Kinetics and Degradation Mechanisms of Persistent Organic Pollutant by Ozonation and Advanced Oxidation Processes

by

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LIST OF ABBREVIATIONS

A	Absorbance
ADMI	American Dye Manufactures Institute
ANOVA	Analysis of Variance
AOPs	Advanced oxidation processes
BBD	Box-behnken design
CAS	Chemical abstract service
CCD	Central composite design
Cl^-	Chloride ion
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
$CO_3^{\bullet-}$	Carbonate ion radical
COD	Chemical oxygen demand
DCM	Dichloromethane
df	Dilution factor
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
FT-IR	Fourier Transform-Infrared
GC-MS	Gas chromatograph mass spectrometer
ΔG	Change in Gibbs free energy
ΔH	Change in enthalpy
H^+	Hydrogen ion
H_2O	Water
H_2O_2	Hydrogen peroxide
H_3O^+	Hydronium ion
HCO_3^-	Bicarbonate ion
HO_2^-	Hydroperoxide ion
$HO_2^\bullet$	Hydroperoxide radical
HR–AOP	Hydroxyl radical-based AOPs
HSO_4^-	Hydrogen sulfate ion
HSO_5^-	Hydrogen sulfate ion
IDLH	Immediately Dangerous to Life or Health Concentrations
IUPAC	International Union of Pure and Applied Chemistry

LD	Lethal Dose
$Na_2S_2O_8$	Sodium persulfate
O_2	Oxygen
$O_2^{\bullet-}$	Superoxide radical
O_3	Molecular ozone
O_3–AOP	Ozone-based AOP
O_3/H_2O_2	Peroxone
O_3/PS	Ozone/persulfate
OH^-	Hydroxide ion
$OH^\bullet$	Hydroxyl radical
ORP	Oxidation-reduction potential
PS	Persulfate, $S_2O_8^{2-}$
R^2	Correlation coefficient
RSM	Response surface methodology
ΔS	Change in entropy
SBR	Sequential batch reactor
SO_4^{2-}	Sulfate ion
$SO_4^{\bullet-}$	Sulfate radical ion
SR–AOP	Sulfate radical-based AOP
STP	Standard room temperature and pressure
TiO_2	Titanium dioxide
TS	Total solid
TDS	Total dissolved solid
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet-Visible

LIST OF SYMBOLS

≈	Almost equal to
%	Percent
% T	Percent of transmittance
°C	Degree Celsius
Abs	Absorbance
C_0	Concentration at time = 0
C_t	Concentration at time = t
Da	Dalton, atomic mass unit
E_a	Activation energy
ΔG	Change in Gibbs free energy
g/mol	Gram per mole
ΔH	Change in enthalpy of activation
h	Plank's constant, 6.626 x 10^{-34} J s.
hv	UV irradiation
J/mol K	Joule per mole kelvin
K	Kelvin
K_B	Boltzman's constant, 1.381 x 10^{-23} J/K
k	Reaction rate
k'_{app}	Apparent rate constant after simplification
k''	Second-order kinetic reaction rate
k''_{app}	Pseudo-first order kinetic reaction rate
k''_{R}	Second-order kinetic reaction rate of radical oxidation
k''_{O3}	Second-order kinetic reaction rate of ozone oxidation
$k''_{O3,\ R}$	Second-order kinetic reaction rate of ozone and radical oxidation
k''_{others}	Second-order kinetic reaction rate of oxidation by others oxidants
k_{app}	Apparent rate constant
k_f	Forward reaction rate
k_b	Backward reaction rate
kJ/mol	Kilojoule per mole
λ	Wavelength
$\lambda_{1/2}$	Half-life
λ_{max}	Maximum absorption wavelength
L	Litre
L O_3/min	Litre O_3 per minute
S	Organic or inorganic compound

Kinetik dan Mekanisma Degradasi Pencemar Organik Kekal oleh Ozonasi dan Proses Pengoksidaan Lanjutan

ABSTRAK

Ozonasi dan proses pengoksidaan lanjutan berkesan dalam pengoksidaan bahan pencemar organik kekal kepada sebatian yang mudah terbiodegradasi atau bahkan mencapai mineralisasi yang lengkap. Selama bertahun-tahun, pengoksidaan molekul ozon (O_3) dan hidroksil radikal ($OH^{\bullet}$) telah banyak dikaji. Baru-baru ini, pengoksidaan radikal sulfat ($SO_4^{-\bullet}$) juga menarik kerana $SO_4^{-\bullet}$ adalah spesies radikal yang kuat tetapi lebih selektif berbanding dengan $OH^{\bullet}$. Tumpuan utama kajian ini adalah untuk menilai kecekapan, kinetik dan mekanisma ozonasi, perokson, dan ozon/persulfat dalam mengoksida pencemaran organik kekal (p-cresol). Penemuan menunjukkan bahawa ozonasi, perokson, dan ozon/persulfat berkesan dalam pengoksidaan 81.9% – 96.8% daripada 100 mg/L p-cresol. Selain itu, peningkatan ketara diperhatikan dalam kecekapan degradasi p-cresol dan keupayaan oksidatif bagi medium tindakbalas apabila medium pH meningkat kepada pH alkali. Penemuan ini mencadangkan bahawa spesies pengoksida utama dalam medium tindakbalas bertukar kepada spesies pengoksida yang lebih kuat pada pH tinggi. Di samping itu, keputusan eksperimen menunjukkan bahawa keadaan operasi optimum dalam ozonasi, perokson, dan ozon/persulfat adalah seperti berikut: pH 11, 30°C, 1.0 L O_3/min, 1.0 mM H_2O_2 atau persulfat. Kaedah gerak balas permukaan reka bentuk Box-Behnken juga digunakan untuk menyiasat tindakbalas antara parameter operasi. Penemuan menunjukkan bahawa tindakbalas antara pH dan suhu operasi dapat meningkatkan atau menghalang prestasi proses; manakala kadar aliran gas O_3 mempunyai pengaruh yang sangat kecil kepada parameter lain. Kajian kinetik menunjukkan bahawa degradasi p-cresol oleh ozonasi, perokson, dan ozon/persulfat mematuhi kinetik tindak balas tertib pseudo-pertama. Secara ringkas, kinetik degradasi p-cresol mempunyai hubungan linear positif dengan pH dan suhu, hubungan linear negatif dengan peningkatan kepekatan awal, dan hubungan tak linear dengan kadar alir gas O_3 dan dos pengoksida. Berdasarkan analisis kromatografi massa kromatografi gas, produk perantaraan degradasi p-cresol oleh ozonasi, perokson, dan ozon/persulfat didapati semua kurang toksik berbanding p-cresol. Produk perantaraan aromatik yang dikesan termasuk 4-methylcatechol, 4-hydroxy-4-methyl-cyclohexadien-1-one, 4-methylbenzyl alcohol, 4-hydroxybenzaldehyde, 5-methylfuran-2(3H)-one, 5-methyl-2-furaldehyde, 3,4-dihydroxy-benzaldehyde, dan 3,4-dihydroxy-benzoic acid. Semua produk perantaraan terdegradasi kepada rantai asid karboksilik yang lebih pendek dengan pengoksidaan lanjut. Penemuan ini juga menunjukkan bahawa laluan degradasi utama p-cresol adalah melalui pengoksidaan cincin benzena; sementara pengoksidaan rantaian sampingan hanya berlaku dalam perokson dan ozon/persulfat. Kehadiran sebatian furanik mendedahkan bahawa produk pembuka cincin boleh menjalani tindakbalas penggantian nukleofilik intramolekul, kemudian mengubah struktur sebatian alifatik ke struktur berkitar.

