REMOVAL OF TETRACYCLINE HYDROCHLORIDE ANTIBIOTIC FROM WATER USING AN OZONATION ALONE AND COMBINATION OF OZONATION AND SONOLYSIS

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by

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LIST OF SYMBOLS

k_{app}	Apparent rate constant
k	Constant of the first order reaction rate
R^2	Correlation coefficient
C_t	Antibiotic concentration at any instant time
C_o	Initial antibiotic concentration
t	Reaction time

LIST OF ABBREVIATIONS

Abs	Absorbance
AOPs	Advanced Oxidation Process
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
H_2O_2/Fe^{2+}	Fenton
FW	Formula Weight
GAC	Granular Activated Carbon
HCl	Hydrochloric Acid
H_2O_2	Hydrogen Peroxide
OH•	Hydroxyl Radical
Fe_2O_3	Iron (III) Oxide
O_3	Ozone
PPCPs	Pharmaceutical and Personal Care Products
UV/ H_2O_2/Fe^{2+}	Photo-Fenton
pH	Potential of Hydrogen
RO	Reverse Osmosis
NaOH	Sodium Hydroxide
SMX	Sulfamethoxazole
TC	Tetracycline
UV	Ultraviolet
UV/Vis	Ultraviolet Visible Light
λ_{max}	Wavelength of Maximum Absorbance

PENGELUARAN ANTIBIOTIK TETRACYCLINE HYDROCHLORIDE DARI AIR MENGGUNAKAN OZONASI SAHAJA DAN KOMBINASI OZONASI DAN SONOLISIS

ABSTRAK

Tetracyclines (TC) adalah kelas pelbagai antibiotik yang mempunyai pelbagai aplikasi dalam rawatan manusia, veterinar, dan akuakultur. Sisa TC ada di tanah, air permukaan, air bawah tanah, dan bahkan air minum kerana pembebasan sisa TC ke alam sekitar dan penyingkiran yang tidak efektif melalui sistem rawatan konvensional. Pembentukan ketahanan TC dalam pelbagai jenis bakteria menunjukkan keparahan pencemaran TC. Degradasi antibiotik TC menggunakan ozonasi sahaja dan gabungan ozonasi dengan sonolisis dibincangkan dalam penerbitan ini. Kepekatan, pH, dan berat pemangkin adalah tiga kriteria yang telah dikaji untuk menentukan kecekapan penurunan antibiotik yang optimum. Bekalan output ozon tetap berterusan sepanjang eksperimen. Untuk kepekatan awal antibiotik, hasil yang diperoleh menunjukkan bahawa ozon dapat menurunkan antibiotik TC dengan lebih cepat pada kepekatan yang sangat rendah, 30 ppm dan kecekapan degradasi adalah 85.96% dalam 5 minit dari reaksi. Hasil kajian menunjukkan bahawa untuk kepekatan yang lebih tinggi, masa tindak balas yang diperlukan meningkat. Pada pH awal 9, penurunan antibiotik menunjukkan peratusan kecekapan degradasi yang lebih tinggi. Lebih daripada 79% antibiotik terdegradasi setelah 5 minit tindak balas. Untuk berat pemangkin tertinggi, iaitu 0.25 g, kecekapan penurunan antibiotik TC mencapai 84.75% juga dalam 5 minit tindak balas. Analisis kinetik menunjukkan bahawa ozonasi antibiotik TC mewakili reaksi urutan pertama. Hasil reaksi ozon bersama dengan sonolisis lebih berkesan berbanding dengan ozon sahaja. Kecekapan penurunan antibiotik TC pada kepekatan 60 ppm pada 5 minit tindak balas adalah 92.1% dengan sonolisis dan 89.8% untuk

ozon sahaja. Sinergi yang diamati dalam skema gabungan, terutamanya disebabkan oleh kesan sonolisis dalam meningkatkan penguraian O_3, menyebabkan mineralisasi lebih tinggi selama 2 jam rawatan dan tahap mineralisasi yang jauh lebih tinggi untuk jangka masa rawatan yang lebih pendek. Hasil yang diperoleh sebelum dan selepas sonolisis dan ozonasi digunakan bersama-sama didapati sebagai teknologi yang menjanjikan untuk penurunan TC dalam larutan air sisa. Ini disebabkan oleh peningkatan O_3 adalah degradasi oleh gelembung yang runtuh yang dapat menghasilkan radikal bebas tambahan. Penemuan kajian ini diperiksa, dan beberapa penyelidikan masa depan mengenai penurunan antibiotik disarankan untuk pendekatan yang lebih berkesan.

REMOVAL OF TETRACYCLINE HYDROCHLORIDE ANTIBIOTIC FROM WATER USING AN OZONATION ALONE AND COMBINATION OF OZONATION AND SONOLYSIS

ABSTRACT

Tetracyclines (TCs) are a class of diverse antibiotics that have a wide range of applications in human, veterinary, and aquaculture treatment. TCs residues are ubiquitous in soil, surface water, groundwater, and even drinking water due to the ongoing release of TCs residues into the environment and insufficient removal through conventional treatment systems. The establishment of TCs resistance in a wide range of bacteria demonstrates the severity of the TCs pollution. The degradation of TC antibiotic using ozonation alone and a combination of ozonation and sonolysis is discussed in this publication. Concentration, pH, and catalyst weight are three criteria that have been studied to determine the optimal antibiotic degradation efficiency. The ozone output supply was constant throughout the experiment. For an initial concentration of antibiotic, the results obtained shown that gnvhh can degrade TC antibiotic faster at a very low concentration, 30 ppm and the degradation efficiency was 85.96% within 5 minutes of the reaction. The results shown that for higher concentration, the reaction time needed increases. At an initial pH of 9, the degradation of antibiotic showed higher percentage of degradation efficiency. More than 79% of antibiotic was degraded after 5 minutes of the reaction. For highest weight of catalyst, which is 0.25 g, the degradation efficiency of TC antibiotic achieved 84.75 % also within 5 minutes of reaction. Kinetic analysis showed that the ozonation of the TC antibiotic represented the first order reaction. The results reaction of ozone together with sonolysis was more effective compared to ozone alone. The degradation efficiency of TC antibiotic at concentration of 60 ppm at 5 minutes of reaction was

92.1% with sonolysis and 89.8% for ozone alone. The synergy observed in the combined schemes, mainly due to the effects of ultrasound in enhancing the O_3 decomposition, led to a higher mineralization for 2 hours treatment and to a significantly higher mineralization level for shorter treatment duration. The results obtained before and after sonolysis and ozonation applied jointly found to be a promising technology for TC degradation in wastewater solution. This is attributed to the enhanced O_3 are degradation by collapsing bubbles that may yield additional free radicals. The study's findings were examined, and some future research in antibiotic degradation was suggested for more effective approaches.

