AQUACULTURE WASTEWATER TREATMENT USING A COMBINATION OF OZONATION PROCESS AND ACTIVATED CARBON ADSORPTION

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by

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LIST OF SYMBOLS

Symbol	Description	Unit
c_1	Initial concentration	mg/L
c_2	Final concentration	mg/L
c_e	Dye concentration at time intervals	mg/L
c_o	Initial dye concentration	mg/L
c_t	Dye concentration at time intervals	mg/L
k	Pseudo-first order rate constant	L/mg.min
t	Reaction time	min
V_1	Initial volume (stock volume)	mL
V_2	Final volume	mL

LIST OF ABBREVIATIONS

AC	Activated carbon
AOPs	Advanced oxidation process
ARS	Alizarin red s.
BOD	Biological oxygen demand
COD	Chemical oxygen demand
COP	Catalytic ozonation process
CW	Constructed wetland
FWS	Free water surface
H_2O_2	Hydrogen peroxide
IVCW	Integrated vertical-flow constructed wetland
MB	Methylene blue
MTZ	Metronidazole
NH_3	Ammonia
O_3	Ozone
SBBR	Sequencing batch biofilm reactor
SBR	Sequencing batch reactor
SBR	Sequencing batch reactor
SDGs	Sustainable development goals
SOP	Single ozonation process
SSF	Subsurface flow
TOC	Total organic carbon
TSS	Total suspended solid
UV-vis	Ultraviolet visible light

RAWATAN AIR SISA AKUAKULTUR MENGGUNAKAN GABUNGAN PROSES OZONATION DAN KARBON TERAKTIF

ABSTRAK

Larutan pewarna sintetik, metilena biru dizonasikan menggunakan penjana ozon bagi menggambarkan penyingkiran warna air sisa akuakultur. Eksperimen ini dijalankan di bawah dos ozon malar iaitu sebanyak 600 mg/jam dan eksperimen ini telah dijalankan sepanjang 60 minit. Faktor – factor yang mempengaruhi proses degradasi juga disiasat, iaitu, kesan kepekatan awal pewarna (mg/L) dan kesan pH. Selain itu, perbandingan antara ozonasi dan kombinasi ozonasi – karbon teraktif disiasat. Ozonasi dilakukan dalam bikar 1L dengan larutan pewarna 500 mL. Kepekatan awal yang dikaji adalah 30 mg/L, 45 mg/L dan 60 mg/L sementara itu pH yang dikaji adalah pH 3, pH 7 dan pH 9 untuk kajian pH. Hasil daripada eksperimentasi menyatakan, kepekatan awal perwarna sebanyak 60 mg/L mengambil masa tindak balas terpanjang untuk mencapai 90% kecekapan penyingkiran warna diikuti oleh 45 mg/L dan 30 mg/L. Ini berlaku adalah kerana ozon telah menjadi bahan pembatas dalam tindak balas kerana dos ozon yang diberikan tetap sama. Kesudahannya, dalam masa 60 minit, semua warna berjaya diturunkan untuk semua kepekatan awal. Selain itu, degradasi biru metilena menggunakan ozon mempunyai penyingkiran warna tertinggi pada pH 9 iaitu di bawah alkali kondisi manakala terendah pada pH 3 iaitu di bawah kondisi berasid. Ozonasi dilakukan dengan baik dalam keadaan alkali kerana lebih banyak radikal hidroksil dapat dihasilkan berbanding dengan keadaan berasid. Kadar degradasi juga ditingkatkan menggunakan kombinasi karbon teraktif bersama perlakuan ozonasi.

AQUACULTURE WASTEWATER TREATMENT USING A COMBINATION OF OZONATION PROCESS AND ACTIVATED CARBON ADSORPTION

ABSTRACT

This study investigates the effectiveness of ozonation treatment alone and combination of ozonation treatment with activated carbon adsorption to treat the synthetic aquaculture wastewater. The solution of a synthetic dye, methylene blue was ozonated using an ozone generator in order to illustrate the color removal of aquaculture wastewater. The experiment was conducted under a constant ozone dosage of 600 mg/h and the concentration was observed throughout 60 minutes. The factors affecting the process of degradation were investigated, i.e., the effects of initial dye concentration (mg/L) and effects of pH. Apart from that comparison between ozonation and ozonation-activated carbon adsorption was observed. The ozonation was done in 1L beaker with 500 mL dye solution. The initial concentration studied in this work were 30 mg/L, 45 mg/L and 60 mg/L meanwhile pH 3, pH 7 and pH 9 for pH studies. As a result, the initial dye concentration of 60 mg/L took the longest reaction time to achieve 90% of color removal efficiency followed by 45 mg/L and 30 mg/L. This happened as ozone became the limiting substances in the reaction since the ozone dosage supplied was kept constant. Eventually, within 60 minutes, all color were successfully removed for all the initial concentrations. Apart from that, the degradation of methylene blue with ozone treatment had the highest color removal at pH 9 which was under basic condition and the lowest at pH 3 which was under acidic condition. Ozonation performed best under alkaline condition as more hydroxyl radicals could be generated compared in acidic condition. Besides that, the rate of degradation was enhanced with the combination of activated carbon adsorption and ozonation treatment.

CHAPTER 1

INTRODUCTION

Chapter 1 shows the overview for this research where it comprises of research background of aquaculture wastewater, advanced oxidation process and activated carbon, problem statement and the objectives of this final year project.

1.1 Background

1.1.1 Aquaculture

The worldwide decline of ocean fisheries has provided positive evolvement in aquaculture industry that gives a great potential towards the contribution of the country's total fish requirement. Aquaculture itself can be defined as the manipulation of the aquatic environment, either natural or artificial in order to augment the production of aquatic organisms that is proved to be useful to mankind (Jones, 1987). Between 1987 and 1997, global production of farmed fish and shellfish reached more than doubled in weight and value that contributes to the world fish supplies (Wu et al., 2016).

