ENHANCED PHOTOCATALYTIC DEGRADATION OF BISPHENOL A UNDER VISIBLE LIGHT IRRADIATION USING NANO DISC RICE HUSK ASH SILICA-TEMPLATED OXYGEN DOPED MESOPOROUS CARBON NITRIDE AND CARBON DOTS MODIFIED GRAPHITIC CARBON NITRIDE

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by

SHITTU FATIMAH BUKOLA

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TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SCHEMES

Page

LIST OF SYMBOLS

e^-	Electrons
g-C_3N_4	Graphitic carbon nitride
h^+	Positive holes
HF	Hydrofluoric Acid
HNO_3	Nitric acid
k	Rate constant
$O_2^{\bullet -}$	Superoxide radical
$^{\bullet}OH$	Hydroxyl radical
OH^-	Hydroxyl ion
TiO_2	Titanium oxide
ZnO	Zinc oxide

LIST OF ABBREVIATIONS

AA	Ascorbic acid
AOP	Advanced Oxidation Processes
AR	Androgen receptor
BBB	Blood-brain barrier
BET	Brunauer, Emmett and Teller
BJH	Barett, Joyner and Halenda
BPA	Bisphenol A
C_o	Initial concentration
C_t	Final concentration
CB	Conduction band
CDs	Carbon dots
CDs	Compact discs
Clx-BPA	Chlorinated derivatives
CNTs	Carbon nanotubes
CQDs	Carbon quantum dots
DFT	Density Functional Theory
EDTA	Ethylenediaminetetraacetic acid
EDCs	Endocrine disrupting compounds
Eg	Band gap
EOCs	Emerging organic contaminants
EPA	Environmental Protection Agency
ER	Estrogen receptor
EU	European Union
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
G	Graphene
GA	Gallic acid

HRTEM	High Resolution Transmission Electron Microscopy
IUPAC	International Union of Pure and Applied Chemistry
KBr	Potassium bromide
LC/TOF/MS	Liquid chromatography/time-of-flight/mass spectrometer
LH	Langmuir–Hinshelwood
MeOH	Methanol
MCN	Mesoporous Carbon Nitride
MW	Microwave
NAD	N_2 Adsorption-Desorption
NDS	Nano disc silica
NLDFT	Non-Local Density Functional Theory
O-MCN	Oxygen doped mesoporous carbon nitride
PL	Photoluminescence
POPs	Persistent organic pollutants
PPCPs	Pharmaceutical and personal care products
PTS	Persistent toxic substances
PZC	Point of zero charge
QS	Quinine sulphate
QY	Quantum yield
RH	Rice husk
RHA	Rice husk silica
ROS	Reactive oxygen species
SEM	Scanning Electron Microscopy
SDAs	Structure directing agents
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric Analysis
THR	Thyroid hormone receptor
TOC	Total organic carbon
TWW	Treated wastewater
UV-Vis DRS	UV-Visible diffuse reflectance spectroscopy

VB	Valence band
VB-XPS	Valence band X-ray photoelectron spectroscopy
WHO	World Health Organization
XRD	Powder X-ray Diffraction

LIST OF APPENDICES

PENINGKATAN PENGURAIAN FOTOPEMANGKINAN BISFENOL A DI BAWAH SINARAN CAHAYA NAMPAK MENGGUNAKAN KARBON NITRIDA BERLIANG MESO TERDOP OKSIGEN BERTEMPLAT NANO CAKERA SILIKA ABU SEKAM PADI DAN TITIK KARBON DIUBAH SUAI NITRIDA KARBON GRAFIT

ABSTRAK

Satu siri karbon nitrida berliang meso terdop oksigen (O-MCN) dengan kandungan oksigen yang berbeza dan titik karbon diubah suai grafit karbon nitrida (CDs/g-C_3N_4) disintesis melalui kaedah polimerisasi termal dan kaedah polimerisasi termal dibantu gelombang mikro, masing-masing, untuk fotodegradasi bisphenol A (BPA) di bawah sinaran cahaya nampak. O-MCN dilabel sebagai *x*O-MCN (*x* = 0.1, 0.2, 0.3, 0.4, dan 0.5 g glukosa) manakala CDs/g-C_3N_4 dilabel sebagai *y*CDs/g-C_3N_4 (*y* = 0.5, 1.0 dan 1.5 ml CD). Spektroskopi inframerah transformasi Fourier (FTIR), difraksi sinar-X (XRD), mikroskopi elektron imbasan (SEM), mikroskopi elektron transmisi (TEM), penjerapan-penyahjerapan nitrogen (NAD), spektroskopi pantulan sinar UV/Sinar nampak (UV-vis DRS), spektroskopi fotopendarcahaya (PL), dan Spektroskopi fotoelektron sinar-X (XPS) digunakan untuk mencirikan nanokomposit. 0.2O-MCN mempunyai penyingkiran BPA tertinggi (97%) pada keadaan optimum (40 mgL^{-1} 0.2O-MCN, 10 mgL^{-1} BPA, pada pH 10). Kadar penyingkiran adalah 0.0132 min^{-1}, iaitu 1.8 kali ganda daripada g-C_3N_4 tulen. Analisis XPS mengesahkan atom oksigen menggantikan atom nitrogen dalam rangka g-C_3N_4. Ujian hapus sisa menunjukkan bahawa + adalah spesies yang paling aktif, diikuti oleh superoksida ($O_2^{\bullet-}$) dan radikal hidroksil ($^{\bullet}OH$). Nanokomposit dapat

digunakan semula sehingga lima kali tanpa kehilangan ketara dalam aktiviti fotopemangkinanya. Dengan kadar fotodegradasi 0,01014 min^{-1} dan kecekapan penyingkiran 90% BPA dalam 180 minit, nanokomposit 1.5CDs/g-C_3N_4 yang dioptimumkan menunjukkan penurunan BPA fotopemangkinan yang luar biasa. Peningkatan aktiviti fotopemangkinan 1.5CDs/g-C_3N_4 disebabkan oleh kesan sinergistik ciri-ciri CD, yang mengakibatkan peningkatan pemisahan pembawa cas dan struktur jalur yang dapat ditala. CD disambungkan ke permukaan g-C_3N_4 melalui pautan C-O. CD yang terikat mengurangkan struktur celah pita g-C_3N_4, lalu mencegah pengumpulan semula cas. Spesies aktif serupa seperti di O-MCN dikenal pasti bertanggungjawab dalam fotopenguraian BPA. Pemangkin hibrid menunjukkan kebolehgunaan semula yang baik sehingga lima kitaran. Pengantara yang dikenal pasti melalui melalui kromatografi cecair / spektrometri masa / penerbangan / masa (LC/TOF/MS) digunakan untuk mendalilkan mekanisme penguraian BPA. Penyelidikan ini memberikan pemahaman yang lebih mendalam mengenai modifikasi struktur elektronik dan mekanisme seperti fotosensitisasi dalam sistem fotopemangkinan bahan berasaskan g-C_3N_4.