CHAPTER 1

INTRODUCTION

1.1 Introduction

This study contrasts advanced oxidation processes with the efficiency of ozonation alone and the combination of ozonation and sonolysis during antibiotic degradation in wastewater. The other major objectives are to determine the effect of the difference in ozone flows on antibiotic degradation, the optimum amplitude needed during sonolysis for the removal of antibiotics, and the time required for the full removal of antibiotics for both sonolysis and ozonation. This study helps to recognize the more effective technique of antibiotic degradation in wastewater and promotes further optimization of ozonation and sonolysis as an antibiotic wastewater treatment technique.

1.2 Background of the study

Antibiotics were discovered in 1929 to treat many forms of emerging diseases and are still in use so far. A new problem called antibiotic-resistant has been created by antibiotics released into the environment, mainly through human, animal, aquaculture, and agricultural activities (Birosova et al., 2014). Antibiotic pathways in the ecosystem are shown below in Figure 1.1 (Homem & Santos, 2011):

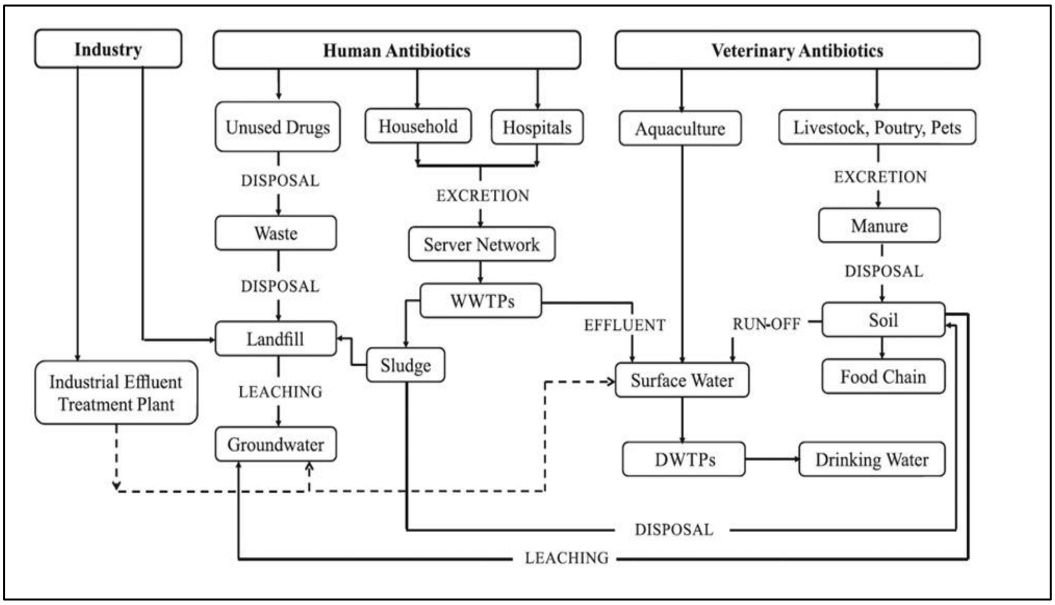

Figure 1.1 Pathways of the antibiotics in the environment (Homem & Santos, 2011).

Although the concentrations recorded in surface waters are normally at the level of micrograms per litre, this form of exposure is of great concern as it favours the production of resistant bacteria (Boreen et al., 2004). The human food chain is also concerned because antibiotic residues, sulphonamides, are present in milk products and meat because these drugs are used to prevent infections in livestock (Dost, 2000). Via runoff from manure that can access ground water and probably drinking water, these pharmaceuticals can also enter the food chain (Kummerer, 2003).In order to prevent the release of antibiotic resistant bacteria into surface water, wastewater treatment is considered a significant obstacle.

Advanced oxidation processes (AOPs) are one of the wastewater treatments described by Glaze et al. (1987) as the process performed close to environmental conditions at pressure and temperature, involving the production of hydroxyl radicals in sufficient quantity to interact with the medium's organic compounds and thus reduce the antibiotic concentrations in the environment.In order to avoid risks to the aquatic environment and human health, the introduction of advanced oxidation processes (AOPs) such as ozonation and acoustic sonolysis is of the utmost importance today in reducing antibiotic disposal in wastewater (Wilt, 2018).

1.3 Problem Statement

As pointed out in UNICEF's second United Nations study on the production of world Water supplies in 2006, poor water quality slows down economic growth and can have a detrimental impact on health and livelihoods. In some developing countries, chemical pollution of surface water, largely due to industrial and agricultural discharges, is also a major health risk. Pollution and industrial waste affect water supplies, damages and kills the world's ecosystems (UNICEF, 2012).

There is also an increasing understanding of antibiotic development in addition to water disinfection, as their discharge into the environment can contribute to environmental, food crops, pollution and also cause bacterial resistance. Antibiotic resistance is mainly increasing because traditional wastewater treatment methods do not fully break down antibiotics (Aydin et al. 2018; Michael et al. 2013; Rodriguez-Mozaz et al. 2015; Sabri et al. 2018; Szekeres et al. 2017). Since bacteria are exposed to antibiotics that do not kill them because of selective pressure, they become resistant and develop resistance, a major health concern. The Centers for Disease Control and Prevention says it is one of the big public health challenges facing today (CDC, 2013b). Antibiotics need to be eliminated from the wastewater to prevent this from happening.

