REMOVAL OF
HUMIC ACID FROM WATER USING AN OZONATION ALONE AND COMBINATION OF OZONATION AND ADSORPTION

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by

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LIST OF ABBREVIATION

AC	Activated Carbon
AOP	Advance Oxidation Process
BOD	Biochemical Oxygen Demand
$CHBr_3$	Bromoform
$CHBrCl_2$	Bromodichloromethane
$CHCl_3$	Chloroform
COD	Chemical Oxygen Demand
DBP	Disinfection By-Product
DOC	Dissolved Organic Carbon
e^-	electron
E. Coli	Escherichia coli
Eh	Oxidation Potential
EPS	Extracellular Polymeric Substances
Fe^{3+}	Iron (III)
H^+	Hydrogen ion
H_2O_2	Hydrogen Peroxide
HA	Humic Acid
HAA	Haloacetic acid
HO_2	Water
$HO2^-$	Hydroperoxyl
HOCl	Hypochlorous Acid
HS	Humic Substances
$HS0_5^-$	Peroxymonosulfate anion

MnO_4^-	Permanganate ion
NOM	Natural Organic Matter
O2	Oxygen
O3	Ozone
OCl2	Dichlorine Monoxide
OH	Hydroxide
OH·	Hydroxyl radical
pH	Potential of Hydrogen
S_2O^{-2}	Persulfate anion
SDG	Sustainability Development Goal
$SO4^{\cdot -}$	Sulfate radical
TOC	Total Organic Matter
THM	Trihalomethanes
TiO_2	Titanium Dioxide
TOM	Total Organic Matter
TSS	Total Suspended Solid
UNICEF	United Nations Children's Fund
US	Ultrasonic sound
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
UV/Vis	Ultraviolet Visible Light
V	Voltage
VSS	Volatile Suspended Solid
WHO	World Health Organization

LIST OF SYMBOLS

C_1	initial concentration
C_2	final concentration
C_{HA_e}	final concentration of humic acid
C_{HA_O}	initial concentration of humic acid
C_i	initial concentration of treated pollutant
C_e	effluent concentration of treated pollutant
C_o	initial humic acid concentration
C_t	humic acid concentration at different time interval
k_1	rate of constant of in the reaction of ozonation
V	volume of treated water
V_1	initial volume (stock volume)
V_2	final volume
W	power of oxidation system

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ABSTRAK

Kajian ini menilai prestasi ozonasi sahaja dan proses ozonasi hibrid di mana ozonasi ditambah dengan karbon yang diaktifkan dan batu lava masing-masing. Penyingkiran asid humik dinilai oleh penyerapan UV254. Apabila ozonasi digunakan semata-mata, penyingkiran adalah 54.91% pada kepekatan asid humik 10 mg/L, pH 7 dan masa pengoksidaan 20 minit. Hasilnya menunjukkan bahawa penggunaan karbon diaktifkan sebagai penyerap meningkatkan penyingkiran asid humik berbanding dengan ozonasi sahaja kerana boleh bertindak sebagai penjerap dan pemangkin. Kecekapan penyingkiran adalah 96.36 % pada masa pengoksidaan 20 minit, pH 7 dan pemangkin pemangkin 1 g/L. Eksperimen pengoksidaan juga dijalankan menggunakan batuan lava dan kecekapan penyingkiran adalah 76.76 % pada masa pengoksidaan 20 minit, pH 7 dan pemuatan 5g/L. Ini menunjukkan bahawa ozonasi ditambah dengan karbon diaktifkan sangat berkesan berbanding dengan batu lava. Kesimpulannya, proses ozonasi hibrid menghasilkan lebih baik berbanding dengan ozonasi sahaja.

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ABSTRACT

This study evaluates the performance of ozonation alone and hybrid ozonation process in where ozonation coupled with activated carbon and lava rocks respectively. The removal of humic acid was evaluated by UV_{254} absorbance. When ozonation was used alone, the removal was 54.91% at a humic acid concentration of 10 mg/L, pH 7 and oxidation time of 20 minutes. The results showed that the use of activated carbon as an adsorbent increased the removal of humic acid compared to ozonation alone as it can act as adsorbent and catalyst. The removal efficiency was 96.36 % at oxidation time of 20 minutes, pH 7 and catalyst loading of 1 g/L. The oxidation experiment was also carried out using lava rocks and the removal efficiency was 76.76 % at oxidation time of 20 minutes, pH 7 and loading of 5g/L. This indicates that ozonation coupled with activated carbon is highly effective compared to lava rocks. In conclusion, hybrid ozonation process yields better compared to ozonation alone.