ENHANCED PHOTOCATALYTIC DEGRADATION OF BISPHENOL A UNDER VISIBLE LIGHT IRRADIATION USING NANO DISC RICE HUSK ASH SILICA-TEMPLATED OXYGEN DOPED MESOPOROUS CARBON NITRIDE AND CARBON DOTS MODIFIED GRAPHITIC CARBON NITRIDE

ABSTRACT

A series of oxygen doped mesoporous carbon nitride (O-MCN) was synthesized via thermal polymerization method. Another series of carbon dots modified graphitic carbon nitride (CDs/g-C_3N_4) was also synthesized via microwave assisted thermal polymerization method. Both were used for the photodegradation of bisphenol A (BPA) under visible light irradiation. The O-MCN were labelled as *x*O-MCN (x = 0.1, 0.2, 0.3, 0.4 and 0.5 g glucose) whereas the CDs/g-C_3N_4 were labelled as *y*CDs/g-C_3N_4 (y = 0.5, 1.0 and 1.5 ml CDs). The Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption-desorption (NAD), UV–vis diffuse reflectance spectroscopy (UV-vis DRS), photoluminescence (PL) spectroscopy, and X-ray photoelectron (XPS) spectroscopy were used to characterize the nanocomposites. The 0.2O-MCN have the highest removal of BPA (97%) under optimum conditions (40 mgL^{-1} 0.2O-MCN, 10 mgL^{-1} BPA, at pH 10). The removal rate was 0.0132 min^{-1}, which is 1.8 times that of pure g-C_3N_4. The XPS analysis confirms that the oxygen atoms substituted the nitrogen atom in the framework of g-C_3N_4. The scavenging experiments revealed that h^+ are the most active species, followed by superoxide ($O_2^{\bullet-}$) and hydroxyl radicals ($^{\bullet}OH$).

The nanocomposite was able to be reused up to five times without significant loss in its photocatalytic activity. With a photodegradation rate of 0.01014 min^{-1} and 90% BPA removal efficiency in 180 minutes, the optimized 1.5CDs/g-C_3N_4 nanocomposite demonstrated outstanding photocatalytic BPA degradation. The enhanced photocatalytic activity of 1.5CDs/g-C_3N_4 is due to the synergistic effects of CD characteristics, which resulted in increased charge carrier separation and tunable band structure. The CDs are anchored to the g-C_3N_4 surface via a C–O link. The bonded CDs reduced the bandgap structure of g-C_3N_4, preventing charge recombination. Similar active species as in O-MCN were identified to be responsible in photodegrading the BPA. The photocatalysts show good reusability after five cycles. The identified intermediates by Liquid chromatography/time-of-flight/mass spectrometry (LC/TOF/MS) were used to postulate the mechanisms for BPA breakdown. This research provides a deeper understanding of the electronic structure modification and photosensitization-like mechanism in the photocatalysis system of g-C_3N_4-based materials.

CHAPTER 1 INTRODUCTION AND LITERATURE REVIEW

1.1 Background

Even though water covers about 70% of the earth surface, unfortunately, a significant part of it has been exposed to pollution due to organic evolution and human activities (Beniah Obinna & Ebere, 2019). The emerging organic contaminants (EOCs) are heterogeneous groups of substances that consist of several chemical classes. They are mainly produced or generated from anthropogenic compounds (harmful chemical released into the environment due to human activities). The EOCs have been confirmed to have detrimental effects on life, continuance and progenitive success on living organisms. Some EOCs demonstrate or show disrupting endocrine effects, which changes the hormonal equilibrium of living organisms. These particular groups of famous compound (EOC) are considered to be endocrine-disrupting compounds (EDCs) (Joanna Karpinska and Urszula Kotowska, 2019). One of the frequently detected EDCs in the aquatic environment is bisphenol A (BPA). Bisphenol A (BPA) is a common EDC found in the aquatic environment. BPA is a chemical compound that is commonly used in manufacturing of flame retardants, polycarbonate plastics, and epoxy resins (Frankowski, Zgoła-Grześkowiak, Smułek, & Grześkowiak, 2020). Most water treatment technologies could not remove the total dosage of BPA in water; hence, there is a continuous high risk to humans and other living organisms to this compound (Tursi, Chatzisymeon, Chidichimo, Beneduci, & Giuseppe Chidichimo, 2018).

The treatment of water using conventional techniques such as flocculation, chlorination, precipitation, sedimentation, and filtration usually remove cyanobacteria and low levels of (cyano) contaminant (Serrà, Philippe, Perreault, & Garcia-Segura, 2021) but are unable to remove the EDCs effectively; thus, via the effluent discharges, the EDCs escape intact into the aquatic system (Davididou, Nelson, Monteagudo, Durán, Expósito, & Chatzisymeon, 2018). The cost of operation of the techniques is very high and can produce secondary contaminants that further instigate a more toxic environment. Chlorination, for example, is a chemical procedure that removes organic molecules from water. Chlorine, the most commonly used disinfectant and oxidant for water treatment, results in the development of potentially harmful by-products of disinfection, for example, chlorate, chlorite, halomethane species, and haloacetamides (Rojas & Horcajada, 2020). The high reactivity of BPA with disinfectant hypochlorite and free chlorine radicals results in the development of its more commonly observed chlorinated derivatives (Clx-BPA) and at higher concentrations than BPA in tap water (Martín, Santos, Malvar, Aparicio, & Alonso, 2020). In addition, Clx-BPA is more active in both artificial environment and living organism studies than BPA. It results in several chlorinated intermediate residual concentrations with endocrine and other detrimental biological properties (Frankowski et al., 2020).