Tetracyclines (TCs) are the most common antibiotic drugs in the world. This broad-spectrum family of antibiotics is known to inhibit protein synthesis in bacteria besides combat a variety of bacterial infections. The conventional methods aimed at treating wastewater cannot effectively eliminate large quantities of tetracycline; besides, TCs easily make stable compounds due to their binding potential to Ca^{+2} and other ions. Therefore, a significant portion is detected in wastewater, surface water, groundwater, sludge, and sediments. They are becoming a serious threat to the environment due to their unaccounted use in subtherapeutic animal growth promotion and human treatment (Ahmad, et al, 2021).

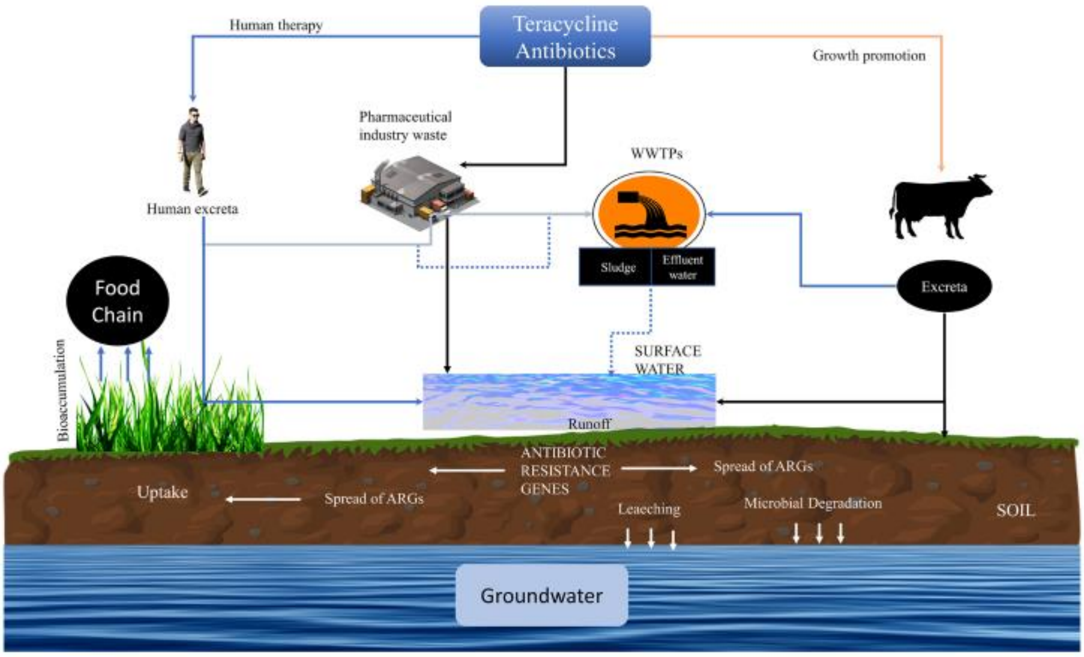

Figure 1.2 Aquatic and terrestrial routes of tetracycline in the environment (Ahmad, et al, 2021).

Advanced oxidation processes (AOPs) are considered to be a good choice for oxidising antibiotics in wastewater. It is a series of chemical treatment procedures that are capable of removing non - biodegradable organic wastewater materials through oxidation reactions with a strong non-selective hydroxyl radical (OH•) that oxidizes conventionally resistant non - biodegradable organic pollutants and can also improve the biodegradability of wastewater (Grieser 2015).

Theoretically, AOPs could completely mineralize organic compounds into carbon dioxide and water according to following equation:

$$R - H + OH \cdot \rightarrow H_2O + R \qquad \text{Equation 1.1}$$

Sonolysis is a promising technology that can be used to degrade organic matter such as antibiotics in waste water (Hartmann et al, 2007; Belgiomo et al,2007; Antoniadis et al, 2007; Naddeo et al, 2007, Naddeo et al, 2009; Naddeo et al, 2010) through the means of using ultrasonic waves. Acoustic cavitations happen as ultrasound waves interact with dissolved gases in a liquid at a high intensity. The bubbles are caused to develop, expand and eventually collapse by this interaction. Ultrasound has been shown to eliminate pollutants from water that form hydroxyl radicals due to cavitation (Dahi, 1976; Ince, 2018; Rayaroth et al. 2016; Xiao, et al. 2014; Yadav N, 2014). Moreover, the energy levels achieved by ultrasound-induced cavitation result in the breaking of chemical bonds in water molecules between oxygen and hydrogen atoms. This contributes to the formation of hydroxyl radicals and hydrogen peroxide (H_2O_2) (Villeneuve, 2008). The temperature reaches several thousand Kelvin during the time of bubble collapse, and the pressure reaches several hundred atmospheres that affect the degradation of antibiotics (Grieser 2015).

The environmental fate of antibiotics has emerged as a research topic in the previous decade till date to address the issue Therefore, in this study, the researcher study on the removal of tetracycline hydrochloride antibiotic using an ozonation alone and combination of ozonation and sonolysis.

1.4 Objectives

1. To study the effect of difference concentration of antibiotic on the degradation efficiency.

2. To investigate the effect of difference pH on the antibiotic degradation efficiency.

3. To determine the effect of difference weight of catalyst on the antibiotic degradation efficiency.

4. To find out the efficiency of ozonation alone and combined of ozonation and sonolysis during degradation of antibiotics.