CHAPTER 1

INTRODUCTION

1.0 Introduction

This research analyses the efficiency of advanced oxidation processes to that of ozonation alone and the combination of ozonation and adsorption in degradation of humic acid. Humic acid will be modelled as a synthetic aquaculture wastewater. The primary objective of the experiment is to study removal efficiency of ozone under certain range of critical process variables with ozone alone and the combination of ozone and adsorption process. This investigation aids in the identification of a more effective humic acid breakdown approach in wastewater and promote global optimization of ozonation and adsorption as a humic acid wastewater treatment technique.

1.1 Background of Study

1.1.1 Aquaculture

Aquaculture is commonly assumed to refer to the farming of aquatic species such as fish, mollusks, crustaceans, and aquatic plants. There are two types of aquacultures: intensive and extensive aquaculture **(**Lucas, 2019). Intensive aquaculture takes place in ponds, cages, and tanks, whereas extensive aquaculture takes place in the ocean, man-made lakes, and rivers. In intense aquaculture, nutrients are obtained through introduced feeds with no usage of natural diets, whereas in extensive aquaculture, nutrients are obtained from natural food organisms or waste. Aquaculture is expanding to grow at a faster rate, as animal nutrients becomes crucial for majority of human beings. Consuming fish becomes cornerstone of many people's cultural customs due to the essential nutrients that present inside it like calcium, omega-3 fatty acids, phosphorus and abundance of minerals. In addition, The American Heart Association said that eating fish at least twice a weak can prevent heart attack and stroke (Norton, 2018). In conclusion, seafood production has reached its peak and eventually the demand for aquaculture raises as it becomes the source for seafood production.

1.1.2 Global Demand for Aquaculture

In 2018, global aquaculture output reached another all-time high of 114.5 million tonnes of live weight and it consists of 82.1 million tonnes of aquatic animals, 32.4 million tonnes of algae and 26000 tonnes of ornamental seashells and pearls (Food and Agriculture Organization of United States, 2020). Out of 82.1 million tonnes of aquatic animals, the number of fish produced is more than half of the value which is 54.3 million tonnes. It can be clearly seen that; production of fish contributes more to the aquaculture sector economically. Aquaculture industries are attracted by the high demand of fish since 46% of total fish production is projected in 2018 with 52% of that value going to human consumption. The production of fish not necessarily used for human consumption but at the same time it will be used to make fish meal and fish oil. By 2029, aquaculture production is expected to reach 105Mt (OECD-FAO Agricultural Outlook 2020-2029, 2021). Based on (Global Newswire, 2021), the aquaculture market is expected to be worth $2.7 billion by 2020 in United States while China, the world's second largest economy, is expected to reach a projected market size of US$177.3 billion by 2027. Hence, aquaculture production expected to increase over the next decade. **Figure 1.1** projects regarding the trends of world aquaculture and capture fisheries and **Table 1.1** shows regarding the projection of fish production to 2030 under baseline scenario.