Photocatalysis has come to light as a captivating approach for the removal of organic contaminants, including EDCs, due to its ability to completely mineralize the pollutants (Chiu, Chang, Chen, Sone, & Hsu, 2019; X. Gao, Kang, Xiong, & Chen, 2020). Photocatalytic water treatment for environmental remediation is a promising Advanced Oxidation Processes (AOP). Photocatalysis efficiently mineralises various troublesome organics by creating active species ($O_2^{\bullet -}$, $^{\bullet}OH$ and h^+) (Lin, Jiang, Chen,

Xu, & Wang, 2020). Photocatalysis occurs when a semiconducting material is exposed to light, thereby forming electron and hole pair (Ameta, Solanki, Benjamin, & Ameta, 2018). Figure 1.1 shows the formation of charge carriers, by exposing a semiconductor to light with the same amount of energy or higher than the band gap of the photocatalyst. The electrons (e^-) separates from the hole and migrates to the conduction band while holes (h^+) remain in the valence band. Molecules that are adsorbed on the photocatalyst surface materials are reduced and oxidised as a result (Rueda-Marquez, Levchuk, Fernández Ibañez, & Sillanpää, 2020). Hence, fashioning out a design to create or modify a photocatalyst to produce the active radicals is very significant in this study (W. Deng, Zhao, Pan, Feng, Jung, Abdel-Wahab, Batchelor, & Li, 2017).

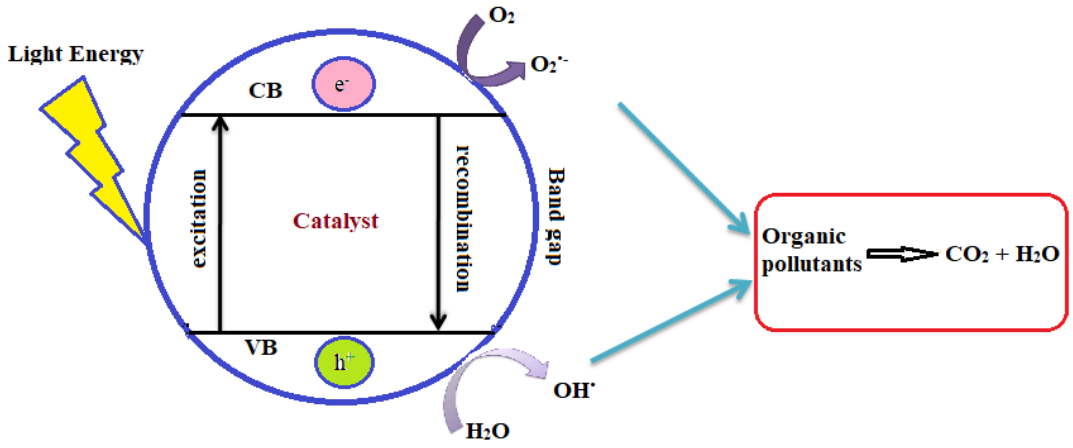

Figure 1.1 Schematic representation of photocatalysis mechanism

The primary factors that influence the photocatalytic performance of a semiconductor are broad bandgap, high surface area, carrier separation, stability and migration efficiency (Photo-oxidation, Yaqoob, Habibah, Serr, Nasir, & Ibrahim,

2020; Quesada-Cabrera & Parkin, 2020). Graphitic carbon nitride (g-C_3N_4) was discovered more recently and it has excellent photocatalytic oxidation technology in water treatment, necessitating researchers to develop and extend the application of g-C_3N_4 (L. Deng, Jiang, Tang, & Li, 2018). The g-C_3N_4 is currently being researched as a new photocatalyst made of carbon nitride for recovering the photocatalytic activity of commonly used photocatalysts like ZnO and TiO_2. It demonstrated excellent photocatalytic behaviour in visible light region without using any metal co-catalyst (Darkwah & Oswald, 2019).

1.2 Literature Review

1.2.1 Water pollution and the environment

Water pollution is defined as water contamination with harmful materials such as industrial effluent wastes, domestic wastes, marine dumping, radioactive waste, and atmospheric deposition (S. Ahmed & Ismail, 2017). Human activities are the main contributor to water pollution. Many water supplies are polluted due to ignorance and are unsuitable for drinking and other purposes. In addition, due to the dumping of untreated contaminants, chemicals and toxic waste from thousands of factories directly into the water body, residual freshwater supplies are increasingly contaminated (Jayaswal, Sahu, & Gurjar, 2018). Severe water contamination has resulted from inadequate regulation of the release of contaminants into the water. The polluting elements in the marine ecosystem have become highly complex relative to conditions in the past, as some rising pollutants contribute to the emergence of a new challenge to water security (Bian, Xiong, & Zhu, 2018). An increase in water consumption, climate changes, and human activities on the environment is already causing a water crisis or environmental catastrophe. In

addition, the widespread use and disposal of chemicals in medicine, industry, and agriculture leads to the accumulation of organic contaminants in water (Sousa, Ribeiro, Barbosa, Pereira, & Silva, 2018).

Toxic organic compounds are mainly from the heavy use of chemical substances in day-to-day activities and unregulated drug access. As a result, there was an increase in waste production and a lot of contamination in the environment from both old and new organic substances (Joanna Karpinska and Urszula Kotowska, 2019). Several organic contaminants that are persistent have been linked to cancer and have other negative consequences in the aquatic environment (Ambauen, Muff, Mai, Hallé, Trinh, & Meyn, 2019). Heavy metals called inorganic compounds enter the marine environment through air deposition, deterioration of the geological matrix, or anthropogenic activities such as industrial waste, residential sewage, and waste produced by mining (S. Thangamalathi & Anuradha, 2018). In general, heavy metals enter the marine environment by atmospheric accumulation, geological matrix degradation or because of anthropogenic activities caused by industrial waste, domestic sewage and mining waste (Kurwadkar, 2019; S. Thangamalathi & Anuradha, 2018).