According to United Nations Food and Agriculture Organization, global human population will eat a total of 30 million tons of fish by 2030 (Bank, 2013). Therefore, over the next 20-30 years, aquaculture output is set to increase in a range of 60% up till 100% to make sure it is able to keep up with the population growth and increasing per capita (Bank, 2013). As in Malaysia, this industry has experienced rapid growth from small scale family-oriented business to large operations. **Table 1.1** summarized the quantity of aquaculture production in Malaysia.

Table 1.1: Aquaculture production by culture environment in Malaysia (*FAO Fisheries & Aquaculture - National Aquaculture Sector Overview - Malaysia*, n.d.).

Year	Environment	Quantity
2016	Marine	39 460
2016	Freshwater	103 848
2016	Brackish water	58 589
2017	Marine	49 001
2017	Freshwater	103 096
2017	Brackish water	72 451
2018	Marine	55 506
2018	Freshwater	101 770
2018	Brackish water	60 617

In 2008, the exportation of aquaculture recorded an increment in growth rates as much as RM 1,323,280 to RM 1,769,305. Since Malaysia is strategically surrounded by busy sea lanes, it has an easy access to fish and fish products. This makes Malaysia as one of the countries with highest fish consumption in the world (Wahab et al., 2009).

The intensive growth in aquaculture production is a mixed blessing, however, wastewater generated from the industry remains as main concern. Waste components such as nitrogenous compounds and phosphorus are causing environmental problems (Turcios & Papenbrock, 2014). Fish respiration and decomposition of excess organic matter will produce ammonia (NH_3) as the main product.

1.1.2 Advanced oxidation process

Discharged water containing various contaminants will cause serious damage. The dissolved oxygen (DO) level and ecological balance of the ecosystem at the nearby receiving water bodies will be badly affected. For example, ornamental aquaculture industry use metronidazole (MTZ), an antibiotic derived from nitroimidazoles, for treatment of infections caused by anaerobic protozoa and bacteria such as *Hexamita* and *Amyloodium*. MTZ have characteristics such highly soluble in water, have low biodegrability and are a potential health hazard as they are mutagenic ad carcinogen (Santana et al., 2017).

Antibiotics can be classified as emerging pollutants and can results in accumulation of this contaminant in aquatic medium. Conventional wastewater treatments are not effective since they could not treat certain compounds. For instance, the MTZ case, conventional wastewater treatment does not eliminate MTZ that have potential to accumulate in aquatic environment. Hence, lower cost and robust processes to decontaminate and disinfect wastewater are required. A lot of studies have been conducted in finding the suitable technology for the wastewater treatment.

In this context, advanced oxidation process (AOPs) have led the way in the treatment of aqueous waste especially for aquaculture wastewater (Mandal et al., 2010). Compared to conventional, they are known for their varied applications such as Bio-degradability improvement biological oxygen demand (BOD)/ chemical oxygen demand (COD) removal as well as odour and color removal and also capable of attacking organic compounds via four pathways, they are hydrogen abstraction, combination or addition of radicals and electron transfer.

Advanced oxidation technologies are based on the in-situ generations of strong oxidants such as hydroxyl radicals for the oxidation of organic pollutants (Ghime & Ghosh, 2020). Hydroxyl radicals has oxidation potential two times stronger than chlorine and they are non-selective in which they attack almost all organic materials. Different AOPs are used for different purposes. Among various types of AOPs, photocatalysis process was less efficient for the seawater matrix treatment. This is because within the 4 hour of treatment, removal of total organic carbon (TOC) was lower than 20%. Better results can be obtained by using ozonation process that combined with oxidant hydrogen peroxide (H_2O_2). The combination of H_2O_2 and ozone gives a complete removal of organics. Moreover, the combination has higher percentage removal of acetic acid than other AOPs used (Ghime & Ghosh, 2020).

1.1.3 Activated Carbon Adsorption

Adsorption process is relevant in environmental pollution and protection with reference to both water and wastewater treatment. Therefore, it can be considered as better alternative in wastewater treatment due to its convenience, the ease of operation and simplicity of design. It is usually applied to remove the dissolved pollutants that remained from the subsequent biological phase or after chemical oxidation treatments in wastewater treatment plants. Adsorption by solids decreases the toxicity of the wastewater or remove the non-safe organic materials from the effluent (Malik, 2004). According to Malik (2004), adsorption onto activated carbon has proven to be one of the most effective and reliable physicochemical treatment methodologies.

1.2 Problem Statement

Aquaculture is a growing industry and became a key role in world supplies. The intensive growth in aquaculture industry has carried an environmental burden as the aquaculture wastewater effluent contain waste components that resulted in water pollution problem. Treatment processes for aquaculture wastewater often depend on conventional methods include coagulation/flocculation, precipitation, biological systems and adsorption that have many drawbacks.

Biological systems such as the utilization of biofilter, sequencing batch reactor (SBR), constructed wetlands and on oxidation pond are not adaptable for wastewater treatment due to their low treatment capacities, high costs, slow processes and high selectively for various pollutants. Therefore, a combination system of advanced oxidation process with adsorption process is proposed in this study due to their ability to destroy a wide variety of contaminants.

In this study, ozonation and activated carbon will be used. Previously, ozonation process coupled with adsorption using activated carbon is proved to be effective for wastewater treatment. A study from (Poblete et al., 2017) proved that AOPs (Solar/H2O2/O_3) with activated carbon adsorption showed an increment in color and COD removals for landfill leachate. In this study, activated carbon adsorption followed by ozonation AOP will be used on aquaculture wastewater in which the activated carbon adsorption is expected to increase the rate of decolorization and the elimination rate of total organic carbon. The treatment for the wastewater using ozonation process only will be compared with ozonation process coupled with activated carbon adsorption.