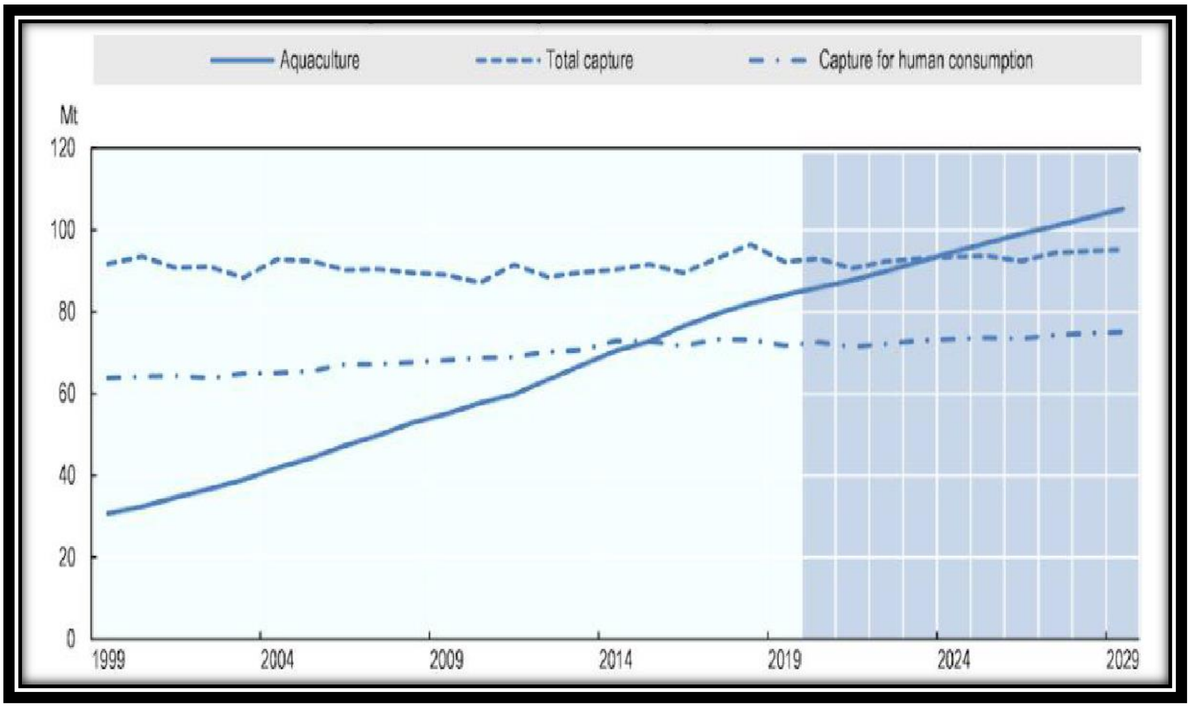

Figure 1.1 World aquaculture and capture fisheries (OECD-FAO Agricultural Outlook 2020-2029, 2021)

Table 1.1 Projection of fish production to 2030 under baseline scenario (Msangi et al., 2013)

	2010-2030 increase in production (million tons)	2010-2030 increase in production (%)	Share of 2010-2030 increase coming from aquaculture (%)
Africa South of the Sahara	0.3	4	64
Middle East and North Africa	0.8	22	97
India	4.8	60	98
Other South Asia	2.4	32	82
Southeast Asia	7.9	38	97
Japan	0.5	-9	-

China	16.5	31	101
Other East Asia and Pacific	0.3	7	105
Latin America and Caribbean	2.1	11	94
North America	0.2	4	103
Europe and Central Asia	0.8	6	122
Rest of the World	0	1	60
Global Total	35.7	24	100

1.1.3 Aquaculture Wastewater

Aquaculture sector is growing rapidly to satisfy the current demand. Although it is growing intensively but it has harmed the environment in producing large number of wastewaters. Based on a study by shrimp aquaculture effluent consists of 87.74 mg/L of total organic matter, (TOM) which is hazardous to the environment and living organisms as well (Arfiati et al., 2021). Aquaculture wastewater can come from a nutrient, fertiliser, pesticide, or herbicide source, or it can come from a nutrient, fertiliser, pesticide, animals or plants. Therefore, organic material will be the pollutant in most of the case. The treated or untreated wastewater will be released to the surface waters. Organic pollutants play a prominent role in wastewater out of other contaminants in wastewater (Zheng et al., 2013). The released wastewater consists of high concentration of organic pollutants with high BOD and COD values. Natural Organic Matter, NOM consists of many functional groups. It is a heterogenous mixture of organic materials that present mostly in aquatic environment (Swietlik et al., 2004). However, humic and fulvic acid contributes more to the NOM (Kan et al., 2016). In conclusion, wastewater treatment needs to be conducted to remove the natural organic pollutants present in the water. Wastewater treatment is critical since fresh water is scarce in some areas, and humans rely on treated wastewater for their everyday activities. According to the 2017 WHO and US EPA census, Australia, California, Texas, Singapore, Namibia, South Africa, Kuwait, Belgium, and the United Kingdom are among the states that reuse treated wastewater for drinking water production and distribution **(**Veolia, 2020). Hence, NOM must be removed from the aquaculture wastewaters which will be reused for other activities.