Amongst these contaminants, toxic organic compounds are numbered in millions with different functional groups, properties, and applications. They are persistent in the environment because they are common industrial organic wastes like organic dyes, pesticides, personal care products, detergents and pharmaceuticals (H. Dong, Qiang, & Richardson, 2019; F. Lu & Astruc, 2020; Richardson & Ternes, 2018; Y. Yang, Ok, Kim, Kwon, & Tsang, 2017). These organic pollutants and their toxic derivatives make the water unhealthy for consumption (Mosharraf, Nazmul

Islam, & M. Rahm, 2012). Hence, there is need to know the classes of the organic compounds, their origins, and the impact they have on the environment and human health. This is to be able to control their entry and instigate strategies in treating the water from persistent organic pollutants.

1.2.2 Toxic organic pollutants

Organic pollutants are chemical contaminants that contain essentially carbon covalently bonded with other compounds. They are considered poisonous or carcinogenic in nature, and large amounts of water create severe and widespread concern (Beniah Obinna & Ebere, 2019). Most organic pollutants are persistent in the environment and resistant to degradation; hence, bioaccumulation poses adverse effects on the ecosystem. This class of organic pollutants are known as persistent organic pollutants (POPs) (Verla, Enyoh, Verla, & Nwarnorh, 2019), which are constantly present in the environment due to increased industrialization and the increase in anthropogenic activities, such as wastewater discharge and incomplete petrochemical combustion (S. Das, Aria, Cheng, Souissi, Hwang, & Ko, 2020). POPs are proclivity toward bioaccumulation, with sluggish metabolism in living organisms. Hence, remain in our body for a long time and makes it highly toxic (Alharbi, Basheer, Khattab, & Ali, 2018).

The four classification of POPs are listed below (Pi, Li, Xia, Wu, Li, Xiao, & Li, 2018);

(a) Persistent toxic substances (PTS): It refers to a class of highly harmful and resistant organic chemical contaminants that are biodegradable in the natural environment. Most PTS are aromatic compounds consisting of two or more benzene rings, usually substituted by chlorine.

(b) Pesticides and herbicides: Almost all pesticides and herbicides are poisonous and persistently stable, significantly destroying habitats and harming human health when impregnated with water. They enter the water by rundown, leaching or spraying (Hassaan & El Nemr, 2020).

(c) Antibiotics: Antibiotic drugs are primarily derived from human excretion, pharmaceutical and hospital sewage discharge, animal feed and aquaculture. In aquatic environments, trace levels of antibiotics can lead to antibiotic resistance and adversely affect marine wildlife, ecosystems, and human health. The widespread use of antibiotics has led to their frequent detection (Q. Li & Zhang, 2020).

(d) Phenols: Phenols are considered toxic and carcinogenic, usually with harmful effects, even in dilute solutions. Phenolic wastewater originates mainly from the petrochemical, resin, plastics, synthetic fibre and coal industries, oil refineries. These phenolic compounds are regarded as priority contaminants because of their toxicity and persistence in the environment and feature on the US Environmental Protection Agency's list of hazardous substances (EPA) (Mainali, 2020).

There is currently growing concern about new organic synthetic compounds in the environment referred to as new or emerging organic contaminants (EOCs). Such compounds have been present in the atmosphere for a long time, but they were not detected until new and more sensitive analytical methods were developed. They are also referred to as emerging POPs (Lorenzo, Campo, & Picó, 2018).

1.2.2(a) Emerging Organic Contaminants (EOCs)

The emerging organic contaminants (EOCs) are any organic chemical that is a man-made or naturally occurring with little or no environmental regulation. However, it has the ability to invade the surroundings and cause documented or suspected negative environmental consequences on human health (Stewart, M. and Tremblay, 2020). The EOCs are mostly human-derived organic chemicals that are extensively distributed in the environment and have terrible health effects (Bernot, Bernot, & Matthaei, 2019). Pharmaceuticals, personal care products, pesticides, surfactants, industrial additives and endocrine-disrupting compounds (EDCs) are among the toxins in the EOCs group, which have serious adverse effects on living organisms and the climate (EDCs) (Stewart, M. and Tremblay, 2020). Since EOCs have been detected at trace levels in different food products (Santarelli, Migliorati, Pomilio, Marfoglia, Centorame, D'Agostino, D'Aurelio, Scarpone, Battistelli, Di Simone, Aprea, & Iannetti, 2018), stringent controls have been implemented by the European Union (EU) on food products entering the European market. Seafood has earned considerable attention among food commodities due to increasing reports on trace organic EOCs in fish, mussels, clams and molluscs from various parts of the world. In seafood samples obtained from European countries' marine and coastal waters, EOCs such as phenolic EDCs, dioxins, polyaromatic hydrocarbons, and pharmaceutical compounds were detected at trace levels (Omar, Aris, Yusoff, & Mustafa, 2019; Philip, Aravind, & Aravindakumar, 2018). It is, therefore, possible to identify EOCs as either pharmaceuticals, nanomaterials, personal care products (PPCPs), or endocrine-disrupting chemicals (EDCs) (Bwapwa & Jaiyeola, 2019).