1.3 Objectives

i. To prepare synthetic aquaculture wastewater, hybrid activated carbon and ozonation process test to effectively treat synthetic aquaculture wastewater.
ii. To study the impact of ozonation process on the rate of decolorization
iii. To evaluate the synergy between activated carbon adsorption and ozonation process for the aquaculture wastewater treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater management used in aquaculture wastewater

There are a lot of conventional wastewater treatment technologies exist throughout the world. Conventional physical, chemical and biological methods have been used in aquaculture systems. Due to the cost and power consumptions, many developing countries could not afford to construct or develop the existing wastewater treatment technologies (Omotade et al., 2019). The following system are considered as the used of these methods are increasing: 1) constructed wetlands system 2) sequencing batch reactor to be further reviewed and discussed.

2.1.1 Constructed Wetland System

Constructed wetland (CW) is one of the effective and well-established wastewater treatment system. It has been widely applied to the treatment of domestic wastewater, mine wastewater, landfill leachate and ground runoff, etc. (Li et al., 2007). It has been demonstrated and proved by researchers that treatment wetland systems can remove significant amounts of suspended solids, organic matter, nitrogen, phosphorus, trace elements and microorganisms contained in wastewater (Y. F. Lin et al., 2002). CWs principle is a highly effective and ecologically sound design which utilize the used of plants, microbes, sunlight and gravity for wastewater recycling and purifying into reusable water (Omotade et al., 2019). This system has advantages in terms of moderate capital costs, low energy consumption and maintenance requirements and benefits of increased wildlife habitat. CWs can be further classified according to the presence/absence of free water surface (FWS), macrophytes used or the direction of the flow (see **Table 2.1**).

Different types of CWs can be integrated i.e. hybrid or combined systems to utilize advantages of the individual features of each system (Omotade et al., 2019). In continuity, the primer problem of the performance of CWs is clogging of the filtration substrate. Hence, it is important to select the right filtration material, distribute the wastewater evenly across the surface of the wetland and also choose the optimum hydraulic loading rate. (Lin et al., 2002) demonstrated a two-stage pilot scale system comprised of free water surface (FWS) and a subsurface flow (SSF) constructed wetlands which are a hybrid constructed wetlands to analyse the removal of nutrients (ammonium, nitrate, nitrite, and phosphate) and the removal of suspended solids, algae and oxygen demand respectively meanwhile (Li et al., 2007) demonstrated an integrated vertical-flow constructed wetland (IVCW) for the aquaculture wastewater treatment to reuse the water for aquaculture and to reduce the discharge of nutrients into natural water body.

From the studies of the hybrid CW systems, the FWS wetland will removed most organics and suspended solids and to denitrification, the SSF wetland will further remove the organics and enhance the denitrification. The systems were able to show a quick start-up behaviour and effective performance in removing the suspended solids, algae and oxygen demand and also nutrients. (Li et al., 2007) also obtained positive results as the system used was able to reduce the concentration of 5-day biochemical oxygen demand, total suspended solids, chlorophyll, ammonium and nitrate nitrogen. However, despite the benefits offered from CWs, the construction cost is significantly high due to the demand of a specific growth substrate (sand or gravel) apart from high land area requirements and the need for a preliminary treatment before the wastewater is treated by the system itself. **Table 2.2** summarize the advantages and limitations of CW system.

Table 2.1: Type of constructed wetlands (Maiga et al., 2019)

Constructed Wetlands	Plants	Flow	Direction
Free water - surface	-Free-floating -Floating-leaved -Submerged -Emergent	-Horizontal	
Subsurface flow	-Emergent only	-Horizontal -Vertical	-Downflow -Upflow

Table 2.2: Advantages and limitations of constructed wetland systems (Omotade et al., 2019).

Advantages	Limitations
CWs are considered as one of the most fertile and productive ecosystems next to rainforest and coral reef.	The technologies are rather underdeveloped.
Can easily be maintained since the system has low maintenance.	Lack of statistical data on the system performance and treatment efficiency.
Create a better habitat for wildlife due to the ability of the natural habitat to generate habitat for a variety of species.	Performance of the system under adverse weather in which cold temperatures slow the treatment process. Meanwhile dry spells and droughts coming from high temperature or lack of rain may damage plants and limit the treatment ability. Heavy rainfalls and snow that melt in spring have the potential to overload the CWs.
Able to treat large volume of aquaculture wastewater as the system has the ability to treat more effluent per area.	High cost and require big surface area of land.
	Skilled daily operation is needed.

2.1.2 Sequencing Batch Reactor

A sequencing batch reactor (SBR) system is a variation of the activated sludge biological treatment process (Boopathy et al., 2007). Multiple steps will take place in the same tank in order to replace the used of multiple tanks. This process accomplishes equalization, aeration and clarification in a timed sequence, in a single-reactor basin

(Lyles et al., 2008). Generally, it incorporates a fill-and-draw type biological wastewater treatment process. A typical SBR treatment process consists of five basic operating stages namely as fill, react, settle, decant/draw and idle (see **Figure 2.1**).

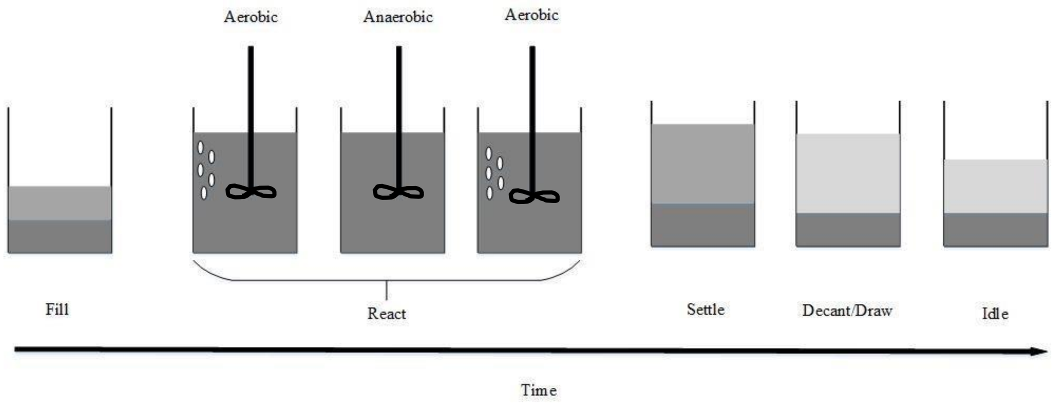


Figure 2.1: Process stages in sequencing batch reactor treatment process (Roy et al., 2010).