Kinetics and Degradation Mechanisms of Persistent Organic Pollutant by Ozonation and Advanced Oxidation Processes

ABSTRACT

Ozonation and advanced oxidation processes are effective in oxidising persistent organic pollutants into readily biodegradable compounds or even achieve complete mineralisation. Over the years, molecular ozone (O_3) and hydroxyl radical ($OH^{\bullet}$) oxidation have been studied extensively. Recently, sulfate radical ($SO_4^{-\bullet}$) oxidation is also of interest because $SO_4^{-\bullet}$ is a strong and more selective radical species compared to $OH^{\bullet}$. The main focus of this research was to assess the efficiencies, kinetics and mechanisms of ozonation, peroxone, and ozone/persulfate in oxidising persistent organic pollutant (p-cresol). The findings demonstrated that ozonation, peroxone, and ozone/persulfate were effective in oxidising 81.9% – 96.8% of 100 mg/L of p-cresol. Besides, significant improvement was observed in p-cresol degradation efficiencies and oxidative capacity of reaction medium when the pH medium increased to alkaline pH. This finding suggested that the predominant oxidant species in reaction medium converted to stronger oxidant species at elevated pH. In addition, the optimum operating conditions in ozonation, peroxone, and ozone/persulfate were as follows: pH 11, 30°C, 1.0 L O_3/min, 1.0 mM of H_2O_2 or persulfate. Response surface methodology Box-Behnken design was also utilized to investigate the interaction between operating parameters. The findings revealed that the interaction between pH and operating temperature can enhance or hamper the process performance; whereas O_3 gas flow rate has negligible influence to other parameters. Kinetic studies indicated that the degradation of p-cresol by ozonation, peroxone, and ozone/persulfate abided to pseudo-first-order of kinetic reaction. Briefly, the kinetics of p-cresol degradation have positive linear relationship with pH and temperature, negative linear relationship with increasing initial concentration, and nonlinear relationship with O_3 gas flow rate and oxidants dosage. Based on the gas chromatography mass spectrum analysis, the detected intermediate products of p-cresol degradation by ozonation, peroxone, and ozone/persulfate were all found less toxic compared to p-cresol. The detected aromatic intermediate products included 4-methylcatechol, 4-hydroxy-4-methylcyclohexadien-1-one, 4-methylbenzyl alcohol, 4-hydroxy-benzaldehyde, 5-methylfuran-2(3H)-one, 5-methyl-2-furaldehyde, 3,4-dihydroxy-benzaldehyde and 3,4-dihydroxy-benzoic acid. All of the intermediate products degraded to shorter chain of carboxylic acids with further oxidation. The findings also indicated that the major degradation pathway of p-cresol was through benzene ring oxidation; whilst side-chain oxidation only occurred in peroxone and ozone/persulfate. The presence of the furanic compounds revealed that ring-opening products could undergo intramolecular nucleophilic substitution reaction, subsequently transforms the aliphatic compound to cyclic structure.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

Environmental pollution is a transnational phenomenon; but it is more often not well-governed in developing countries. It is not surprising that these countries solely focus its resources on economic development. However, one should understand that balanced development in economic, environment, and social are necessity in order to attain sustainability. Excessive economic activities not only could cause environmental pollutions and deteriorate quality of life, but also will lead to adverse effect along with high environmental costs. While on the contrary, overprotection on the environment will retard economic development and does not help in growing competitive community. Therefore, adequate economic development and proper environmental management is equally important in promoting the betterment of society.

Water pollution is among the major issues affecting sustainable development in Malaysia. The occurrence of water pollution could reduce the total water availability consequently impacts the sustainability of water resources (World Wide Fund for Nature Malaysia, 2019). In Malaysia, water pollution is an ongoing environmental issue closely linked with urbanization and modernization (Huang, Ang, Lee, & Lee, 2015). It is also a threat to national water security owing to the fact that 97% of the total water used is contributed by streams and rivers (Afroz, Masud, Duasa, Akhtar, & Duasa, 2014). Over the years, the river water quality in Malaysia has found to be degraded. According to the Department of Environment (DOE), out of 477 rivers monitored in 2017, 46% were found to be clean, 43% slightly polluted, and 11% polluted

(Department of Environment [DOE], 2017). The sources of water pollution could be from point source e.g. effluent discharges at specific locations; and non-point source such as surface runoffs (Huang et al., 2015). The reported main point sources of water pollution were from sewage treatment plants (54.1%), manufacturing industries (38.7%), animal farms (4.48%), and agro-based industries (2.78%) (Afroz et al., 2014).

In line with the United Nations Sustainable Development Goal 6, advancement in wastewater management is essential to ensure availability and sustainable management of water and sanitation for all. Tackling point sources water pollution and adequate wastewater treatment not only help protect public health and the environment but also help prevent the cost of pollution (United Nations, 2018). However, at the present moment, the conventional treatment plants in Malaysia are not keeping pace with the strength and composition of wastewater (Huang et al., 2015). Among the pollutants in wastewater, persistent organic pollutants are of concern because they are toxic, resist to biodegradation, bioaccumulative, could transport great distances with aqueous system, and subsequently cause significant negative impacts to living organisms and the environment (World Wide Fund For Nature, 2019).

Advanced oxidation processes (AOPs) are highly effective techniques for water and wastewater treatments. AOPs are generally defined as oxidation processes involving the generation of hydroxyl radicals ($OH^{\bullet}$) which are responsible for degradation of organic pollutants; but now the concept of AOPs also includes sulfate radical ($SO_4^{\bullet -}$) due to their strong oxidation power (Deng & Zhao, 2015). Studies have shown that AOPs are highly effective in degradation of persistent organic pollutants including phenolic compounds (Suzuki, Araki, & Yamamoto, 2015), pharmaceuticals

(Kanakaraju, Glass, & Oelgemöller, 2018), azo dyes (Razali et al., 2018), and pesticides (Lutze et al., 2015).