Due to rising population, increasing urbanization and climate change-induced changes in precipitation patterns (weather), many regions such as the Middle East,

East Africa, and the U.S. Southwest face unprecedented water crisis. Treated wastewater (TWW) is accepted as a reliable alternative to increasing irrigation to combat water scarcity and meet the increasing demand for water in agricultural production (Q. Fu, Malchi, Carter, Li, Gan, & Chefetz, 2019). In 2017, human-caused global warming reached an average of 1°C above pre-industrial levels, as reported by Intergovernmental Panel on Climate Change. The global mean temperature could rise by 3.5 °C by 2100, with regional average global temperature fluctuations ranging from 1.4 to 5.8 °C. Climate change is predicted to be responsible for roughly 20% of the worldwide increase in water shortage, affecting the growth and functioning of societies worldwide, both socially and economically (Ungureanu, Vlăduț, & Voicu, 2020). Approximately 5.6 billion m^3 of TWW is used globally for irrigation purposes per year, even though it is less than 1% of the global irrigation volume. More than 85 % of the TWW produced in Israel is used for irrigation, while about 38 % of the TWW is used for irrigation in Jordan, and about 46 % of the TWW used in California is used for agricultural land (Ben Mordechay, Tarchitzky, Chen, Shenker, & Chefetz, 2018). The EOCs found in TWW used for irrigation of agricultural products will be absorbed by the crops and eventually join the food chain when humans consume (González García, Fernández-López, Polesel, & Trapp, 2019). A rising number of studies have recorded the absorption and accumulation of pharmaceutical and personal care products (PPCPs) by plants since around 2009 (Q. Fu et al., 2019). Despite the low concentration of PPCPs generally detected, their continuous introduction from various pathways into the environment and their bioactivity and established mode of action make them concern as emerging environmental pollutants that may pose potential ecotoxicological effects in the environment (Christou, Karaolia, Hapeshi, Michael, & Fatta-Kassinos, 2017).

1.2.2(b) Endocrine Disrupting Compounds

Chemicals unwittingly messing with the endocrine communication system and cause detrimental health effects are endocrine-disrupting chemicals (EDCs) (Lucaccioni, Trevisani, Marrozzini, Bertoncelli, Predieri, Lugli, Berardi, & Iughetti, 2020). EDCs are therefore defined as “chemicals that stand in the way of any aspect of the action of hormones” (Lauretta, Sansone, Sansone, Romanelli, & Appetecchia, 2019). EDCs consist of natural and synthetic compounds readily released by household, municipal, hospital, industrial and livestock waste into the environment. Not to mention, in humans, they can imitate and block the endocrine system, causing severe consequences such as cancer, irregular reproductive growth and metabolic disorders and a wide range of human well-being issues (Ismail, Wee, Haron, Kamarulzaman, & Aris, 2020). Several processes can disrupt the endocrine system, including imitating or eliminating natural hormone, synthesis, secretion, transport, metabolism, and imitating hormone activity at the receptor binding and signal transduction levels (Kassotis & Stapleton, 2019; Küblbeck, Vuorio, Niskanen, Fortino, Braeuning, Abass, Rautio, Hakkola, Honkakoski, & Levonen, 2020)

Over 460 million people have type II diabetes, and 650 million adults are obese, according to the World Health Organization (WHO), making these diseases major health issues and a huge economic burden worldwide (International Diabetes Federation, 2019). By 2045, the global burden of diabetes is expected to cross a whopping 629 million people. The WHO expects metabolic disorders to be a major cause of death by 2030, bringing tremendous economic stress on healthcare systems worldwide (Kassotis & Stapleton, 2019). Much evidence shows that EDCs play a significant part in causing cancer, diabetes, obesity, infertility, growth development problems, and metabolic syndrome (De Coster & Van Larebeke, 2012). Even though

they are detected in low concentration, they can cause damages at long-term low-dose exposure (Bao, Huang, Hu, & Yin, 2020).

Since the beginning of the Industrial Revolution in 1784, contaminants have primarily arisen from industrial origin. Water sources, such as rivers, provide a simple way to dispose of industrial waste, and groundwater is frequently contaminated by leaching from dumping sites, potentially exposing people to waterborne diseases. After the original reference in 1965, the presence of EDCs in drinking water was reintroduced as a serious concern in the mid-1970s, albeit there was little investigation after that (Wee & Aris, 2019). It is suspected that EDCs enter the aquatic environment as sewage effluent or other forms of contamination. However, little evidence on the occurrence of these compounds in drinking water is still available. Many of these EDCs are very stable and resistant to water treatment, raising concern that they can move via relatively large amounts of drinking water (Oberflächenwasser, Brueller, Inreiter, Boegl, Rubasch, Saner, Humer, Schuhmann, Hartl, Brezinka, Wildt, & Allerberger, 2018).

Two typical EDCs in the water environment have been reported (X. Gao et al., 2020):

(i) Oestrogen: This substance is found in sewage (ng L^{-1}) at low concentrations but has high oestrogen action, which includes natural steroidal estrogens such as 17β-estradiol (E2) and 17α-ethynylestradiol synthetic contraceptive (EE2).

(ii) Endocrine-disrupting phenolic compounds have low estrogenic activity, but have significant concentration in wastewater, which can reach micrograms per litre such as nonylphenol (NP) and bisphenol A (BPA).

Exposure to these compounds by man and animals is associated with adverse health and reproductive results; hence, the presence of these EDCs in water has become a public health problem. For example, exposure to bisphenol A (BPA) and phthalates reduces fertility in mammals by triggering primordial follicles prematurely and altering sex-steroid hormone levels (Gonsioroski, Mourikes, & Flaws, 2020). BPA is among the best-studied EDCs that may adversely affect the early development stage and one of the most widely produced chemicals in the world. Most individuals are exposed to this chemical daily by eating food and beverages from polycarbonate containers into which BPA has leached, including reusable bottles and baby bottles (Basak, Das, & Duttaroy, 2020).