Some of the benefits using SBR treatment process are increased control over the reliability, precision and versatility of the reactor apart from the infrastructure requires less capital investment and significantly less plumbing and space requirements (Kern & Boopathy, 2012). **Table 2.3** shows the benefits and disadvantages using SBR. Moreover, the operation can be modified according to the characteristics of the influent stream to achieve the desired effluent concentration.

Table 2.3: Advantages and disadvantages of sequencing batch reactor (SBR) (Torczon, 2015)

Advantages	**Disadvantages**
Possibilities having high treatment efficiencies for BOD, COD, TSS, N, P	Has low pathogen removal
High flexibility in operating conditions	Skilled personnel are required in handling SBR with sludge digestion
Electric energy can be produced from biogas coming from SBR and anaerobic sludge digestion	Depend on uninterrupted power supply
Less land is required as tank construction is compact	Need more automation
	Need proper operation since biogas is explosive
	Depend on some foreign spare parts almost inevitable

Boopathy et al. (2007) and Kern & Boopathy (2012) conducted a study using SBR on shrimp aquaculture wastewater to determine and analysed the removal of carbon and nitrogen from the wastewater. Nitrification and denitrification were achieved as well as the removal of carbon. The results from the experiments are summarized in **Table 2.4**. Another study conducted by Hassaan et al. (2017) in studying the impact of carrier on ammonia and organics removal using four different carriers (porous, plastic, bamboo ring, maifan stone and ceramsite) in sequencing batch biofilm reactor (SBBR). Apart from that, they also studied carbon and nitrogen removal rates. They found that ceramsite had the best NH_4^+-N removal rates of 0.093 ± 0.003 kg/ (m^3.d) followed by maifan stone, bamboo ring and plastic with removal rates of 0.089 ± 0.005, 0.065 ± 0.008 and 0.045 ± 0.05 kg/ (m^3.d) respectively.

Table 2.4: Concentration of parameters and days taken to reduce the concentration.

	Shrimp Aquaculture Wastewater			
Parameters	**Initial concentration (mg/l)**	**Concentration (mg/l)**	**Days taken to reduce the concentration**	**References**
COD	120	32	8 days	(Boopathy et al., 2007)
	1593	44	10 days	(Lyles et al., 2008)
	1593	1000	8 days	(Kern & Boopathy, 2012)
Ammonia	101.7	0	3 days	(Boopathy et al., 2007)
	91.0	0	3 days	(Lyles et al., 2008)
	249.7	0	9 days	(Kern & Boopathy, 2012)

2.2 Advanced Oxidation Process

Generally, conventional treatment methods are the common methods applied in wastewater treatment. However, they are not classified advanced enough for inorganic and/or organic compounds in aquaculture wastewater. Conventionally, the methods used can be divided into two main categories: physicochemical and biological methods (Crini & Lichtfouse, 2019). Physicochemical treatment methods include coagulation, precipitation, adsorption using activated carbon.

Crini & Lichtfouse (2019) listed all the benefits and disadvantages of the conventional methods individually which concluded that one of the limitations of physicochemical treatment methods is they can be very costly. Both precipitation and coagulation have high sludge production problem that require additional treatment. As for biological treatment methods, the limitations would be they have very poor decolorization and possibility of sludge bulking and foaming. Therefore, researchers are now concentrating on cheaper effective combinations of systems or new alternatives.

Advanced oxidation processes are one of the emerging removal methods. They are powerful methods that have been widely used to decomposed organic products in industrial wastewater and ground-water where they offered the abilities to mineralize most of the organic contaminants into carbon dioxide and water. Konsowa et al. (2010) mentioned in the article AOPs such as ozonation, UV/H_2O_2, UV/O_3 are highly versatile methods that have proved and been widely used to treat organic contaminants into carbon dioxide and water. AOPs can be classified into homogeneous phase and heterogeneous phase as shown in **Table 2.5**.

Table 2.5: Classification of AOPs major types (Biń & Sobera-Madej, 2012)

Advanced Oxidation Processes (AOPs)			
Homogeneous Phase		**Heterogeneous Phase**	
Photochemical processes	**Chemical processes**	**Photochemical processes**	**Chemical processes**
UV photolysis	O_3/H_2O_2 system	UV/O_2/TIO_2 system	Electro – Fenton reaction
UV/O_3 system	Ozonation in alkaline (O_3/OH^-)	UV/ H_2O_2/TIO_2 system	
UV/H_2O_2 system	Fenton reaction (Fe^{2+}/ H_2O_2)		
UV/ultrasound system	Ultrasound (Sonolysis)		
Photo – Fenton reaction	Ultrasound/ H_2O_2 system		
	Supercritical Water Oxidation – SCWO		
	Wet Air Oxidation – WAO		

Shu & Chang (2005) described how the system works. The degradation of organics in wastewater occurs with the help of dominants species known as free radicals ($OH^{\cdot}$). They added that AOPs account of activation of hydrogen peroxide, or ozone, with UV light to produce hydroxyl radicals which have 2.8 V, higher oxidation potential than that of hydrogen peroxide with 1.78 V. The triumph of the application on wastewater treatment has been reported in many investigations. **Table 2.6** summarized the used of advanced oxidation process on different type of wastewater. For example, UV/H_2O_2 process was demonstrated by Xu et al. (2004) and it was proved able to decolorize the dye used in the experiment meanwhile Yildirim et al. (2011) demonstrated about degradation of C.I. reactive red 194 Azo dye using ozonation, homogeneous catalytic ozonation and photocatalytic ozonation.