Asides from AOPs, membrane separation is also a newly emerging advanced technology for the removal of persistent organic pollutants (Badmus, Tijani, Massima, & Petrik, 2018). Membrane separation is a physicochemical method that utilizes pressure difference to achieve separation and purification (Han, Qiu, Cheng, & Qiu, 2018). The advantages of membrane separation technologies are high removal efficiencies, small footprint, and easy to scale up; however the demerit is the membrane can be easily blocked by pollutants (Villegas et al., 2016). The membrane fouling issues, can be also associated with shorter membrane life and extra costs for energy, chemicals, and feed-water used in membrane pretreatment (Han et al., 2018).

In comparison, AOPs are considered sustainable and clean treatment technology due to its thoroughness and no residues production (Litter, Candal, & Meichtry, 2014; Ribeiro, Nunes, Pereira, & Silva, 2015). Nevertheless, the major concern of AOPs application is that AOPs could lead to a transformation product with new chemical toxicity similar to the parent compound (Sharma, Ahmad, & Flora, 2018). Other than that, economic feasibility of AOPs is also a big challenge that needs to be overcome to ascertain the practicality of the technology in developing countries.

1.2 Problem Statement

Water pollution is a threat to national water resources. Among the pollutants in water and wastewater, persistent organic pollutant poses significant negative effects to living organisms and the environment. p-Cresol is a persistent organic pollutant, group C (possible human carcinogens) priority pollutant, and also a contaminant of emerging concern in water and wastewater. It could cause harm to living organism by affecting organs and the central nervous system of living organism (CDC, 2015). The widespread of p-cresol in the environment is mainly contributed by its high involvement in industries and household products (Wei et al., 2016). Aside from cause harm in living organisms, the presence of p-cresol also deteriorates water quality and surrounding air quality (Zhu & Kolar, 2014).

The most common treatment methods for p-cresol or phenolic wastewater are biodegradation and adsorption methods (Villegas et al., 2016; Zhu, Kolar, Shah, Cheng, & Lim, 2018). However, the limitation of biodegradation in complex wastewater treatment is that the treatment efficiency is highly dependent on the toxicity of substrate and environmental conditions of bioreactor (Gerginova, Zlateva, Peneva, & Alexieva, 2014; Surkatti & El-Naas, 2014). Moreover, biodegradation often requires hours to days to achieve complete mineralization (Reshma & Mathew, 2014). On the other hand, adsorption methods are of simple operation, low operation cost, and highly efficient in organic pollutant removal. Nonetheless adsorption is merely a separation process; the process itself could not destroy pollutants, but instead transfer it from aqueous phase to the adsorbents (Badmus et al., 2018), which requires post-treatment. In comparison, ozonation and AOPs could serve as a sustainable and clean technology for phenolic wastewater treatment because they are highly destructive to phenolic compounds, require much shorter treatment time, and do no cause secondary pollution (Parikh, Parmar, & Upasani, 2018; Villegas et al., 2016).

Ozonation and AOPs have been studied extensively over the years. Nevertheless, only limited studies on degradation of p-cresol by ozonation and hydroxyl radical-based AOP, not to mention the recently arises sulfate radical-based AOP. In ozonation and AOPs, the processes performance often depends on the oxidant species involved, pH of reaction medium, as well as the concentration of treatment target. The combination of O_3 and radical precursors, e.g., hydrogen peroxide (H_2O_2) and persulfate ($S_2O_8^{2-}$) and suitable pH medium for radical formation may enhance the oxidation of p-cresol. Besides, ozonation and AOPs are cost-intensive treatment process and their operating parameters, e.g. oxidant dosage, pH, and operating temperature, could direct influence the treatment efficiency. Furthermore, the interaction effect of processes parameters is rarely discussed although many optimisation studies have been done previously. Other than that, the major concern of oxidation of phenolic compound by ozonation and AOPs is the toxicity of the transformation products produced during the treatment. Accordingly, the identity and hazard of intermediate products in p-cresol degradation need to be clarified. In addition to that, the degradation pathways and mechanisms involved in p-cresol oxidation by ozonation and AOPs are less documented; thus further exploration is necessary in order to fill the research gap.

1.3 Research Objectives

The main objectives of this research is to investigate the performance of ozonation and AOPs studied, e.g., peroxone and ozone/persulfate (ozone/PS); and to study the degradation of p-cresol by using the methods studied. In specific, the research objectives are:

(i) To evaluate the performance of O_3 and AOPs studied in terms of p-cresol degradation and dependency on pH of reaction medium.

(ii) To investigate the influence of process parameters towards the performance of ozonation and AOPs studied.

(iii) To develop kinetic model of p-cresol degradation and establish its relationship with process parameters in ozonation and AOPs studied.

(iv) To identify the intermediate products in p-cresol degradation and elucidate the pathways and mechanisms involved in ozonation and AOPs studied.

1.4 Research Scope

Ozonation, peroxone, and ozone/PS are selected as treatment methods; and p-cresol is used as model pollutant in this study. All experiments were conducted in semi-batch mode using laboratory-scale ozonation reactor. The scope of research includes parameters study such as O_3 gas flow rate, oxidants dosage, pH, and operating temperature. The performance of methods studied was evaluated in terms of p-cresol reduction, COD reduction, and changes of pH and ORP in reaction medium. Whereas, the degradation intermediate products of p-cresol were identified through UV-Vis and IR absorption spectra, total ion chromatograph (TIC), and mass spectra. The research scope in accordance with respective research objective can be well-represented by experimental matrix (Appendix B) and was briefly described as below.

This study focuses on the performance of ozonation, peroxone, and ozone/PS in degrading persistent organic pollutant by using p-cresol as model pollutant. The performance of ozonation and combination of ozonation with H_2O_2 or persulfate was evaluated and compared with respect to increasing initial p-cresol concentrations as well as pH conditions of reaction medium. The processes parameters in ozonation, peroxone, and ozone/PS including O_3 gas flow rate, oxidants dosage, pH as well as operating temperature were optimised in order to enhance the processes performance. Response surface methodology Box-Behnken design (BBD) was also employed to investigate the effect of interaction between parameters. Other than that, the kinetic model of p-cresol degradation was developed; subsequently establish its relationship with processes parameters. The intermediate products in p-cresol degradation were identified through UV-Vis spectrometry, FTIR spectrometry, and GCMS. Accordingly, the degradation pathways of p-cresol were proposed by taking into account of oxidation mechanisms of oxidants involved in the processes.