1.1.4 Humic Acid in Wastewater

Humic acid belongs to humus family in where it is produced from the decomposition of plants and animal residues. The chemical composition of humic acid varies depending on their geographic origin, age, climate, and biological circumstances. Hence, there is a range for their molecular in where it is in the range of 2.0 to 1300 kDa (de Melo et al., 2016). The elements involved are carbon, oxygen, nitrogen and sulphur. There are wide functional groups involved in the humic acid such as acid groups, carboxylic acids, phenolic OH, alcoholic OH, quinoide and methoxy OCH. Under acidic condition (pH<2), it is not soluble in water. Nevertheless, it is soluble at high pH conditions. Humic acid mostly present in the surface waters due to the wide range of functional groups. Based on Stevenson's hypothesis, polymerization reaction between phenolic, amine and aldehyde functional groups can form humic acid in natural water (Sharma et al., 2016). When humic acid is present in water, it affects the colour of the water. Moreover, it acts as a precursor for formation of trihalomethanes and for low and high molecular weight chlorine containing compounds during chlorination process **(**Suffet and Maccarthy, 1988.) Finally, humic acid causes mammalian cells to be carcinogenic which eventually leads to growth retardation. As a result, humic acid needs to be removed during the wastewater treatment. **Table 1.2** below shows the elemental composition and functional group content in humic acid.

Table 1.2 Elemental composition (weight%) and functional group content(mequ/g) in humic acid. (Sharma et al., 2016)

Elemental Composition (Weight %)	
C	53.6-58.7
H	3.2-6.2
N	0.8-5.5
O	32.8-38.3
S	0.1-0.5
Functional Groups (mequ/g)	
Acid groups, total	5.6-8.9
Carboxylic acids	1.5-5.7
Phenolic OH	2.1-5.7
Alcoholic OH	0.2-4.9
Quinoide	0.1-5.6
Methoxy OCH_3	0.3-0.8

1.1.5 Wastewater Treatment

Preliminary, primary, secondary, and tertiary treatment are the four stages of traditional wastewater treatment. Primary treatment removes settleable organic materials and inorganic solids after preliminary treatment removes coarse particulates found in wastewater. During secondary treatment, organic materials and suspended particles are removed even more thoroughly. Finally, tertiary treatment is used to eliminate pollutants that were not removed during secondary treatment and to disinfect the water (Gedda et al., 2021). The treated water from conventional treatment identified with contaminants as some compounds causes problems while undergoing the wastewater treatment. Hence, new technologies are being implemented in wastewater treatment plant to produce high quality water.

1.1.6 Advance Oxidation Process

Glaze et al introduced Advance Oxidation Process, (AOP) in 1987, and it is a preferred technology. To optimize the effluent treatment process, this technology is being introduced. To eliminate organic and inorganic contaminants, (AOP) uses strong oxidising agents or irradiation. The fundamental goal of (AOP) is to produce hydroxyl radicals that will oxidise the pollutants in the wastewater. When hydroxyl radicals react with organic matter, oxygenated molecules such as carbonyl compounds, organic acids, and alcohol are produced, whereas inorganic matter has electrons removed, resulting in a greater oxidation state. In conclusion, introduction (AOPs) such as ozonation is vital in decreasing humic acid in wastewater to prevent hazards to the aquatic environment and human health.