Table 2.6: Summary of used of different type of wastewater on different type of wastewater

Type of AOPs	Type of wastewater	Oxidant for advanced oxidation	Reference
-H_2O_2/UV -H2O2/Fe2+ -H_2O_2/Fe^{2+}/UV	Model dye wastewater	OH·	(Xu et al., 2004)
-O3	Model dye wastewater	OH·	(Yildirim et al., 2011)
-O3 -O3/ H2O2 -O_3/UV -H_2O_2/UV	Groundwater contaminated with trichloroethylene (TCE), tetrachloroethylene (PCE)	OH·	(Glaze & Kang, 1988)
-H_2O_2 -H_2O_2/UV -UV -O3 -Photocatalysis -Fenton -Photo-Fenton	Petroleum refinery sourwater	OH·	(Coelho et al., 2006)

-UV -UV/ H_2O_2 -Fenton -Photo-Fenton	Model compounds of organo-phosphorus	OH·	(Badawy et al., 2006)
-UV -US (sonication) -UV/TiO_2 -US/UV/ TiO_2	Olive mill wastewater	OH·	(Al-Bsoul et al., 2020)

Ozone is a powerful oxidant and is popularly used to decompose organic micropollutants in water. According to Medellin-Castillo et al. (2013), AOPs based on ozone have been developed to enhance the effectiveness of ozonation and to reduce the ozone consumption for a given application since the application of conventional ozonation to wastewater treatment has been hinder with the slow chemical kinetics and having possibility to form intermediate compounds that are even more toxic than the original compound. Ozonation can efficiently eliminate most pathogens that can affect seafood quality in both freshwater and seawater aquaculture systems. In addition, ozonation system can reduce total organic carbon (TOC), nitrate, color and suspended solids (Tango & Gagnon, 2003).

Konsowa et al. (2010) investigated the factors affecting the rate of decolorization of synthetic waste solution containing a water-soluble direct dye by ozonation. The results from the experiment concluded that increasing in ozone concentration, gas flow rate and pH was found to reduce the decolorization time and increasing initial dye concentration was found to increase the decolorization time.

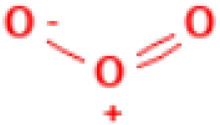
In order to increase the system, ozonation process can be couples with adsorption using activated carbon. Activated carbon adsorption is a technologically simple and adaptable to many treatment formats. Poblete et al. (2017) mentioned in their article that adsorption processes with the usage of activated carbon have been extensively used to remove pollutants from water where they can remove a wide range of both organic and inorganic.

A comparative study was carried out by Poblete et al. (2017) by using AOPs with and without adsorption that was performed using activated carbon. The results showed that AOPs specifically solar/H2O2/O3 with activated carbon adsorption achieved higher color elimination which was at 75.8% compared to AOPs alone which was only at 59.7%. This comparative study concluded that higher percentages of color elimination was obtained when AOPs were preceded by an adsorption process than process directly applied without adsorption pre-treatment.

2.3 Ozonation

Ozone is an allotrope of oxygen that is known as a powerful oxidant. It is even more powerful than chlorine and other oxidants (Bidhendi et al., 2006). It is relatively unstable in aqueous solution and have a half-life of 20 – 30 minutes at 20 degrees centigrade. Properties of ozone can be seen in **Table 2.7** below.

Table 2.7: Ozone properties

Ozone properties	
Molecular formula	O_3
Structure	
Molecular weight	47.988
Melting point	-111.9°C
Physical properties	
▪ Appears as a colorless to bluish gas that condenses to a dark blue liquid, or blue – black crystal. ▪ Has a characteristic odor in concentrations less than 2 ppm. ▪ Used as a disinfectant for air and water; for bleaching waxes; for textiles and oils; ozonolysis of unsaturated fatty acids to pelargonic and other acids; manufacture of ink; catalyst; water treatment for taste and odor control; mold and bacteria inhibitor in cold storage; bleaching agent	

When it is added into the water, enhancement of protein can occur apart from water clarity, UV transparency and the processes of coagulation, filtration and nitrification are improved (Spiliotopoulou et al., 2017). In engineering perspective, ozonation treatment has its own advantages. The devices are generally small and versatile leading the ozonation treatment become a more promising in on – site treatment of waste effluents (Hu et al., 2019). The benefits and disadvantages of ozonation can be seen in **Table 2.8**.

Table 2.8: Advantages and disadvantages of ozonation treatment (Pirani, 2011).

Advantages	**Disadvantages**
Reacts rapidly with bacteria, viruses and protozoa over a wide pH range	Equipment is expensive
Has stronger germicidal properties than chlorination	Large amount of energy is needed
No chemicals are needed	By – products from the process are still being evaluated and some of them have the possibilities are carcinogenic
Efficient for organics degradation and inorganics removal	No residual effect is present in distribution system
Has the ability to remove colour, taste and odour	Ozone generation has fire hazard potential

Ozone process can be accomplished in two pathways: direct ozone oxidation and indirect free hydroxyl radical oxidation (Chiang et al., 2006). The two pathways are illustrated in **Figure 2.2**.