1.5 Novelty of Research

The main focus of this research was to assess the efficiencies, kinetics and mechanisms of ozonation, peroxone, and ozone/PS in oxidising p-cresol. Even though many researchers have been worked on oxidation of p-cresol by ozone (O_3) and hydroxyl radical based AOPs, as far as authors are aware, there is no published work on p-cresol oxidation by ozone/PS or sulfate radical based AOPs. Indeed, at present, general research in sulfate radical based AOPs is still in its infancy. This data can be served as reference for latter research.

Besides, the interaction effect of process parameters in ozonation and AOPs is rarely discussed although optimisation studies of ozonation and AOPs are well-established for wastewater treatment. In the present work, the interaction effect between O_3 gas flow rate with pH and operating temperature on p-cresol reduction is studied extensively by using BBD. The BBD result is also used to reaffirm the significance or contribution of each process parameters in the model of designed experiment.

Other than that, according to the author's knowledge, no comprehensive work was dedicated to degradation mechanisms of p-cresol degradation by ozonation, peroxone, and ozone/PS. In this study, the identity and hazard classification of intermediate products in p-cresol degradation are identified. Subsequently, the degradation mechanisms and pathways of p-cresol degradation in ozonation, peroxone, and ozone/PS are elucidated.

1.6 Thesis Outline

In Chapter 1, the importance of wastewater management in Malaysia; the concerns of phenolic compounds in the environment; as well as the limitation of existing treatment methods were described. Based on the problem statement, the research objectives were rationalized along with the scope of research. Chapter 2 starts with a brief introduction on AOPs, followed by an overview of methods studied (ozonation, peroxone and ozone/PS) and model pollutant (p-cresol) in this study. Chapter 3 presents the materials and methods including chemical and reagents, experimental set-up and procedures, experimental flow chart as well as analytical methods employed in this study. In Chapter 4, the performance of ozonation, peroxone, and ozone/PS in degrading p-cresol and dependency on pH of reaction medium were evaluated. The effects of operating parameters towards processes performance were studied and the optimum operating conditions were justified based on its performance in degrading p-cresol. The interaction effect between process parameters was also elaborated in accordance with results obtained from Box-Behnken design (BBD) in response surface method. Besides, the kinetic model of p-cresol degradation was developed subsequently established the relationship between p-cresol degradation kinetics and process parameters. Other than that, the degradation intermediate products of p-cresol by methods studied as well as its hazard classification were identified. Accordingly, the degradation pathways of p-cresol in ozonation, peroxone, and ozone/PS were proposed. The plausible oxidation mechanisms involved were also elaborated considering the oxidants involved in respective process. The thesis end with Chapter 5, which comprises of a thesis overview, conclusion, significance of the research, and the recommendations for future work.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

Chapter 2 starts with a brief introduction on AOPs including the types of AOPs, affecting factors affecting the performance of AOPs, and the costs associated with AOPs. In addition, an overview of ozonation and AOPs studied (peroxone and ozone/PS) were discussed; followed by comparison between the three processes. Furthermore, an overview of the model pollutant used (p-cresol) in this study were presented along with its environmental hazards and available treatment methods.

2.2 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) is an emerging technology for treatment of various types of contaminant in wastewater. The current concept of AOPs involves the formation of $OH^{\bullet}$ or $SO_4^{\bullet -}$ and the oxidation of organic compounds by the radicals produced (Deng & Zhao, 2015). The formation of strong and highly reactive radicals in AOPs make it possible to oxidize recalcitrant compounds by degrading it to more readily biodegradable compounds, and subsequently easier to achieve mineralization (Amor, Marchão, Lucas, & Peres, 2019). Table 2.1 shows the types AOPs categorized based on radical species and initiator involved in the process.

In AOPs, the oxidants applied or free radical species produced during oxidation processes can directly affect the AOPs performance. Accordingly, radical precursors are often used in combination in AOPs to improve its performance. For example, the application of H_2O_2 and persulfate in AOPs could generate $OH^•$ and $SO_4^{•-}$ (Abu Amr, Aziz, Bashir, Aziz, & Alslaibi, 2015). Table 2.2 presents the common oxidants or radical species in AOPs and their respective oxidation potentials. Amongst all, $OH^•$ has the highest oxidation potential (E^0 = 2.80 V), thus hydroxyl radical-based AOP (HR-AOP) have been the focus of AOPs study in decades. However, $OH^•$ has high reactivity with all compounds, thus is more likely to be scavenged by water and wastewater matrices (Gligorovski, Strekowski, Barbati, & Vione, 2015). Recently, attention is also given to sulfate radical-based AOP (SR-AOP) because $SO_4^{•-}$ also has strong oxidation power (E^0 = 2.60 V) but higher selectivity compared to $OH^•$ (Oh, Dong, & Lim, 2016).

Table 2.1 Types of AOPs based on radical species and initiator involved

Type	Combined system	Catalytic	Photolytic / Thermal
O_3–AOP	O_3/H_2O_2	-	-
	O_3/PS [a]		-
HR–AOP	$O_3/H_2O_2/Fe^{2+}$ [a]	Fe^{2+}/H_2O_2	O_3/UV
	-	-	UV/H_2O_2
SR–AOP	-	Fe^{2+}/PS	PS/UV [b]
	-	PS/Alkaline [b]	PS/Thermal [b]

Source: Deng and Zhao (2015); [a] Abu Amr et al. (2015); [b] J. Wang and Wang (2018)

Table 2.2 Oxidant used or radical produced in AOPs and its oxidation potential

Oxidant / Radical species		Oxidation potential, E^0 (V)
Hydroxyl radical	$OH^•$	2.80
Sulfate radical	$SO_4^{•-}$	2.60
Ozone	O_3	2.08
Persulfate	$S_2O_8^{2-}$	2.12
Hydrogen peroxide	H_2O_2	1.78

Source: Oh et al. (2016)

2.2.1 Factors affecting AOPs Performance

AOPs performance can be influenced by the presence of radical precursors and catalysts; UV irradiation; pH; temperature; and radical scavengers. In general, the application of radical precursors, catalysts, and UV irradiation could enhance AOPs performance; in contrast, the presence of radical scavengers could hamper the process itself. Whereas, an increased in pH and temperature can either enhance or inhibit AOPs performance, depending on the radical production mechanisms involved in AOPs.