1.5 Sustainability of Wastewater Treatment

The Sustainable Development Goals (SDGs) are a collection of 17 global goals altogether. The objectives of these SDGs are to act as blueprint to be able to achieve a better future in terms of sustainability for all. These aims are designed to eliminate poverty and other forms of deprivation by collaborating on sustainable methods that address health, education, inequality, economic growth, climate change mitigation, and the preservation of natural resources such as lands, oceans, and forests. The 17 Sustainable Development Goals are goals are (SDG1) No Poverty, (SDG2) Zero Hunger, (SDG3) Good Health and Well-being, (SDG4) Quality Education, (SDG5) Gender Equality, (SDG6) Clean Water and Sanitation, (SDG7) Affordable and Clean Energy, (SDG8) Decent Work and Economic Growth, (SDG9) Industry, Innovation and Infrastructure, (SDG10) Reducing Inequality, (SDG11) Sustainable Cities and Communities, (SDG12) Responsible Consumption and Production, (SDG13) Climate Action, (SDG14) Life Below Water, (SDG15) Life On Land, (SDG16) Peace, Justice and Strong Institutions and (SDG17) Partnership For The Goals.

Wastewater treatment should very efficient that removes almost all unwanted contaminants. The system should achieve zero waste by transforming wastewater contaminants into valuable product such as clean water. Thus, it paves a way towards cleaner and greener environment. This can be linked to SDG 6 on Clean Water and Sanitation, which aims to provide everyone with universal and equitable access to clean and affordable drinking water. This goal also aims to enhance water quality globally by decreasing pollution, eliminating dumping, and avoiding the release of dangerous chemicals and materials, halving the share of untreated wastewater, and significantly increasing recycling and safe reuse.

Moving on, wastewater should be treated before releasing to the environment. Thus, proper treatment should be carried out in order to alleviate effect and consequences of wastewater. As release of the untreated wastewater can damage the lives of the underwater species. This point can be closely be related to Goal 14 Life Below Water. This SDG is to ensure to conserve the usage of seas, oceans and marine resource in sustainable manner. Release of the untreated wastewater directly to inland waters may tremendously affect the lives underwater. Hence, wastewater should be treated adequately to protect the biodiversity and the lives of aquatic animals and the same time the quality of the water that they survive in. This also helps provide a sustainable future for the fishing industry in Malaysia. This study has uploaded the aim of SDG goal 6 and 14 towards clean water that leads to better quality of life below water to conserve and sustainably use the oceans.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The researcher addresses the ozonation and sonolysis of advanced oxidation processes during degradation of antibiotics in the wastewater in this chapter. The following subtopics are used for the literature review below: Wastewater, Antibiotics, Antibiotic Occurrence in Wastewater and Persistent Antibiotics, Antibiotic Resistance and Advanced Oxidation Processes (AOPs).

2.2 Wastewater

Wastewater is any water that has been adversely impacted by anthropogenic activity in terms of quality. Waste water is commonly associated with sewage, but sewage is a more general term that refers to all polluted water, including waste water that can include organic and non-organic substances, industrial waste, infiltrated and mixed with contaminated water, storm, runoff, and other related liquids (Miretzky et al. 2004). This also covers the discharge of liquid waste from residential households, industrial facilities, factories, or agriculture, which can include a broad range of potential toxins and concentrations. Municipal wastewater, which contains a wide range of pollutants arising from the mixture of wastewater from multiple sources, is the most widespread application (Hamdan, 2010).

Discharges from residential and industrial areas are the primary sources of domestic wastewater. The origin of the wastewater in the treatment plant would have a serious impact on the characteristics of the wastewater. As an example, restaurant or hawker centre wastewater will contain more oil and grease, as well as detergent material, while hospital wastewater will contain antibiotics, antibacterial soups and cleaning agents (Hamdan, 2010).

It is very useful to understand the classification of domestic wastewater to ensure that the design potential as well as the operation and maintenance of the treatment plant are met. Wastewater characteristics are determined not only by the sources, but also by the atmosphere or climate. It is possible to separate the volumetric flow of wastewater into the regular and peak seasons. An average COD of no more than 400 mg/L, which was considered to be low intensity domestic wastewater, will be present in the normal season. The rainwater will dilute the domestic wastewater into a large amount of low organic content during the peak rainy season (Mara, 2013).

2.3 Antibiotics

Humans and animals, including bacteria, viruses, fungi and protozoa, function as hosts for disease-causing organisms. Simple diseases frequently resulted in death in the past and before the advent of antibiotics. Compounds have been found to exhibit antimicrobial properties over time and to treat infections. Mercury, silver, and cyanide contain compounds that have traditionally been used to combat diseases. In 1928, Alexander Fleming made the paramount antibiotic discovery. He was attempting to extract Staphylococcus aureus and it infected one dish. Fleming found that near the invading material, which he later described as a typical mold of the genus Penicillium, bacteria did not spread. Fleming revealed the antimicrobial properties of the substance now known as penicillin after cultivating the mould and collecting a limited amount of excreted liquid (Shuler et al., 2002).

2.3.1 Antibiotic in Wastewater

Wastewater effluents, bio-solids, industrial wastewater, and sewage are the primary causes of antibiotic entry into the ecosystem. Antibiotic wastewater includes a number of organic components that are not biodegradable and can be high in the demand for chemical oxygen (COD) and very low in the demand for biochemical oxygen (BOD). It is possible to divide the processes involved in the manufacture of antibiotics into four categories: (a) fermentation, (b) biological and natural extraction, (c) chemical synthesis and (d) combining, compounding and formulation (US EPA, 2006). The composition of antibiotic wastewater will also vary greatly based on the mechanism involved, from one effluent to another.

Regrettably, no research on the characterization of antibiotic wastewater in Malaysia has been published, although the number of pharmaceutical companies is more than 100 and most of these companies manufacture antibiotics. Mixing antibiotic wastewater with pharmaceutical wastewater to be biologically processed is normal practise in Malaysia, which could cause the production of antibiotic resistant bacteria or discharge antibiotic wastewater to evaporation ponds that could contaminate the soil and groundwater. In China (Zhang et al. 2006) and Turkey, only a few studies have recorded the characteristics of antibiotic wastewater (Alaton and Dogruel, 2004; Cokgo et al., 2004).