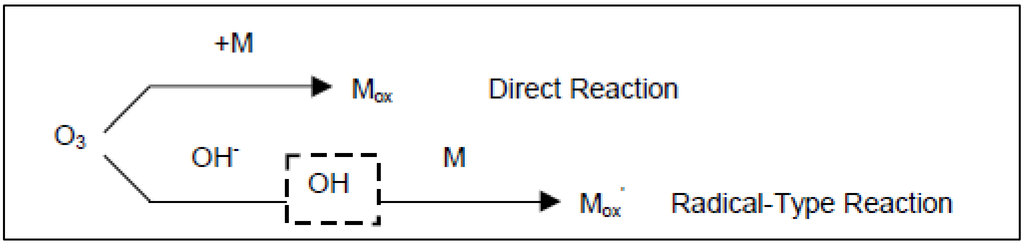


Figure 2.2: Ozone reactivity in aqueous solution (Langlais et al., 1991)

In real life, both reactions will take place. Depending on various factors, i.e., temperature, pH and chemical composition of the water, one of them will dominate.

2.3.1 Direct ozone oxidation

Direct ozonation is a selective reaction with a slow reaction rate constants in a range of 1.0-10^6 $M^{-1}s^{-1}$ (S. N. Malik et al., 2020). Under acidic conditions, direct oxidation is more selective and predominates. In the overall ozone reaction, three ozone molecules are needed to produce two hydroxyl radicals as shown as below:

$$3O_3 + OH^- + H^+ \rightarrow 2OH^\circ + 4O_2 \tag{2.1}$$

Based on **Figure 2.3** below, three types of reactions usually occur. They are cyclo addition, electrophilic addition and nucleophilic addition.

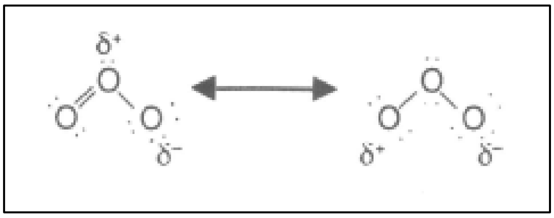


Figure 2.3: Ozone resonant structure (Langlais et al., 1991)

2.3.1(a) **Cyclo addition (Criegee mechanism)** (Langlais et al., 1991)

An ozone molecule has the capability to undergo a 1-3 dipolar cyclo addition with saturized compounds (double or triple bonds) leading to the formation of compound called ozonide (I), see

Figure 2.4. In protonic solvent like water, primary ozonide will decompose into a carbonyl compound (aldehyde or ketone) and a zwitterion (II). This quickly led to a hydroxy – hydroperoxide (III) stage in which in turn, decompose into carbony compound and hydrogen peroxide. The reactions are illustrated in **Figure 2.5**.

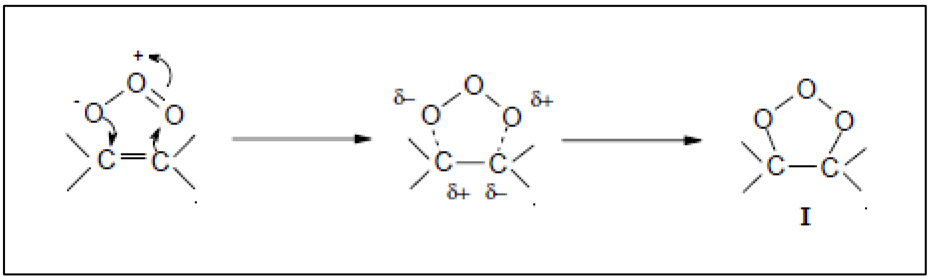


Figure 2.4: Dipolar cyclo addition (Langlais et al., 1991)

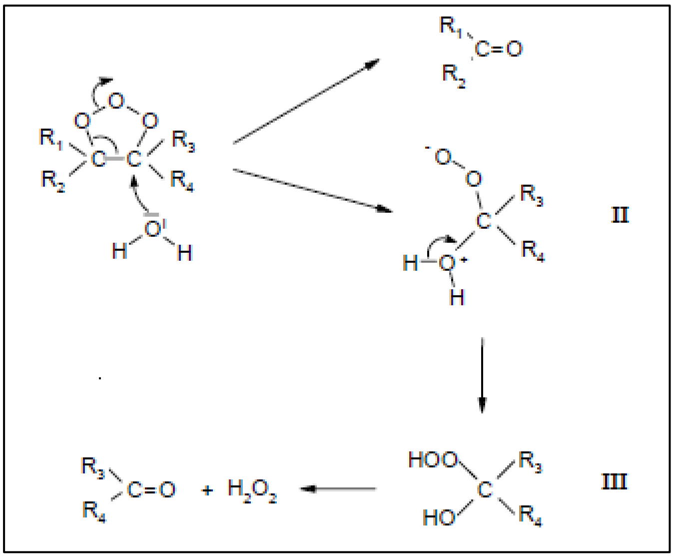


Figure 2.5: Criegee mechanism (Langlais et al., 1991)

2.3.1(b) Electrophilic reaction

Electrophilic addition is the primary principle for the initial reaction of ozone and the reactions occur in molecular solutions with electron – rich organic compounds including aromatic rings substituted with electron – donating groups, phenols/phenolates and polyaromatic compounds (Wei et al., 2017). The ozone molecule's initial attack is focused on the least deactivated meta position leading to aromatic compounds to bear the electron donor groups D, i.e., phenol and aniline react quickly with ozone. The reaction is presented in **Figure 2.6** where the first formation of ortho- and para-dydroxylated by-products will be produced from the initial attack of ozone molecules. The compounds will form quinoid and aliphatic products with carbonyl and carboxyl functions as they are highly susceptible to further ozonation.