2.2.1.1 Radical Precursors, Catalysts, and UV Irradiation

The combination of ozonation or AOPs with radical precursors, catalysts, and UV irradiation enhance the radical production by providing more resources and additional pathways for radical production. The addition of H_2O_2 in ozonation or AOPs could enhance $OH^{\bullet}$ production in the system. For instance, in peroxone system, the dissociation form of H_2O_2, HO_2^-, initiates the production of $OH^{\bullet}$ through Equation (2.1 – 2.6) (Staehelin & Hoigne, 1982). On the other hand, the combination of persulfate with ozonation or AOPs could introduce additional radical species, $SO_4^{\bullet-}$, in the system. The $OH^{\bullet}$ present in ozonation or AOPs could activate the persulfate and through Equation (2.7) and (2.8) (J. Wang & Wang, 2018).

$$H_2O_2 + H_2O \rightarrow HO_2^{-} + H_3O^{+} \tag{2.1}$$

$$O_3 + HO_2^{-} \rightarrow O_3^{\bullet-} + HO_2^{\bullet} \tag{2.2}$$

$$HO_2^{\bullet} \leftrightarrow O_2^{\bullet-} + H^{+} \tag{2.3}$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \tag{2.4}$$

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet} \quad (2.5)$$

$$HO_3^{\bullet} \rightarrow OH^{\bullet} + O_2 \quad (2.6)$$

$$S_2O_8^{2-} + OH^{\bullet} \rightarrow SO_4^{2-} + SO_4^{\bullet -} + \frac{1}{2}O_2 + H^+ \quad (2.7)$$

$$SO_4^{2-} + OH^{\bullet} \rightarrow SO_4^{\bullet -} + OH^- \quad (2.8)$$

On the other hand, the presence of catalyst and UV irradiation in AOPs provides another pathway to generate free radicals. For instance, Fe^{2+} can catalyse H_2O_2 and persulfate to form $OH^{\bullet}$ and $SO_4^{\bullet -}$ in single step (Brienza & Katsoyiannis, 2017; Elloy, 2014), via reaction (2.9) and (2.10). The radical produced accelerates the decomposition of H_2O_2 and persulfate, and propagates the radical production (Zhao, Liao, Yan, & Huling, 2013). Whereas, UV irradiation at wavelength 200 nm – 300 nm can activate O_3, H_2O_2, and persulfate via reaction (2.11 – 2.13) (Ao & Liu, 2017; Oturan & Aaron, 2014). In addition, UV irradiation above 300 nm in Fenton process could regenerate Fe^{2+} from the ferrous ion complex ($Fe(OH)^{2+}$)) subsequently recycle the Fenton reaction (2.9) (Villegas-Guzman et al., 2017). Moreover, direct photolysis of target treatment compounds by UV irradiation can also enhance oxidative destruction (Oturan & Aaron, 2014).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (2.9)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + Fe^{3+} \quad (2.10)$$

$$O_3 + H_2O \xrightarrow{hv} O_2 + H_2O_2 \quad (2.11)$$

$$H_2O_2 \xrightarrow{hv} 2OH^{\bullet} \quad (2.12)$$

$$S_2O_8^{2-} \xrightarrow{hv} 2SO_4^{-} \quad (2.13)$$

2.2.1.2 pH

AOPs performance is highly dependent on pH. This because solution pH can influence decomposition of O_3 (Khuntia, Majumder, & Ghosh, 2015), H_2O_2 (Pędziwiatr, Mikołajczyk, Zawadzki, Mikołajczyk, & Bedka, 2018), and persulfate (J. Wang & Wang, 2018), oxidative species formed, and availability of free radicals in reaction medium (Villegas-Guzman et al., 2017). In ozonation, O_3 is stable in acidic condition thus is predominant and responsible for oxidation of organic compounds (Deng & Zhao, 2015). As pH increased to neutral or alkaline pH, the available OH^- increased leading to more HO_2^- formation via reaction (2.14). Subsequently, the formation of $O_2^{\bullet-}$, $HO_2^{\bullet}$, and OH accelerate the decomposition of O_3, propagate the chain reactions, and induce more $OH^{\bullet}$ production, as shown in Equation (2.15 – 2.21) (Staehelin, Buhler, & Hoigne, 1984; Van & Trinh, 2013).

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (2.14)$$

$$O_3 + HO_2^- \rightarrow O_3^{\bullet-} + HO_2^{\bullet} \quad (2.15)$$

$$HO_2^{\bullet} \leftrightarrow O_2^{\bullet-} + H^+ \quad (2.16)$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \quad (2.17)$$

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^{\bullet} \quad (2.18)$$

$$HO_3^{\bullet} \rightarrow OH^{\bullet} + O_2 \quad (2.19)$$

$$O_3 + OH^{\bullet} \rightarrow HO_4^{\bullet} \quad (2.20)$$

$$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \quad (2.21)$$

In HR–AOP, pH may enhance or hamper the HR–AOP performance depending on mechanisms involved. As in Fenton reactions, the optimum pH range is 2.5 < pH < 3, where Fe^{2+} reacts rapidly with H_2O_2 to generate $OH^{\bullet}$ (Badmus et al., 2018). In particular, at pH less than 3, the production of $OH^{\bullet}$ decreases due to the formation of $Fe(OOH)^{2+}$ (reaction (2.22)); and at pH greater than 4, the formation of $Fe(OH)^{2+}$ (reaction (2.23)) could alter the decomposition of H_2O_2 and subsequently retards the production of $OH^{\bullet}$ (Villegas et al., 2016). On the other hand, H_2O_2 could deprotonate into HO_2^- at elevated pH (pH > pKa 11.6); however its role in AOPs is minor as H_2O_2 can be activated to yield $OH^{\bullet}$ in one step, thus induces H_2O_2 decomposition and propagates the radical chain reaction.

$$H_2O_2 + Fe^{3+} \rightarrow Fe(OOH)^{2+} + H^+ \leftrightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (2.22)$$

$$OH^- + Fe^{3+} \rightarrow Fe(OH)^{2+} \leftrightarrow Fe^{2+} + OH^{\bullet} \quad (2.23)$$

Whereas in SR–AOP, persulfate reacts with water molecule at 2 < pH < 7 to produce HSO_4^- and H_2O_2 via reaction (2.7) (Zhao et al., 2013), providing radical precursor for $OH^{\bullet}$ generation. In ozone/PS, pH affects persulfate decomposition through altering $OH^{\bullet}$ production in O_3 decomposition. In PS/Fe^{2+} system, the way pH affecting the persulfate decomposition is similar with H_2O_2 decomposition in Fenton's reaction; at pH above 4, persulfate decomposition is altered by hydrolysis of Fe^{2+} (reaction (2.24)), thus has lower $SO_4^{\bullet -}$ production (Oh et al., 2016). Whereas, base-catalysed hydrolysis of $S_2O_8^{2-}$ produces $SO_4^{\bullet -}$ and HO_2^-; the HO_2^- can further react with $S_2O_8^{2-}$ to generate more $SO_4^{\bullet -}$; as depicted in Equation (2.25) and (2.26) (Furman, Teel, & Watts, 2010). At pH greater than 12, the $SO_4^{\bullet -}$ produced can react with OH^- to produce $OH^{\bullet}$, via reaction (2.27) (Zhao et al., 2013).