1.2.3 Bisphenol A (BPA)

Bisphenol A [2, 2-bis (4-hydroxyphenyl) propane] (BPA), as shown in Figure 1.2, is an organic compound that belongs to bisphenols and derivatives of diphenylmethane. It has a molecular weight of 228.18 g mol^{-1}. The BPA is a white crystalline solid at room temperature. It melts at 156 ºC and boils at 220 ºC. Its solubility in water is 120 mg L^{-1} at 25 ºC. A Russian chemist, Alexander P Dianin was the first to synthesize BPA in 1891 using a condensation reaction of two phenol molecules and one acetone molecule with hydrogen chloride and ion exchange resin as a catalyst (Ohore & Songhe, 2019). Since the 1940s, BPA has been widely used to manufacture plastic containers, thermal papers, can liners/coats, and DVDs. The BPA is classified as endocrine-disrupting compounds because of its estrogenic properties (Almeida, Raposo, Almeida-González, & Carrascosa, 2018; Ohore & Songhe, 2019). Dowds and Lawson, who discovered their estrogenic properties in vivo, obtained the first evidence of BPA's mechanisms of action in 1936 (Cimmino, Fiory, Perruolo, Miele, Beguinot, Formisano, & Oriente, 2020). Estrogenic

compounds have similar properties to the 17βE2 hormone, whose effects are induced by interactions with the oestrogen receptor and cell systems. 17βE2 hormone is the main natural ovarian-generated oestrogen (Pamplona-Silva, Mazzeo, Bianchi, & Marin-Morales, 2018). Therefore, even at very low concentrations, BPA can induce estrogenic effects, causing reproductive and developmental disorders in both humans and wild animals by operating and blocking the physiological activity of oestrogen receptors analogously or acting as testosterone antagonists in the cell (Cimmino et al., 2020). BPA belongs to the Endocrine Disruptive Chemicals (EDCs) group and is acutely toxic to living organisms because of its strong evidence of disruptive endocrine activity (Adeyi & Babalola, 2019).

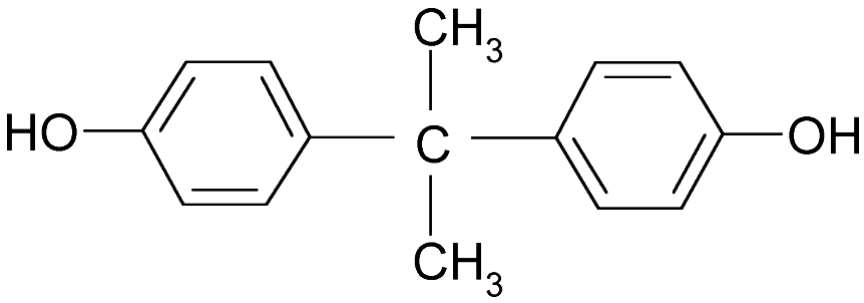

Figure 1.2 Structure of Bisphenol A

1.2.3(a) Sources of BPA

The BPA is one of the most rapidly and perhaps the most representative member of the emerging organic pollutants in the environment due to its excessive use (up to tens of thousands of ng L^{-1} in surface water and thousands of ng g^{-1} in sediments) (Z. Huang, Zhao, Yang, Jia, Zhang, Chen, Liu, Yang, Xie, & Ying, 2020). Around 8 million tonnes of BPA are produced and used annually, mainly in the manufacturing of epoxy resins and polycarbonate polymers (Radwan, Ibrahim,

Adel, & Farouk, 2020). Polycarbonates are hard plastics used in toys, bottles of water, glass lenses and compact discs (CDs), and epoxy resins as strong adhesives, dental sealants, and protective linings in cans (Löfroth, Ghasemimehr, Falk, & Vult von Steyern, 2019). Because they can withstand high temperatures and high-impact collisions, BPA-based polycarbonate plastics are rigid and stable. Because they have the ability to withstand heating in microwave ovens, these properties make them useful as safety equipment and food packaging materials. BPA extends the life-span of food and beverage products by being an ingredient in epoxy resins used to make protective coatings such as the insides of aluminum and metal cans (as well as the lid closures of glass jars and bottles) (Campanale, Massarelli, Savino, Locaputo, & Uricchio, 2020). The extensive use of BPA has contributed to its exposure to human and marine animals through the leaching of packaging materials into food and water, thus its declaration by regulatory authorities in several countries as a hazardous material (Alam & Deen, 2020).

The widespread occurrence of BPA in the ecosystem has been documented to include wastewater discharge, river water and sediments, given the comprehensive applications of BPA (Q. Chen, Lan, Shi, Liu, Zhu, Sun, & Duan, 2019). Due to its vast amount utilised as raw materials in the production of epoxy and polycarbonate resins, BPA pollution is found everywhere, water, soil and air. BPA sources are mostly traced from either wastes gotten from its production, transports and processing or waste from BPA-based products, waste water, and environmental breakdown of plastics (Reddy, Kim, Kavitha, Kumar, Raza, & Kalagara, 2018).

Due to the growing scarcity of freshwater supplies, reclaimed water is an alternative water resource commonly used for irrigation. Still, it may become an

essential source of BPA contamination for food crops and groundwater (Gonzales-Gustavson, Rusiñol, Medema, Calvo, & Girones, 2019).

BPA has also been associated with fissure sealants and composite materials in a dental context where its existence is likely due to impurity from the manufacturing process. BPA is used as a raw material to synthesise many resin monomers in dentistry (Berge, Lygre, Lie, Lindh, & Björkman, 2019). Since the use of such materials in dental care, increased BPA concentrations in saliva and urine have been shown. In contrast, other materials do not offer BPA leaching, suggesting that BPA leaching is material based (Becher, Wellendorf, Sakhi, Samuelsen, Thomsen, Bølling, & Kopperud, 2018). People are subjected to BPA in their everyday lives due to its wide variety of applications, likely without being aware of it.

1.2.3(b) Toxicity of BPA

In humans and animals, exposure to this chemical occurs mainly via the oral (approximately 90 %), gastrointestinal, and dermal routes (Amjad, Rahman, & Pang, 2020; Encarnação, Pais, Campos, & Burrows, 2019). In humans, terrestrial and aquatic animals, BPA exposure has been linked to diabetes, cardiovascular disease, breast cancer, brain development abnormalities, hypertension, obesity, thyroid dysfunction, infertility, and other health problems (Amjad et al., 2020). Many mechanisms, including oxidative stress, affect endocrine and reproductive organs and the immune and central nervous systems (M. S. Rahman, Kang, Arifuzzaman, Pang, Ryu, Song, Park, & Pang, 2019). Oxidative stress refers to the body's imbalance between oxidation and antioxidation, in which oxidation predominates, leading to inflammatory invasion of neutrophils, increased secretion of proteases, and the development of several oxidative intermediates (K. Wang, Zhao, & Ji, 2019). BPA

can cause oxidative stress by entering the body and creating high reactive oxygen species (ROS), causing biological macromolecules to be destroyed, facilitating the production of oxygen-free radicals and raises the amount of oxidative stress in the body or cells and the consequence of the degree of antioxidant gene expression directly or indirectly decreases the antioxidant enzymes and results in oxidative damage to the body by the impaired antioxidant system of biological organisms (X. Zhang & Liu, 2018).