2.3.2 Antibiotic Occurrence in Wastewater and Persistent Antibiotics

The occurrence of pharmaceutical substances in water, especially drinking water, is discussed in several papers. Although this issue is widely debated, there are currently no federal requirements for pharmaceuticals in wastewater or drinking water. Only a list of pharmaceuticals under consideration for drinking water requirements has been made by the Environmental Protection Agency (Bienkowski 2013). One of the issues about getting pharmaceuticals in wastewater is that these pharmaceuticals find their way into drinking water as the water is pumped back into the water cycle. The issue then becomes the concentration of pharmaceuticals that human beings consume in drinking water. It's been said that because the concentration of pharmaceuticals is so limited in drinking water, in order to achieve the therapeutic dose of the pharmaceuticals, humans will have to consume an exaggerated amount of water in a day, which is not normal or practical. On the other hand, something about pharmaceuticals is overlooked when this claim is made. Antibiotics, which fall within the large range of pharmaceuticals, may indirectly have harmful effects on humans in wastewater. Small quantities of antibiotics in wastewater find their way to drinking water and the origin of antibiotic resistant bacteria is these micro levels of antibiotics. When this occurs, humans, as well as animals, tend to lose their battle against bacterial infections that may lead to death or other health problems. For this reason, it is critical that antibiotics exist in the environment and there is nothing to be taken lightly.

2.3.3 Antibiotic Resistance

Antibiotic resistance is the capacity of microorganisms to withstand the effects of infection-fighting antibiotics. The production and propagation of antibiotic resistance in bacteria is of public health significance because by contacting a resistant organism or having a resistant microbe appear in the body when antibiotic therapy starts, a patient may develop an antibiotic resistant infection (Lewis, 1995). In 1971, Huber stated criticizing the non-medical application of antibiotics and identifying antimicrobial agents as possible environmental pollutants and a public health danger (Huber, 1971). Since then, multiple studies have confirmed the presence of resistant antibiotic species in the ecosystem (Pillai et al., 1997; Ash et al., 2002).

Latest experiments have demonstrated the presence in multiple water bodies of antibiotic resistant bacteria. Gallert et al. (2005) observed fecal coli-forms and enterococci resistant to antibiotics in the influence and effluent of wastewater treatment plants. Antibiotic resistance provides microorganisms with a survival edge which makes it impossible to remove the infections they cause. It is difficult to treat infections caused by antibiotic resistant bacteria. Therefore, to treat illnesses, doctors need to administer higher dosages of substitute antibiotics. High doses have side effects and the ability to produce strains of bacteria that are more antibiotic-resistant.

Drug inactivation or modification, alteration of the target site, alteration of the metabolic pathway, and decreased drug accumulation are involved in the antibiotic resistance process (Katzung 2004), as shown in the following:

2.3.3(a) Drug inactivation or modification

Bacteria synthesise enzymes that eliminate the antibiotics' antimicrobial function. For instance, β-lactamases synthesised by antibiotic-resistant bacteria hydrolyse the penicillin β-lactam ring to inactivate the antibiotic (Katzung, 2004).

2.3.3(b) Alteration of target site

Penicillin affects bacteria by adding proteins that bind to penicillin that are necessary for the synthesis of the bacterial cell wall. By overproduction of penicillin-binding proteins, bacteria create resistance to penicillin (Katzung, 2004).

2.3.3(c) Alteration of metabolic pathway

In order to dodge the effect of antibiotics, bacteria may change their metabolic pathways. Sulfonamides, for example, inhibit folic acid synthesis, and sulfonamide resistant bacteria develop alternative routes of folic acid synthesis (Katzung, 2004).

2.3.3(d) Reduced drug accumulation

Bacteria that develop antibiotic resistance are able to minimise antibiotic intake either by modifying the drug's permeability or by improving the active efflux of the drug (Katzung, 2004).

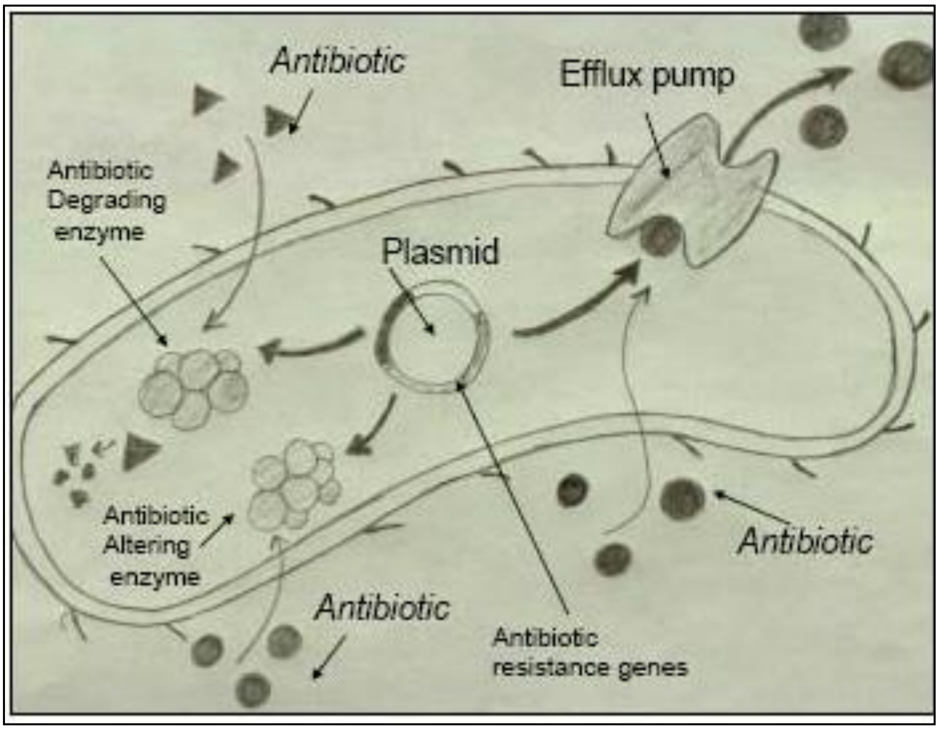

Figure 2.1 Antibiotic resistance mechanisms (Yim,2007).

