided to the system, FOG continued to reduce from the wastewater. At the end stage of experiment, ozone dosage at 16,757 mgO_3/L, the removal percentage achieved at 57.14%.

Removal percentage of BOD_5, COD, TOC and FOG at the end stage of experiment, ozone dosage at 16,757 mgO_3/L, were 50.00%, 69.55%, 26.82% and 57.14% respectively. It can be seen that COD had the highest removal capacity following by FOG and BOD while TOC had the lowest removal result (Appendix Figure D6).



Appendix Figure D5 BOD$_5$, COD, TOC and FOG Removal by mg/L in pH 13 wastewater



Appendix Figure D6 Effect of BOD$_5$, COD, TOC and FOG Removal Percentage in pH 13

Appendix E

Additional information of ozone

Advantages and Disadvantages of Ozonation

The advantages of ozonation include:

1. Odor elimination
2. Reduces oxygen demanding matter, turbidity and surfactants
3. Removes most colors, phenolics and cyanides
4. Increases dissolved oxygen
5. Production of no significant toxic side products
6. Increases suspended solids reduction

The disadvantages of ozonation include:

1. High capital cost
2. High electric consumption
3. Highly corrosive, especially with steel or iron and even oxidizes Neoprene

To minimize the disadvantages of ozonation in wastewater treatment plants, some innovations have been developed: use and recycle of oxygen feed to air gap and improved design of ozone contactors.

These innovations, of course, are efforts to increase the effectiveness of ozonation systems while minimizing costs associated with ozone generation. Typically, once-through air feed/air cooled systems require about 6 to 9 kwh/lb while recycled oxygen feed/air cooled systems require about 2.5 to 3.5 kwh/lb. It can be seen from these power consumption figures that if pure oxygen is readily available, the cost of ozone generation can be cut dramatically.

Disinfection using ozone

Ozone is thirteen times more soluble in water than oxygen. When first introduced into wastewater, very little disinfection occurs. The ozone is rapidly consumed, satisfying the ozone demand of inorganic salts and organic matter dissolved in the wastewater. The disinfecting properties of the ozone come into play only after the ozone demand is satisfied. When the demand is satisfied, research studies suggest that ozone brings about disinfection 3100 times faster than chlorine. It has also been found that disinfection occurs within contact times of 3 - 8 seconds. Typical ozone dosages needed to reach the disinfection stage vary with the quality of the effluent. Dosages between 5 - 15 mg/L are commonly cited for disinfection of secondary wastewater effluents. Ozone also exhibits excellent virocidal properties at these dosages, with longer contact time of about 5 minutes needed. It has also been found that any residual ozone in the effluent of the contactor disappears in a matter of seconds outside the contactor.

Other uses of ozone in wastewater treatment

1. Ozone has the ability to remove solids from wastewater by oxidation and physical floatation. Foam develops when wastewater is ozonated. It has been found that this foam traps a significant amount of solids and nutrient material such as phosphates and nitrates.

2. pH has been found to increase very slightly because of ozonation. This is probably the affect of carbon dioxide being driven out of the solution by the gas feed in the ozone contactor.

3. Color and turbidity are reduced by the addition of ozone. This is brought about by chemical oxidation of the substance causing the color or turbidity.

4. Some minor nitrification occurs, but not at levels high enough to consider ozonation as an effective nitrification process.

Safety of ozone

The Maximum Allowable Concentration (MAC) of ozone in air, as established by the American Council of Governmental Industrial Hygienists, is 0.1 ppm by volume for continuous human exposure. The threshold odor of ozone is 0.01

ppm. This means that a person working near an ozone-handling area should be able to detect the presence of ozone at levels far below the MAC. Ozone odor has been described as being similar cloves, newly mowed hay, nitric acid, etc., depending on the concentration. Concentrations greater than 1 ppm are extremely pungent and are considered unsafe for prolonged human exposure, and therefore should be avoided. (http://water.me.vccs.edu/courses/ENV149/ozonation.htm)

Advanced Oxidation Process for Water Treatment

In natural gas exploration, Ecosphere Ozonix™ can treat effluent to oxidize, separating hydrocarbons and heavy metals, recovering clean water without the need for distillation or chlorination at offsite plants. (http://www.ecospheretech.com/index.php/technology/ozonix-process).