1.2.3(b)(i) Toxicity of BPA in Animals

Growing evidence from laboratory animal studies reveal the toxic effects of BPA on animals and indicates that BPA changes the reproductive function of males and females even at extremely low exposure levels (Vandenberg, Hunt, & Gore, 2019). In a study, adult male Wistar rats were exposed to BPA to investigate the role of gallic acid (GA), a recognised antioxidant, in rat testicular oxidative stress induced by BPA. In this study, the activity of antioxidant enzymes in rats was significantly reduced by BPA and a substantial increase in the levels of reactive oxygen species (ROS) (Olukole, Ola-Davies, Lanipekun, & Oke, 2020). BPA uptake was reported to damage the oxidant-antioxidant equilibrium in mouse colons and livers by causing oxidative stress and lowering antioxidant activity, as seen in Figure 1.3 (K. Wang et al., 2019).

The toxic effect of BPA on porcine embryonic growth was addressed in another report. Increased ROS levels resulting in oxidative stress were triggered by BPA exposure to embryos. Mitochondrial and DNA damage is caused by oxidative stress, which contributes to autophagy (cell degradation). Furthermore, BPA exposure can cause alterations in DNA methylation that may affect the health of

offspring (J. Guo, Zhao, Shin, Niu, Ahn, Kim, & Cui, 2017). The BPA was found to cause damage in the brain, kidney, liver, epididymal sperm and other organs in rodents. It also causes structural changes and many enzymes and receptor protein to not function well in cell signaling. The BPA causes damage to DNA, deformities, and genotoxicity in the liver of mice and rats. Early exposure to BPA during developmental stages could lead to changes in nonhuman primates' mitochondrial activity, thereby causing disease evolution later in life. The degree of toxicity of BPA depends on the dose, exposure age, frequency of exposure and individual differences (Kourouma, Quan, Duan, Qi, Yu, Wang, & Yang, 2015). In another report, an increase in doses of BPA increases immature spermatozoa in rats. A dose of 10 mg/kg of BPA in adult male rats aggravates the vulnerability of its prostate gland to develop hormonal carcinogenesis, reduction in sperm counts and testosterone hence a great fertility consequence. As for neonatal mice, the effects of BPA exposure depend on the amount administered. BPA exposure to neonatal mice could affect the framework of its brain, sexual dimorphism and adult neuronal phenotypes (Mas, Egido, & González-Parra, 2017).

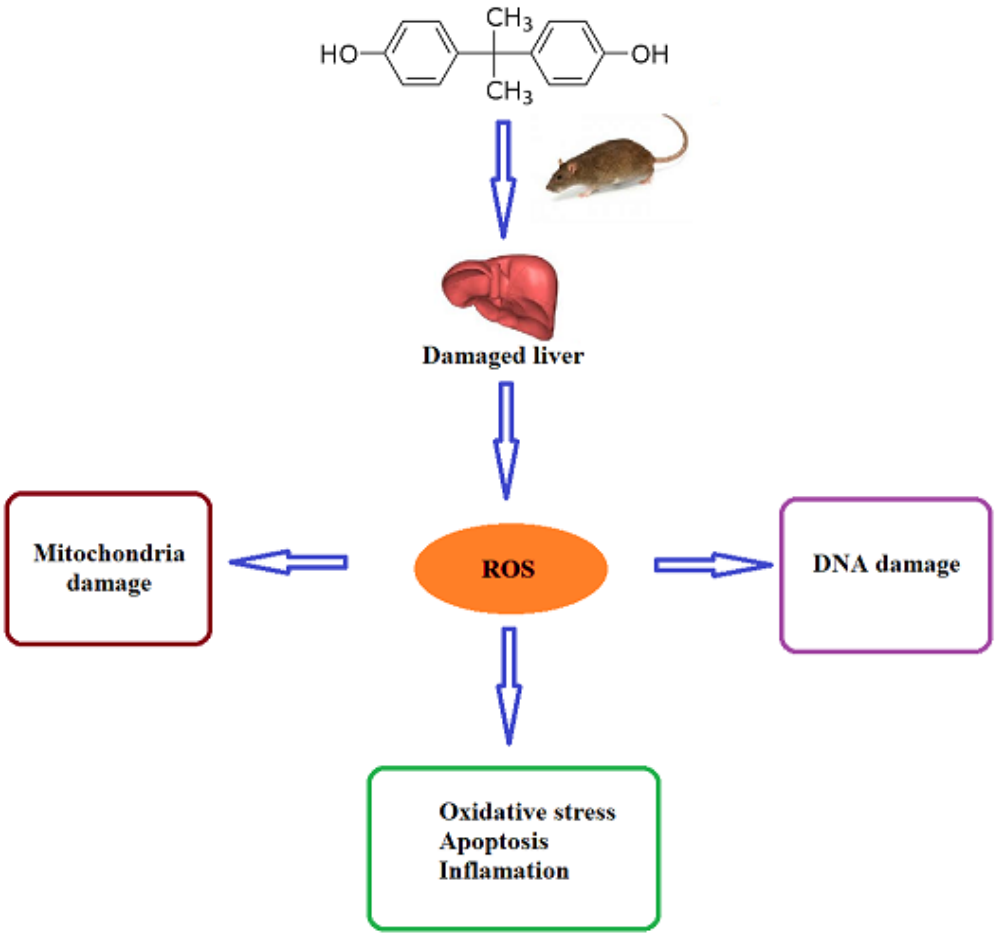

Figure 1.3 Schematic diagram of an adverse effect of BPA

Water polluted with BPA has been reported to instigate histopathological changes in fish. The first organ to be affected is its gills because it is responsible for respiration, osmoregulation and excreting nitrogenous waste products. The histopathological abnormality in gills depends on how long the fish get exposed to BPA. Exposure to BPA may also cause fish to be traumatized, leading to rupture of lamellar capillary and bleeding (Mohammed, Elshaer, Khalaf-Allah, & Bakry, 2013). Fish have been reported to be exposed to BPA via the gills (respiration), leading to estrogenic effects, hence inducing egg yolk protein precursor vitellogenin in male

fishes (Canesi & Fabbri, 2015). In the aquatic environs, marine species react in different ways depending on the concentration of BPA. Table 1.1 lists the effects of BPA doses on different aquatic species.