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 \downarrow + 3H^+ \quad (2.24)$$

$$S_2O_8{}^{2-} + 2H_2O \xrightarrow{OH^-} HO_2{}^- + 2SO_4{}^{\bullet -} + 3H^+ \tag{2.25}$$

$$HO_2{}^- + S_2O_8{}^{2-} \rightarrow SO_4{}^{\bullet -} + SO_4{}^{2-} + H^+ + O_2{}^{\bullet -} \tag{2.26}$$

$$SO_4{}^{\bullet -} + OH^- \rightarrow OH^{\bullet} + SO_4{}^{2-} \tag{2.27}$$

2.2.1.3 Temperature

In general, increasing temperature could enhance AOP performance by accelerating reactions rate and radical production. However, temperature also has great influence towards the oxidants involved in the oxidation process. In O_3–AOP, high operating temperature could accelerate O_3 decomposition and speed up $OH^{\bullet}$ production (Ershov & Morozov, 2009), but temperature more than 30°C could hamper the process because O_3 has shorter retention time at higher temperature (Andoyo et al., 2018). Similarly, H_2O_2 also decomposes faster to form water and oxygen at higher temperature (Pędziwiatr et al., 2018), which do not benefits in radical production. As for SR–AOP, an increase in operating temperature could enhance AOPs performance due to thermal activation of persulfate. Previous studies by Hilles, Abu Amr, Hussein, El-Sebaie, and Arafa (2016) also reported that persulfate can be easily activated at temperature above 30 °C to yield two $SO_4{}^{\bullet -}$ in one step via reaction (2.28) owing to the low bond dissociation energy (BDE) of peroxide bond in persulfate.

$$S_2O_8{}^{2-} + \text{heat} \rightarrow 2SO_4{}^{\bullet -} \tag{2.28}$$

2.2.1.4 Radical Scavenger

Radical scavenger is any unwanted species that reacts with radicals produced, limits or/and terminates the radical chain-reactions (Trapido, 2011). The presence of scavengers could alter $OH^{\bullet}$ production, subsequently affect the oxidation of target treatment compounds. In AOPs, the radical scavenger might include but not limited to alkalinity, dissolved organic matter (DOM), inorganic compounds, and reduced metals.

Alkalinity affect the AOPs performance through the scavenging reactions of bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}) (AwwaRF, 1998). HCO_3^- is predominant at pH range of 4.3 to 8.3; at pH above 8.3, HCO_3^- dissociates to CO_3^{2-} and complete the reaction at pH 10.2 (Kow et al., 2018). At pH greater than 9, HCO_3^- and CO_3^{2-} competed for $OH^{\bullet}$; the formation of carbonate ion radical ($CO_3^{\bullet -}$) can interfere the $OH^{\bullet}$ production by consuming H_2O_2 and HO_2^- to regenerate HCO_3^- and CO_3^{2-} (Acero & Gunten, 2000). The scavenging reactions of $OH^{\bullet}$ by HCO_3^-, CO_3^{2-} and its radicals proceed until termination of radicals. The reactions involved were shown as follows.

$$HCO_3^- + OH^{\bullet} \rightarrow HCO_3^{\bullet} + OH^- \quad (2.29)$$

$$CO_3^{2-} + OH^{\bullet} \rightarrow CO_3^{\bullet -} + OH^- \quad (2.30)$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \quad (2.31)$$

$$HCO_3^- + H^+ \rightarrow CO_3^{2-} \quad (2.32)$$

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \quad (2.33)$$

$$HCO_3^{\bullet} \leftrightarrow CO_3^{\bullet -} + H^+ \quad (2.34)$$

$$CO_3^{\bullet -} + H_2O_2 \rightarrow HCO_3^- + HO_2^{\bullet} \quad (2.35)$$

$$CO_3^{\bullet -} + HO_2^- \rightarrow CO_3^{2-} + HO_2^{\bullet} \quad (2.36)$$

DOM consists of large macromolecular organic compounds such as humic and fulvic substances. The presence of DOM in AOPs could promote or inhibit ozone decomposition process depending on the nature of DOM (Y. Liu et al., 2015). Besides, the concentration of DOM also can influence its role as a promoter; at lower DOM concentration, reaction between O_3 and DOM may generate $OH^{\bullet}$ in contrary with high concentration of DOM (Ghazi, Lastra, & Watts, 2014), as presented in reaction (2.37) and (2.38) respectively.

$$\mathrm{DOM} + \mathrm{O_3} \rightarrow \mathrm{OH^{\bullet}} + \mathrm{byproduct} \quad (2.37)$$

$$\mathrm{DOM} + \mathrm{OH^{\bullet}} \rightarrow \mathrm{O_2}^{\bullet -} + \mathrm{byproduct} \quad (2.38)$$

Inorganic compounds such SO_4^{2-} and Cl^- can scavenge $OH^{\bullet}$ by reacting with it to form less reactive inorganic radicals (Deng & Zhao, 2015; Van & Trinh, 2013). However, in the case of SO_4^{2-}, the scavenging effect is minor since the product, $SO_4^{\bullet -}$, is also of high oxidation power, $E^0 = 2.70$ V. The scavenging reactions of Cl^- were shown in Equation (2.39 – 2.44) (Neta, Madhavan, Zemel, & Fessenden, 1977).

$$\mathrm{Cl^-} + \mathrm{OH^{\bullet}} \leftrightarrow \mathrm{ClOH^{\bullet -}} \quad (2.39)$$

$$\mathrm{ClOH^{\bullet -}} + \mathrm{H^+} \leftrightarrow \mathrm{HClOH^{\bullet}} \quad (2.40)$$

$$\mathrm{HClOH^{\bullet}} \leftrightarrow \mathrm{Cl^{\bullet}} + \mathrm{H_2O} \quad (2.41)$$

$$\mathrm{Cl^{\bullet}} + \mathrm{Cl^-} \leftrightarrow \mathrm{Cl_2}^{\bullet -} \quad (2.42)$$

$$\mathrm{Cl_2}^{\bullet -} + \mathrm{H_2O} \leftrightarrow \mathrm{HClOH^{\bullet}} + \mathrm{Cl^-} \quad (2.43)$$

$$\mathrm{Cl_2}^{\bullet -} + \mathrm{OH^-} \leftrightarrow \mathrm{ClOH^{\bullet -}} + \mathrm{Cl^-} \quad (2.44)$$