- Oxidizes soluble and insoluble organics from effluent and suspended solids to less than 1 ppm
- Oxidizes bio slimes and oil sheens
- Oxidizes heavy metals including iron and magnesium
- Decomposes dissolved ammonia

Appendix F

Standards for the discharge of wastewater from industrial plants and industrial estates set by Thailand Pollution Control Department

Appendix Table F1 Standards for discharge wastewater from industrial plant and industrial estate set by Thailand Pollution Control Department

Parameters	**Standard Values**	**Method for Examination**
1. pH value	5.5-9.0	pH Meter
2. Total Dissolved Solids (TDS)	- not more than 3,000 mg/l depending on receiving water or type of industry under consideration of PCC but not exceed 5,000 mg/l - not more than 5,000 mg/l exceed TDS of receiving water having salinity of more than 2,000 mg/l or TDS of sea if discharge to sea	Dry Evaporation 103-105 °C, 1 hour
3. Suspended solids (SS)	not more than 50 mg/l depending on receiving water or type of industry or wastewater treatment system under consideration of PCC but not exceed 150 mg/l	Glass Fiber Filter Disc
4. Temperature	not more than 40°C	Thermometer during the sampling
5. Color and Odor	not objectionable	Not specified
6. Sulphide as H_2S	not more than 1.0 mg/l	Titrate
7. Cyanide as HCN	not more than 0.2 mg/l	Distillation and Pyridine Barbituric Acid Method

Appendix Table F1 (continued)

Parameters	**Standard Values**	**Method for Examination**
8. Fat, Oil & Grease (FOG)	not more than 5.0 mg/l depending of receiving water or type of industry under consideration of PCC but not exceed 15.0 mg/l	Solvent Extraction by Weight
9. Formaldehyde	not more than 1.0 mg/l	Spectrophotometry
10. Phenols	not more than 1.0 mg/l	Distillation and 4-Aminoantipyrine Method
11. Free Chlorine	not more than 1.0 mg/l	lodometric Method
12. Pesticides	not detectable	Gas-Chromatography
13. Biochemical Oxygen Demand (BOD)	not more than 20 mg/l depending on receiving water or type of industry under consideration of PCC but not exceed 60 mg/l	Azide Modification at 20 °C , 5 days
14. Total Kjedahl Nitrogen (TKN)	not more than 100 mg/l depending on receiving water or type of industry under consideration of PCC but not exceed 200 mg/l	Kjeldahl
15. Chemical Oxygen Demand (COD)	not more than 120 mg/l depending on receiving water of type of industry under consideration of PCC but not exceed 400 mg/l	Potassium Dichromate Digestion

Appendix Table F1 (continued)

Parameters	**Standard Values**	**Method for Examination**
16. Heavy metals		
1. Zinc (Zn)	not more than 5.0 mg/l	Atomic Absorption Spectro Photometry; Direct Aspiration or Plasma Emission Spectroscopy ; Inductively Coupled Plama : ICP
2. Chromium (Hexavalent)	not more than 0.75 mg/l	
3. Copper (Cu)	not more than 2.0 mg/l	
4. Cadmium (Cd)	not more than 0.03 mg/l	
5. Barium (Ba)	not more than 1.0 mg/l	
6. Lead (Pb)	not more than 0.2 mg/l	
7. Nickel (Ni)	not more than 1.0 mg/l	
8. Manganese (Mn)	not more than 5.0 mg/l	
9. Arsenic (As)	not more than 0.25 mg/l	
10. Selenium (Se)	not more than 0.02 mg/l	
11. Mercury (Hg)	not more than 0.005 mg/l	Atomic Absorption Cold Vapor Technique

Remarks:

1. PCC: Pollution Control Committee
2. The standards were summarized from the Notification of the Ministry of Science, Technology and Environment, No. 3, B.E. 2539 (1996) and it specifies that pollution sources that the above standards are to be applied are factories group II and III issues under the Factory Act B.E.2535 (1992) and every kind of industrial estates.
3. Notification of the Pollution Control Committee, No. 3, B.E. 2539 (1996) dated August 20, B.E. 2539 (1996) has issued types of factories (category of factories issued under the Factory Act B.E.2535 (1992) that are allowed to discharge effluent having different standards from the Ministerial Notification No. 3 above as follows :
    1. BOD up to 60 mg/l
        - animal furnishing factories (category 4 (1))
        - starch factories (category 9 (2))
        - food from starch factories (category 10)
        - textile factories (category 15)
        - tanning factories (category 22)
        - pulp and paper factories (category 29)
        - chemical factories (category 42)
        - pharmaceutical factories(category 46)
        - frozen food factories (category 92)
    2. COD up to 400 mg/l
        - food furnishing factories (category 13 (2))
        - animal food factories (category 15 (1))
        - textile factories (category 22)
        - pulp and paper factories (category 38)
    3. TKN
        - 100 mg/l - effective after 1 year from the date published in the Royal Government Gazette of the Ministerial Notification No. 4

- 200 mg/l - effective after 2 year from the date published in the Royal Government Gazette of the Ministerial Notification No. 4 for the following factories:
    1. food furnishing factories (category 13 (2))
    2. animal food factories (category 15 (1))

Source: Notification the Ministry of Science, Technology and Environment, No. 3, B.E.2539 (1996) issued under the Enhancement and Conservation of the National Environmental Quality Act B.E.2535 (1992), published in the Royal Government Gazette, Vol. 113 Part 13 D, dated February 13, B.E.2539 (1996)

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