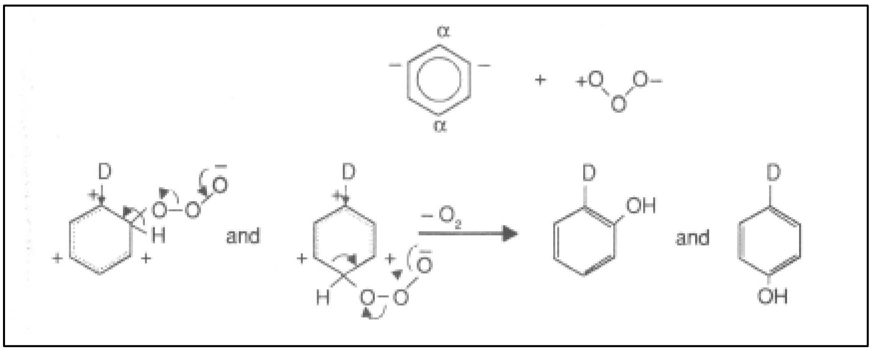


Figure 2.6: Aromatic compounds that undergo electrophilic reaction (Langlais et al., 1991)

2.3.1(c) Nucleophilic reaction

Since ozone also has the possibilities to behave as a nucleophilic reagent, it is capable to react with electron-deficient positions of carbonyl groups, carbon-nitrogen triple or double bonds (Wei et al., 2017). Based on **Figure 2.7**, ozone molecules are extremely selective and they are limited to unsaturated aromatic and aliphatic compounds as well as to specific functional groups.

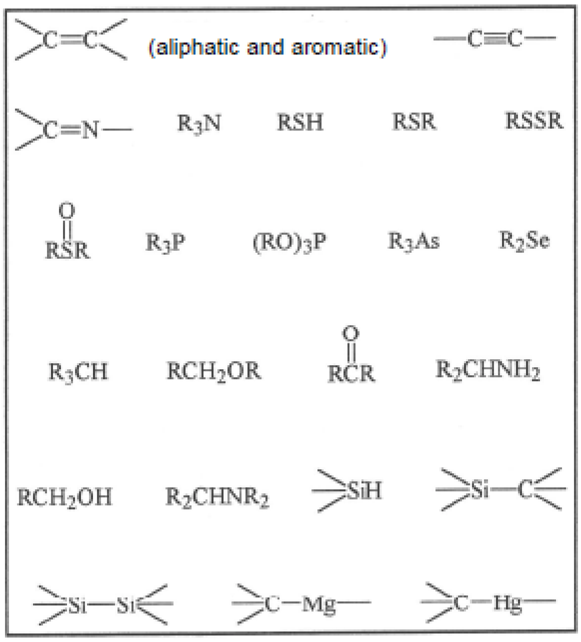


Figure 2.7: Organic group opens that can be attacked by ozone (Langlais et al., 1991)

2.3.2 Indirect reactions

Other than direct reactions mentioned earlier, oxidation can also be achieved through indirect reaction with oxygen-containing radicals generated from homogeneous and heterogeneous catalytic decomposition of ozone. The homogeneous catalytic ozone decomposition mechanisms in aqueous solution that involved SHB Bühler et al. (1984) and TFG (Tomiyasu et al., n.d.) models. The models' initiation steps, propagation and termination steps are as below:

Table 2.9: Reactions for indirect oxidations

	SHB models		
Chain initiation	$O_3 + OH^- \rightarrow HO_2^\bullet + O_2^{\bullet-}$	$k = 70\ l/(mol.s)$	(2.1)
Chain propagation	$HO_2^\bullet \rightarrow H^+ + O_2^{\bullet-}$	$k = 7.9\ \times 10^5\ \ l/(mol.s)$	(2.2)
	$H^+ + O_2^{\bullet-} \rightarrow HO_2^\bullet$	$k = 5\ \times 10^5\ \ l/(mol.s)$	(2.3)
	$H^+ + O_3^{\bullet-} \rightarrow HO_3^\bullet$	$k = 5.2 \times 10^{10}\ \ l/(mol.s)$	(2.4)
	$HO_3^\bullet \rightarrow\ \ H^+ + O_3^{\bullet-}$	$k = 3.3\ \times 10^2\ \ s^{-1}$	(2.5)
	$HO_3^\bullet \rightarrow\ \ O_2 + OH^\bullet$	$k = 1.1\ \times 10^5\ \ s^{-1}$	(2.6)
	$O_3 + OH^\bullet \rightarrow HO_4^\bullet$	$k = 2\ \times 10^9\ \ s^{-1}$	(2.7)
	$HO_4^\bullet\ \rightarrow HO_2^\bullet +\ O_2$	$k = 2.8\ \times 10^4\ \ s^{-1}$	(2.8)
Chain termination	$HO_4^\bullet + HO_4^\bullet \rightarrow H_2O_2^\bullet +\ 2O_3$	$k = 5\ \times 10^9\ \ l/(mol.s)$	(2.9)
	$HO_4^\bullet + HO_3^\bullet \rightarrow H_2O_2^\bullet +\ O_3 + O_2$	$k = 5\ \times 10^9\ \ l/(mol.s)$	(2.10)
	TFG models		
Chain initiation	$O_3 + OH^- \rightarrow HO_2^- + O_2^-$	$k = 40\ l/(mol.s)$	(2.11)
Chain propagation	$O_3^{\bullet-} +\ H_2O\ \ \rightarrow \bullet\ OH + O_2 +\ OH^-$	$k = 20 - 30\ l/(mol.s)$	(2.12)
	$O_3^{\bullet-}\ + \bullet\ OH\ \ \rightarrow HO_2^\bullet + O_2^{\bullet-}$	$k = 6\ \times 10^9\ \ l/(mol.s)$	(2.13)
Chain termination	$CO_3^{\bullet-} + \bullet\ OH \rightarrow\ \ HO^-\ + CO_3^{\bullet-}$	$k = 4.2\ \times 10^8\ \ l/(mol.s)$	(2.14)
	$CO_3^{\bullet-} + O_3^{\bullet-}\ \ \rightarrow\ \ O_3 + CO_3^{\bullet-}$	$k = 6\ \times 10^7\ \ l/(mol.s)$	(2.15)
	$HCO_3^-\ + \bullet\ OH \rightarrow\ \ HO^-\ + CO_3^{\bullet-}$	$k = 8.5\ \times 10^6\ \ l/(mol.s)$	(2.16)
	$HCO_3^\bullet \rightarrow\ \ H^+\ + CO_3^{\bullet-}$	$k = 500\ \ s^{-1}$	(2.17)

CHAPTER 3

MATERIALS AND METHODS

3.1 Research methodology

This final year project focused on the experiment of aquaculture wastewater treatment using a combination of ozonation process and activated carbon adsorption. **Figure 3.1** shows the activity of the research.