Reduced metals such as Fe^{2+}, Cu^{+}, and Mn^{2+} may affect AOPs performance by consuming $OH^{\bullet}$ or oxidants involved in AOPs. Fe^{2+} and Cu^{+} reacts with $OH^{\bullet}$ to form Fe^{3+} and Cu^{2+}, which later transform to their respective organic complexes (Friedrich, Zanta, Machulek Jr, Silva, & Quina, 2012). As for Mn^{2+} in the presence of Fe^{2+}, the formation of Mn^{3+} could consume O_3 to generate permanganate ion (MnO_4^-) (Gunten, 2003), as shown in reaction (2.45) and (2.46).

$$Fe-O^{2+} + Mn^{2+} + H_2O \rightarrow Fe(OH)_2{}^{+} + Mn^{3+} \tag{2.45}$$

$$Mn^{3+} + 2O_3 + 2H_2O \rightarrow MnO_4{}^{-} + 2O_2 + 4H^{+} \tag{2.46}$$

Whereas, scaling agent only affect AOPs involving irradiation. The presence of scaling agent could cause fouling or inefficiency in UV system by absorbing UV light or blocking penetration of UV light during irradiation, and subsequently results in lower yield of radical production (Krishnan, Rawindran, Sinnathambi, & Lim, 2017). The scaling agents may include humic and fulvic acids, iron (200 – 400 nm), nitrate (230 – 240 nm), and nitrite (300 – 310 nm) (Kow, Fahmi, Abidin, & Ong, 2016).

2.2.2 Treatment Cost of Ozonation and AOPs

Figure 2.1 presents the cost estimation for ozonation and AOPs treatment in real industrial conditions based on cost evaluation input data in Table 2.3 (Bilińska, Gmurek, & Ledakowicz, 2016). The investment costs included ozonation plant and UV lamp equipment; and the operating costs were related to the O_3 dose and chemicals used in the treatment. Figure 2.1 shows AOPs utilising UV radiation generally have higher investment costs and treatment costs compare to others. Whereas, the cost of chemical

(H_2O_2) is negligible compared to ozonation and UV application. In comparison, O_3-based AOPs are more economically feasible compared to UV-assisted AOPs.

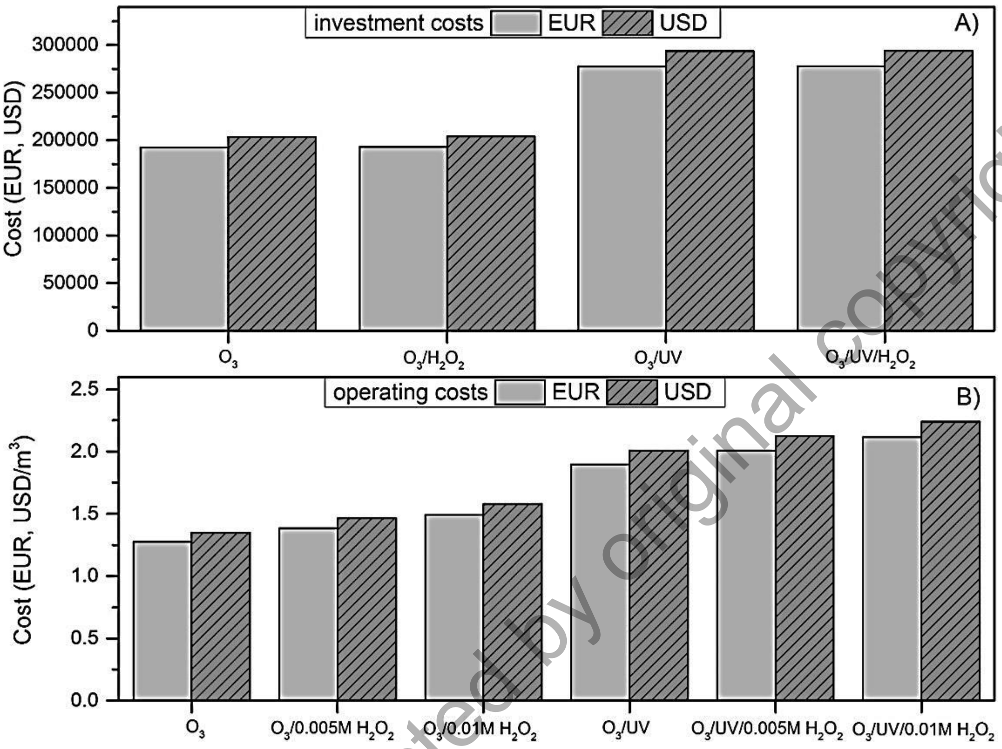


Figure 2.1 Cost estimation for ozonation and AOPs treatment
Source: Bilińska et al. (2016)

Table 2.3 Cost evaluation input data

Parameter	Value
Ozone dose in gas phase	250 g/Nm^3
Gas flow-rate	10 Nm^3/h
Reaction time	0.67 h
Reactor volume	1 m^3
UV lamp energy	16 kW
H_2O_2 0.005 M	0.51 L(H_2O_2 30% a.s.)/m^3
H_2O_2 0.01 M	1.02 L(H_2O_2 30% a.s.)/m^3

Source: Bilińska et al. (2016)

2.3 An Overview of Ozonation and AOPs Studied

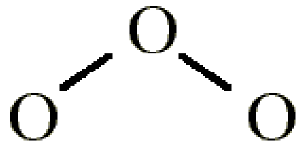
In this study, the treatment methods employed were ozonation and the combination of O_3 with H_2O_2 and persulfate. The involvement of radical precursor could introduce new oxidants species in the reaction medium, improve radical production, and subsequently enhance the treatment efficient. The chemistry and processes mechanisms including radical production and oxidation routes involved in O_3 and AOPs studied were discussed and compared in this section.

2.3.1 Ozonation

Ozonation is the most conventional AOPs and is widely used for water treatment, disinfecting and as oxidizing or reducing agents in industries (Interstate Technology & Regulatory Council, 2005; USEPA, 2014). In ozonation, O_3 and/or radical produced during O_3 decomposition could be used for the oxidation of organic compounds (Hoigne & Bader, 1976). Table 2.4 shows the properties and characteristic of O_3. O_3 can be produced via atmospheric reaction and irradiation of O_2 or other O_3 precursors; however in industries, O_3 gas is often produced onsite from compressed oxygen by using O_3 generator and purged into liquid medium (National Center for Biotechnology Information [NCBI], 2015).