2.4 Adsorptive Treatment - Advanced Oxidation Processes (AOPs)

Advanced oxidation methods (AOPs), which are oxidation methods, are distinguished by their radical production (Parsons 2004). The purpose of oxidation, which is to kill electrons, is to 'mineralize' micro-pollutants so that they are converted into basic and less destructive molecules such as carbon dioxide and water (Parsons 2004). If the contaminant, which is the optimal solution, is not fully mineralized, it can then be converted into a simpler, biodegradable compound. Hydroxyl radicals are a special type of oxidizing organisms that target organic compounds and are generally used to be environmentally friendly (Kurt et al. 2017). Hydroxyl radicals are formed by an excited atomic oxygen reaction with water and are very potent oxidants at high concentrations. The efficacy of AOPs is determined by the generation of these strong hydroxyl radicals (E_0 = 2.80 V), which are non-selective and extremely reactive, with a reaction rate constant of approximately 109 L mol-1 s-1 (Ribeiro et al. 2015).

AOPs are known to be very promising methods for the treatment of polluted soil, land and wastewater containing organic contaminants that are not biodegradable. Because of the hazardous characteristics of non-biodegradable organic contaminants, such as antibiotics, a traditional biological method may not be appropriate for treating wastewater contaminated by these compounds. Moreover, separation technologies such as coagulation-filtration, activated carbon absorption and reverse osmosis only transfer, without removing, the pollutants from one step to the next. AOPs are promising approaches for the treatment of polluted wastewater containing organic contaminants that are non-biodegradable (recalcitrant) (Kurt et al. 2017).

By considering the stage where the process takes place, AOPs can be categorized, so homogeneous or heterogeneous processes can be distinguished. The classification of AOP can also take into account the various potential forms of generating hydroxyl radicals. Photochemical and non-photochemical procedures can be differentiated in this manner ((Kurt et al. 2017). Those containing Fenton, ammonia, ozone and hydrogen peroxide, electrochemical oxidation, cavitations, supercritical water oxidation, non-thermal plasma based electrical discharge, gamma-ray, x-ray, and electron-beam contain non-photochemical processes.

Hydrogen peroxide has a potential of 1.78 V, ozone of 2.07 V and hydroxyl radicals of 2.80 V when looking at advanced oxidation processes and contrasting oxidation potentials, indicating that hydroxyl radicals have more oxidation capacity. Overall, hydroxyl radicals are the second most powerful oxidising species with fluorine as the first, 3.03V (Parsons 2004). Fluorine is not widely used as it is poisonous, corrosive and prone to aggressive reaction (Braeunig, 1996). For instance, hydroxyl radicals are significantly faster when comparing oxidising rate constants for ozone and hydroxyl radicals for different organic compounds. This is why the development of hydroxyl radicals in water is the objective of most AOPs. In oxidation, when photolysis, ozone, hydrogen peroxide, etc are involved, the rate of reaction (k), which is the rate at which reactants are converted into products depends on the radical, oxygen, and pollutant concentration. Temperature, pH, type of pollutant, ion presence, and scavenger presence are some variables that can affect radical concentration (Parsons 2004). Molecules known to react in a predictable manner with radicals are referred to as radical traps or scavengers. Such compounds are common in most waters and absorb hydroxyl radicals, so scavengers compete for radical hydroxyl reactions with organic pollutants (Ribeiro et al. 2015).

In the past, comprehensive studies have been undertaken to investigate the effectiveness of AOPs in the elimination of prescription toxins in treated wastewater (Westerhoff et al., 2005, Rosenfeldt and Linden, 2004, Drewes et al., 2008b). These researches have shown that in comparison to UV radiation or ozonation alone, AOPs are efficient treatment procedures to remove selected pharmaceutical contaminants and provide enhanced removal efficiency. Although few studies on the effectiveness of AOPs for oxidising antibiotics are available, AOPs appear to be successful for oxidising antimicrobial contaminants as well. Studies using laboratory and full-scale ozone/H_2O_2 treatment methods have shown that the concentrations of erythromycin, ofloxacin, sulfamethoxazole and trimethoprim in tertiary treated wastewater have significantly reduced (Drewes et al., 2008b).

More than 90% of these antibiotics were removed from tertiary treated wastewater by the 7 mg/L ozone, 3.5 mg/L H_2O_2 and 2 min contact time AOP process. Metronidazole degradation using UV, UV/ H_2O_2, H_2O_2/Fe^{2+} (Fenton) and UV/ H_2O_2/Fe^{2+} (photo-Fenton) photochemical oxidation has been investigated (Shemer et al., 2006). This study showed that although the removal of metronidazole was insignificant only by UV irradiation (600 mJ/cm2 dose and 5 min retention), the removal efficiency was significantly improved by the addition of ferrous ions. However, all samples in this study were spiked deionized water samples, and the ability of photochemical oxidation for the treatment of metronidazole in wastewater is expected to decrease due to increased turbidity and intrusion of matrix compounds.

For any AOP, the total degree of oxidation depends on the contact time and concentration of scavengers in the water such as non-target oxidize-able species. In drinking water, dissolved organic carbon (DOC) and bicarbonate are typically the most relevant scavengers. High DOC and carbonate/bicarbonate levels will make micro-pollutant mineralization very inefficient (von Gunten, 2003). Hydroxyl radical formation can be initiated by the presence of natural organic material, while humic acid and bicarbonate can scavenge the radicals (Drewes et al., 2008b). Pre-treatment methods, such as granular activated carbon (GAC) or reverse osmosis (RO), however, greatly decrease DOC concentrations, thereby improving the efficiency of oxidation.