1.2 Problem Statement

Freshwater is essential for human health and social growth. There are approximately 332.5 million cubic miles of water on the planet, but only around 1% of it is readily available for home and commercial use as freshwater. Furthermore, only two-thirds of the available water is drinkable, with the remainder being unusable owing to pollution (Abdul Aziz and Abu Amr, 2019). 780 million people lack access to drinking water, according to WHO and UNICEF statistics, with 185 million relying on surface water to satisfy their daily requirements in certain developing countries, chemical pollution of surface waterways, mostly owing to industrial and aquaculture wastes, poses a considerable health danger. Natural organic matter, (NOM) plays a prominent role in wastewater. NOM concentrations in surface waters vary from 0.1 to 20 mg/L, with humic compounds such as humin, fulvic acid, and humic acid accounting for the majority. Humic acid (HA) is one of the most challenging NOM fractions to remove, accounting for over 50–90% of total organic matter in surface water (Kan et al., 2016). Hence, humic acid is modelled to be the synthetic wastewater in this study.

The presence of humic acid in drinking water can give it an unappealing colour and flavour. Furthermore, during the disinfection process, the reaction of humic acid with chlorine produces disinfection by- products (DBPs). The main DPBs formed during the disinfection process are trihalomethanes (THM) and haloacetic acid (HAA). DBPs were linked to an increased risk of cancer. DBPs can also be quickly absorbed across the gastrointestinal tract. Hence, the presence of humic acid can cause serious health problem for living organisms.

Conventional wastewater treatment includes coagulation has some difficulties in removing the humic acid. Humic acid is hydrophobic fraction of (NOM) and it carries high charge density and a higher level of negative charge as it consists of carboxylic and phenolic groups (Tak et al., 2018). As a result, humic acid tends to dominate the colloidal charge nature of water, making it more susceptible to coagulation removal. Membrane technology is very commonly employed nowadays. Ultrafiltration and nanofiltration have been used extensively to remove humic acid, with a high proportion of the humic acid being removed. However, humic acid adds to membrane fouling, which reduces membrane function and necessitates a high-cost treatment (Yuan et al., 2000). The decrease of water quality, owing in part to NOM pollution, has resulted in more restrictive water quality laws and an increasing demand for effective water treatment technology. As a result, the Advanced Oxidation Process (AOP) can be used in wastewater treatment plants to improve humic acid removal since traditional wastewater treatment has trouble eliminating humic acid and lowering DPB levels in wastewater. AOPs are highly successful wastewater treatment technology for eliminating humic acid, which are extremely resistant to biodegradation. The AOP process produces hydroxyl radicals (OH·), which are very efficient, strong, abundant in nature, nonselective, and electrophilic, with a redox potential of 2.8V. It will degrade and mineralize them into carbon dioxide and water. By removing a hydrogen atom from aliphatic carbon or adding a hydrogen atom to double bonds and aromatic rings, it speeds up the oxidation and breakdown of humic acid in wastewater (Kumar and Vineet, 2021).

Hence, advance oxidation process particularly ozonation is the best choice for degradation of humic acid in wastewater. Ozone is a highly oxidising agent that capable of converting organic contaminants into smaller compounds such as carbon dioxide and water. It has redox value of 2.07 V. Ozone will react with organic compounds through direct or indirect reaction. Hydroxyl radical is generated during indirect ozonation. Reaction of organic matter with ozone or hydroxyl radical, can significantly mineralize the organic compound (Gulyas et al., 1995). However, there is some limitations as ozone has low dissolution and mass transfer rate. As a result, less amount of ozone is utilized to degrade the humic acid and it will increase the demand for high ozone dosage. Thus, high cost is needed since the generation of ozone from pure oxygen will consumes high energy.

Adsorption is used with ozonation to improve the ozonation process since it is more sustainable and efficient for wastewater treatment that contains refractory organic components. According to research by (Karamah et al., 2018), ozonation alone removes 53.15 % of phenol, whereas ozonation combined with adsorption removes 78.62 %. As a result of the presence of granular activated carbon, the diffusion limitation of ozone is reduced, and the adsorption and desorption of ozone onto the adsorbent is accelerated, resulting in the transformation of ozone into active molecular radical components and the formation of hydroxyl radical. In addition, to remove heavy metals and organic debris from wastewater, a low-cost adsorbent such as lava rocks is used with ozonation in a packed column. Lava rocks have a lot of surface area, a lot of porosity, a lot of adsorption capacity, and they're cheap. The presence of lava rocks allows for a huge contact area between ozone and water, increasing gas-liquid mass transfer. As a result, the amount of ozone necessary to accomplish the appropriate humic acid elimination is