Figure 2.2 shows the process mechanism involved in ozonation. O_3 could react with pollutants via direct oxidation or indirect oxidation through radical produced in the process. However, the role of O_3 in oxidation decreases with increasing pH as a result of the formation of strong radical, $OH^{\bullet}$. The main reactions pathway in decomposition

Table 2.4 Properties and characteristic of O_3

IUPAC name	Ozone
Skeletal formula	
Molecular formula	O_3
CAS	10028-15-6
Chemical name	Ozone; triatomic oxygen; ozon
Molecular Weight (g/mol)	47.998
Physical Description	Colourless to bluish gas with characteristic odor
Density (g/L)	1.962
Melting point (^oC)	- 193
Boiling point (^oC)	-111.35
Solubility	Slightly soluble in water; soluble in alkaline solvents, oils

Source: Lide (2004); NCBI (2015)

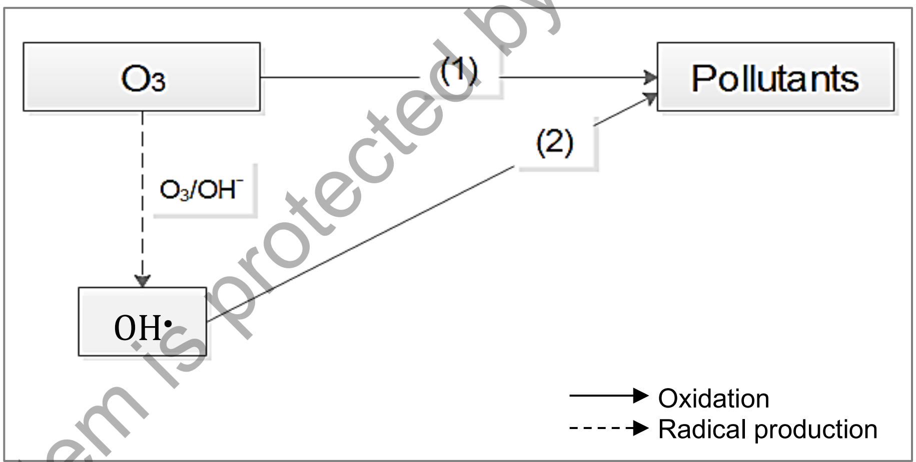


Figure 2.2 Process mechanism involved in ozonation

model of O_3 proposed by Staehelin and coworkers (1984) as well as Tomiyasu Fukutomi, and Gordon (1985) were presented in Equation (2.47 – 2.65). In brief, the formation of $OH^{\bullet}$ involves O_3 decomposition where O_3 reacts with OH^- and HO_2^- to produce $O_2^{\bullet-}$ which eventually leads to $OH^{\bullet}$ formation (Y. Liu et al., 2015). In alkaline condition, $OH^{\bullet}$ can be produced directly via reaction (2.55), but at a slower reaction rate (Tomiyasu et al., 1985). The involvement of $OH^{\bullet}$, $HO_2^{\bullet}$, and $O_2^{\bullet-}$ accelerate O_3

decomposition and propagate the chain reactions of $OH^{\bullet}$ production (Ershov & Morozov, 2009); until the radical reactions are terminated via routes (2.63) – (2.65).

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (2.47)$$

$$O_3 + HO_2^- \leftrightarrow HO_5^- \quad (2.48)$$

$$HO_5^- \rightarrow O_3^{\bullet -} + HO_2^{\bullet} \quad (2.49)$$

$$HO_2^{\bullet} \leftrightarrow O_2^{\bullet -} + H^+ \quad (2.50)$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \quad (2.51)$$

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet} \quad (2.52)$$

$$HO_3^{\bullet} \rightarrow OH^{\bullet} + O_2 \quad (2.53)$$

$$HO_3^{\bullet} \rightarrow O_3^{\bullet -} + H^+ \quad (2.54)$$

$$O_3^{\bullet -} + H_2O \rightarrow OH^{\bullet} + O_2 + OH^- \quad (2.55)$$

$$O_3 + OH^{\bullet} \rightarrow HO_4^{\bullet} \quad (2.56)$$

$$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \quad (2.57)$$

$$HO_2^- + H^+ \leftrightarrow H_2O_2 \quad (2.58)$$

$$O_3^{\bullet -} + OH^{\bullet} \rightarrow HO_2^{\bullet} + O_2^{\bullet -} \quad (2.59)$$

$$O_3 + OH^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \quad (2.60)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (2.61)$$

$$OH^{\bullet} + HO_2^- \rightarrow HO_2^{\bullet} + OH^- \quad (2.62)$$

$$HO_4^{\bullet} + HO_4^{\bullet} \rightarrow H_2O_2 + 2O_3 \quad (2.63)$$

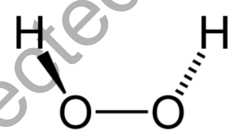
$$HO_4^{\bullet} + HO_3^{\bullet} \rightarrow H_2O_2 + O_2 + O_3 \quad (2.64)$$

$$O_3 + OH^{\bullet} \rightarrow O_3 + OH^- \quad (2.65)$$

2.3.2 Peroxone

Peroxone (O_3/H_2O_2) is a combination of O_3 with $OH^{\bullet}$ precursor, H_2O_2. The properties and characteristic of H_2O_2 were presented in Table 2.5. The common applications of H_2O_2 including as oxidizing and bleaching agents, plating and surface treating agents, cleansing and degreasing solvents, antiseptic, and propellant (ITRC, 2005). In peroxone system, the addition of H_2O_2 in O_3 does not only provides source for $OH^{\bullet}$ production, but also enhances the transformation O_3 to produce $OH^{\bullet}$ via peroxone reaction subsequently improve O_3 transfer from gas to liquid phase as a results of increasing O_3 reaction rate (Staehelin & Hoigne, 1982).

Table 2.5 Properties and characteristic of H_2O_2

IUPAC name	Hydrogen peroxide
Skeletal formula	
Molecular formula	H_2O_2
CAS	7722-84-1
Chemical name	Hydrogen peroxide; oxydol; perhydrol; superoxol; hydroperoxide; inhibine
Molecular Weight (g/mol)	34.015
Physical Description	Dry powder; colourless liquid with a slightly sharp odour
pH	Weak acid; H_2O_2 concentration (wt %)= 35, 50, 70, 90; corresponding true pH= 4.6, 4.3, 4.4, 5.1
Density (g/cm^3)	1.44
Melting point (^oC)	- 0.43
Boiling point (^oC)	150.2
pK_a	11.6
Solubility	Miscible with water; soluble in ether and alcohol; insoluble in petroleum ether

Source: Lide (2004); NCBI (2015)