2.4.1 Ozonation of Antibiotics

Although antibiotics are an emerging class of pathogens, antibiotics have already been investigated in the treatment processes of wastewater, drinking water, and grey water. In fact, ozone has been successfully used for the treatment of antibiotics, as well as unique industrial wastewater, in these water sources (Hernandez et al, 2011; Glaze,1987; Perkowski et al,1996; Rice, 1996).

Ozone is an excellent choice for the transformation of antibiotics in water and waste water sources due to the selective oxidation reactions provided by ozone over other widely used oxidants, as well as the dual oxidant capabilities available from the key decomposition product of ozone such as hydroxyl radicals. Ternes et al (2003), who researched ozonation of a number of the pharmaceutical and personal care products (PPCPs) in wastewater matrices, conducted one of the first reports of antibiotic removal by ozone. The compounds examined included, among others, trimethoprim, sulfamethoxazole, clarithromycin, erythromycin, and roxithromycin. All five antibiotics were reduced to concentrations below the quantification limits with an ozone dose of 5 mg/l, suggesting that macrolide, sulfonamide, and trimethoprim antibiotics effectively compete with organic matter for ozone reactions.

Another early research by Adams et al.(2002), found that after only 1.3 min of gaseous ozonation (2% w/w) in Missouri River water, 95 percent elimination of a suite of seven antibiotics (carbadox, sulfachloropyradazine, sulfadimethoxine, sulfamethazine, sulfamethazine, sulfathiazole, and trimethoprim) was achieved. In Switzerland, a project has shown that macrolides and sulfonamides have been efficiently converted (>95%) into secondary effluents at pH 7 at ozone doses of 2 mg/l (Huber et al, 2005). Okuda et al, (2008). found that the overall mass concentration of pharmaceuticals, including several antibiotics, declined from approximately 3800 ng/l to less than 50 ng/l with an ozone dose of 3 mg/l .Transformation of sulfonamide and macrolide antibiotics using a supply of gaseous ozone supplying 5.3 percent ozone at

1.6 l/min was able to achieve 90 percent efficiency of transformation in 20 minutes(Lin et al., 2009). All of these studies suggest that even in the presence of far higher DOM concentrations, antibiotics react rapidly with ozone.

Efficient ozonation treatment for the removal of antibiotics in water and wastewater effluents has also been documented in several previous studies (Adams et al., 2002, Huber et al., 2005, Ternes et al., 2003). The study by Adams et al. (2002) found that in 1.3 min contact time at an ozone dose of 7.1 $mg.L^{-1}$, ozonation eliminated more than 95 percent of many sulfonamides and trimethoprim from river water. Huber et al. (2005) also found that 90% ->99% of sulfonamides and macrolides in secondary wastewater effluents were oxidised using ozonation at doses >2 $mg.L^{-1}$.Second-order rate constants for ozone and hydroxyl radicals have been reported for fluoroquinolones, sulfonamides, β-lactams, macrolides and trimethoprim (Dodd et al., 2009).As a result of this analysis, the authors indicated that at standard ozone doses used for disinfection, that is 5-10 $mg.L^{-1}$ ozone with 5-23 $mg.L^{-1}$ DOC, 99% elimination of antibiotics from river water and wastewater effluents should be achievable.

Oxidative degradation of organic chemicals during ozone treatment can occur either by direct reaction with molecular ozone (O_3) or indirectly through hydroxyl radicals (Staehelin and Hoigne, 1985). Many antibiotics, including sulfonamides, macrolides, fluoroquinolones and tetracyclines, have been shown to be mainly transformed by direct ozone reaction during wastewater ozonation (Dodd et al., 2006), while cephalexin, penicillin, and N4-acetyl sulfamethoxazole have been mostly transformed by hydroxyl radicals (Dodd et al., 2006). The ratio of molecular ozone and hydroxyl radicals, the resulting reaction kinetics, and the presence of organic matter would depend on the relative supremacy of the real oxidative pathway (von Gunten, 2003, Elovitz et al., 2000).Through attacking or modulating their pharmaceutically active functional groups, ozone and/or hydroxyl radicals deactivate the bactericidal properties of antibiotics, such as N-etheroxime and dimethylamino macrolide groups (Lange et al., 2006, Dodd et al., 2009), sulfonamide aniline moieties (Huber et al., 2005), penicillin thioether groups, cephalosporin unsaturated bonds and phenol ring bonds (Huber et al., 2005) (Dodd et al., 2009).

For those compounds with electron-rich aromatic systems, such as hydroxyl, amino, acylamino, alcoxy and alkyl aromatic compounds, as well as those with deprotonated amine and non-aromatic alkene groups, strong removal by ozonation was observed, because these main structural monomers are highly adaptable to oxidative attacks (Dickenson et al., 2009). However, the possible transformation into products that remain biologically active and resistant to further ozonation is a major concern with regard to the use of ozone for antibiotic oxidation. Dodd et al (2009) stated that after primary oxidation reactions, the ozonation products of β-lactam antibiotics are still biologically active, but hydroxyl radicals or ozone may be further deactivated if the residual ozone concentration is adequate. In the case of roxithromycin, however the main ozonation products have been retained by the bactericidal dimethylamino groups and are very persistent at very high ozone doses for further degradation (Radjenovic et al., 2009).

2.4.2 Acoustic Sonolysis/ Cavitations / Ultrasonic of Antibiotics

Cavitations are one of the possible technologies for eliminating antibiotics. Although several studies have already investigated this chemical-free way of dealing with chemicals in wastewater, this is not a novel technology. There are two kinds of cavitations available: hydrodynamic and acoustic cavitations. When there is a quick formation and collapse of bubbles, hydrodynamic cavitations in water are formed. It occurs as the static pressure becomes lower than the vapor pressure of the material. The bubble implodes and folds inwards during cavitations, causing high temperatures that isolate the molecules of water. One of the ways to make cavitations happen can also be ultrasound, or high pitch echo. Ultrasound is a signal that is not audible by most human ears at frequencies above 20 kHz (Torres Palma and Serna-Galvis, 2018).