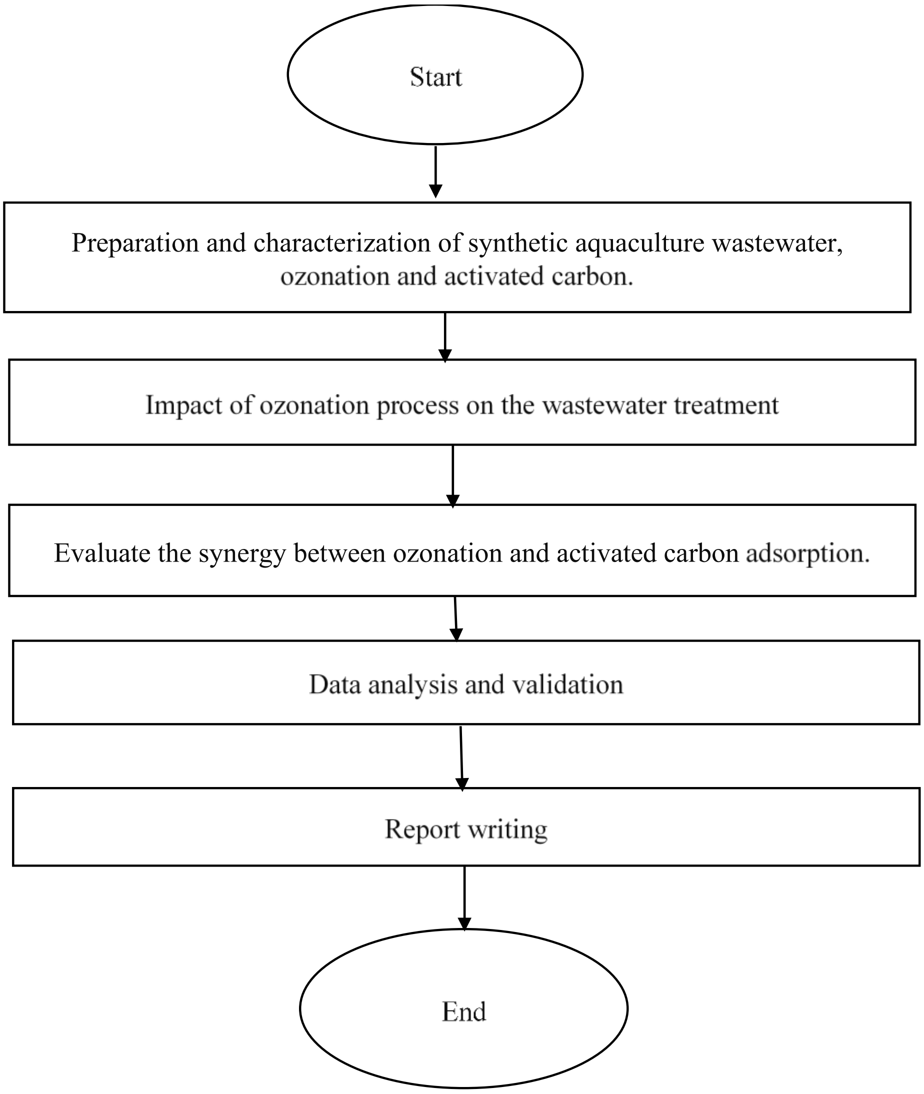
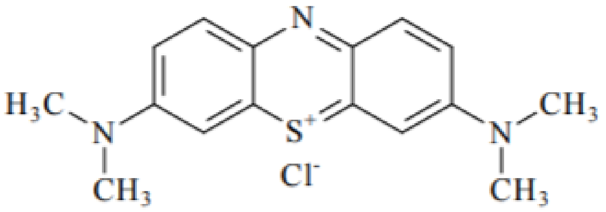


Figure 3.1: Flow diagram of research project

3.2 Reagent, Solutions and Material Used

The commercially dye utilized in this experiment without further purification was Methylene Blue and it was supplied by Fischer Scientific UK, Bishop Meadow Road, Loughborough. It is soluble in water and has properties as listed **Table 3.1**. Distilled water was used throughout this experiment to prepare all the solutions needed. Ozone was generated from ozone generator (power supply: 220V, 50Hz; power consumption: 12 W; function time controller: 5-60 min) with a fixed ozone production of 600 mg/h. The initial pH of the dye solution was altered using 0.1M sodium hydroxide and 0.1M hydrochloric acid to the necessary pH.

Table 3.1: Properties of methylene blue (MB) (Koch, 2016)

Commercial name	Methylene blue
Trade names	Urelene blue, Proveblue, Provable
Molecular weight (g/mol)	319.85
Molecular formula	$C_{16}H_{18}CIN_3S$
Structure	
CHEMICAL AND PHYSICAL PROPERTIES	
Description	▪ Dark green crystals or crystal line powder with bronze lustre; ▪ Odourless; ▪ Stable in air; ▪ Deep blue solution in water or alcohol; ▪ Form double salts
Melting point	100-110 ˚C
Density	1.0 g/mL (20 ˚C)
Solubility	43.6 g/L in water at 25 ˚C; soluble in ethanol
Vapour pressure	1.30 x 10^{-7} mm Hg at 25 ˚C (estimated)