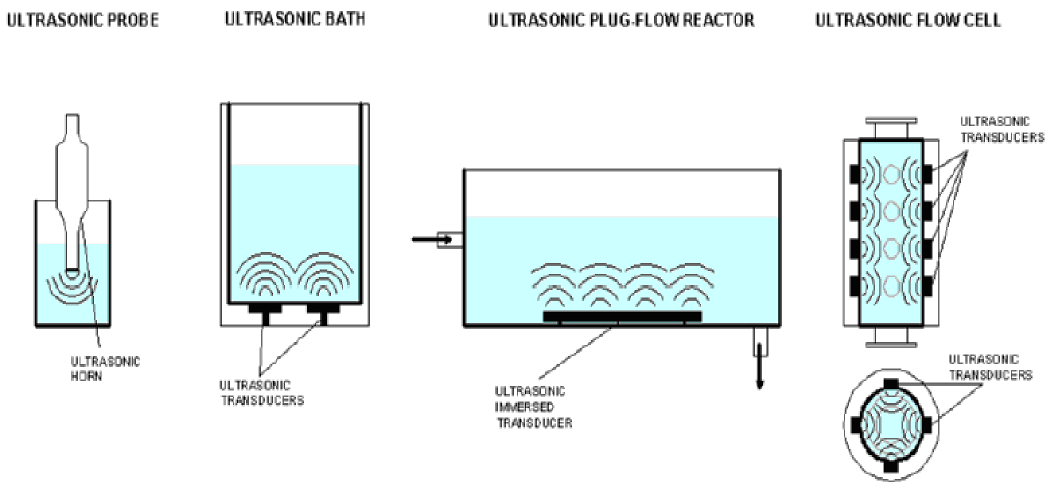

Figure 2.2 Ultrasonic systems typically used for sonochemical treatment (Naddeo, et al, 2014).

Tiny gas bubbles appear when water is irradiated under ultrasonic conditions, when the water pressure becomes negative. It happens when the acoustic pressure amplitude is greater than the ambient air pressure, the acoustic pressure amplitude being the sound oscillation amplitude. This pressure reduction generates a force, a force that expands the liquid. This allows the dissolved gases to become gas bubbles in the liquid, so they can no longer be dissolved in the liquid under negative pressure. The bubble expands when the pressure exceeds the liquid pressure on the bubble's surface. It bursts when the bubble reaches a critical size and a shock wave is sent into the fluid because of the sudden release of localised pressure. Acoustic cavitations are the growth and collapse using ultrasound of such micro-bubbles. There is little or no thermal transfer between the inside of the collapsing bubbles and the surrounding fluid during the rapid collapse of the bubbles, making it an adiabatic process. For this cause, within the falling bubbles, temperature and pressure hit very high values (Grieser 2015).

Some researchers have said that temperature and pressure values can be in the range of 10,000 K and 10 GPa (99,000 atm) or 5,000 K and 1,000 atm. This high temperature and high pressure conditions allow chemical processes, such as chemical bond splitting (Torres-Palma and Serna-Galvis 2018), to dissociate water vapor and oxygen within the bubble and to form oxidants such as hydroxyl radicals, hydrogen peroxide, oxygen atoms, ozone, and molecular hydrogen. Light pollution can also result from high temperatures and high pressure conditions. The oxidants formed within the bubble will then also move through the interface area into the surrounding liquid and react with the solute molecules outside the bubble. These chemical reactions are termed sono-chemical reactions and hydroxyl radicals are the major oxidants. Furthermore, the oxidation-reduction ability of hydroxyl radicals is much greater than that of hydrogen peroxide, indicating that hydroxyl radicals play a more significant role. It is suggested that the concentration of hydroxyl radicals on the bubble wall is approximately 5×10^{-3} M in the absence of solutes and their lifetime is approximately 20 ns at this concentration (Grieser 2015). In the other hand, in the absence of solutes, the lifespan of hydrogen peroxide is long.

In three distinct regions, sono-chemical reactions can occur. Area one is the area inside a collapsing gas bubble with high temperatures and high pressure. The interface region between hot gas and bulk liquid is region Two. The third area is the bulk of the ambient temperature solution where hydroxyl radicals have escaped from the inside of the bubble and react with organic solutes (Grieser 2015). In the sonochemical phase, the pollutant form determines the route of its degradation .In the bulk solution, hydrophilic pollutants accumulate, non-volatile hydrophobics accumulate in the interface zone and volatiles cross into the cavitation bubble within .Therefore, after the bubble collapses, hydroxyl radicals entering the bulk solution can destroy the hydrophilic compounds (Torres-Palma and Serna-Galvis 2018).

Radicals and/or thermal reactions in the interface region degrade hydrophobic, non-volatile compounds. Within the bubbles, volatile pollutants are degraded by pyrolysis. Both frequency and ultrasonic strength are dependent on the number of bubbles produced by cavitations. Frequency modifies the bubble's scale and collapse duration. The increase in frequency allows the collapse of the bubble faster resulting in more cavitations happening per unit of time (Torres-Palma and Serna-Galvis 2018). If the frequency grows, the smaller the bubbles are produced and higher intensities are required to collapse (Grieser 2015). At frequencies of around 200-350 kHz, the highest radical forming takes place. However, the influence of frequency on the deterioration of pollutants depends on the form of contaminant. The majority of moderate hydrophobic and hydrophilic pollutants are degraded at frequencies where hydroxyl radicals are rapidly formed which is between 200 to 350 kHz. Sono-degradation of volatile or very hydrophobic pollutants is favoured at high frequencies which is more than 350 kHz. The growth of sono-chemical activity is promoted by rising ultrasonic strength, or amplitude. For all types of compounds (hydrophobic, hydrophilic and volatile), the reaction to amplitude is the same. Increased amplitude contributes to faster