Table 1.1 Toxicity of BPA on aquatic species

Aquatic species	**BPA Dose**	**Mechanism of Action**	**Ref.**
Frog (*Siluranatropicali*)	2.3 μg L^{-1}	Inhibition of metamorphosis	(Kashiwagi, Utsumi, Kashiwagi, Ohta, Sugihara, Hanada, & Kitamura, 2008)
Swordtail fish	7 μgL^{-1}	Reduced tail length	(Kwak, Bae, Lee, Lee, Lee, Kang, Chae, Sung, Shin, Kim, Mar, Sheen, & Cho, 2001)
Zebrafish	0.2 - 2.2 μg L^{-1}	Reduced sperm	(J. Chen, Saili, Liu, Li, Zhao, Jia, Bai, Tanguay, Dong, & Huang, 2017)
Freshwater Ramshorn snail	>1.0 μg L^{-1}	Super feminization, oviduct rupture and mortality	(Flint, Markle, Thompson, & Wallace, 2012)
Zebrafish embryos	22 mg L^{-1} - 6.8 mg L^{-1}	DNA methylation	(Olsvik, Whatmore, Penglase, Skjærven, D'Auriac, & Ellingsen, 2019)
Seahorse (Hippocampus erectus)	10, 100, and 1000 μg L^{-1}	Ovarian failure, apoptosis of follicular cells, and reproductive dysfunction	(Y. Liu, Wu, Qin, Chen, Wang, & Lin, 2021)
Catfish	- 0.05μg L^{-1} - 2.76μg L^{-1}	- Elevated serum - Cholesterol level	(Makinwa & Uadia, 2017)
Nile tilapia	0.0, 1.64, or 3.28 μg L^{-1}	Liver and kidney dysfunction	(Abdel-Tawwab & Hamed, 2018)
Gobiocypris rarus (Fish)	15 μg L^{-1}	Disrupted the integrity of Sertoli cell barrier	(S. Tao, Wang, Zhu, Liu, Wu, Yuan, Zhang, & Wang, 2019)
Oyster	2 mg L^{-1}	Affects gonadal development	(L. Luo, Zhang, Kong, Huang, & Ke, 2017)

1.2.3(b)(ii) Toxicity of BPA to human

The BPA is believed to cause endocrine disruption in humans by interacting with a variety of biological receptors, including the androgen receptor (AR), estrogen receptor (ER), and thyroid hormone receptor (THR). As a result of these disrupting effects, there are health risks to the reproductive system, nervous system, metabolic function, immune function, and offspring's growth and development (Ma, Liu, Wu, Yuan, Wang, Du, Wang, Marwa, Petlulu, Chen, & Zhang, 2019). The presence of BPA in human has been detected in urine, plasma, saliva, semen, breast milk, serum, and adipose tissues. Low concentration of BPA was found to have a detrimental effect in humans mostly concerning human development, metabolic activities, reproduction and inflammatory pathways (Usman & Ahmad, 2016; Valentino, D'Esposito, Ariemma, Cimmino, Beguinot, & Formisano, 2016)

Humans are being subjected to BPA levels in different amounts (0.27–10.6 ng/ml) either directly or indirectly. The global BPA intake from dermal exposure, dust inhalation, and ingestion was estimated at 30.76 ng/kg per body weight per day. In humans, the most common route of BPA exposure is through ingestion, which accounts for about 90% of BPA exposures (Ohore & Songhe, 2019). The consequences are numerous, with hormonal abnormalities being the most commonly reported. BPA has been linked to the onset of sexual characteristics and obesity at a young age (Supornsilchai, Jantarat, Nosoognoen, Pornkunwilai, Wacharasindhu, & Soder, 2016). Exposure to high BPA serum concentrations (1.53–2.22 $\mu g\ L^{-1}$) in males, particularly during the stage of development, male foetuses were feminised as a result, testicular and epididymal atrophy, sperm parameter changes, and testosterone levels reduction (Castellini, Totaro, Parisi, D'Andrea, Lucente, Cordeschi, Francavilla, Francavilla, & Barbonetti, 2020; Karnam, Ghosh, Mondal, &

Mondal, 2015). According to an epidemiological report, men exposed to BPA have a higher risk of low sperm quality than men who are not exposed to BPA. Increased urinary BPA levels were related to reducing sperm concentration, total sperm count, sperm viability, and motility in particular (Cariati, D'Uonno, Borrillo, Iervolino, Galdiero, & Tomaiuolo, 2019). In females, high BPA serum concentrations (1.53–2.22 μg/L) cause changes in estradiol E2, causing hormonal imbalance and anomalies in metabolism such as menstrual irregularities, puberty in its early stages, increased endometriosis risk, Implant failure is more common., and ineffective gonadotropin fertility treatment (Ohore & Songhe, 2019).

Breast milk is an essential source of nutrition for babies. For several years, the World Health Organization (WHO) has advocated for exclusive breastfeeding for the first six months of a baby's life as the best way to provide nutrition (Nasser, Omer, Al-Lenqawi, Al-Awwa, Khan, El-Heneidy, Kurdi, & Al-Jayyousi, 2018). BPA can accumulate in the mammary glands' fat and be ingested by babies during breastfeeding because of its lipophilic properties. For exclusively breastfed infants (0–6 months), the mean amount of BPA was calculated to be 0.3 μg/kg body weight per day, which decreased after the introduction of solid foods (Ma et al., 2019). The BPA can get through the blood-brain barrier (BBB), causing deformity in the central and peripheral nervous system, thereby causing abnormalities in humans (Guida, Troisi, Ciccone, Granozio, Cosimato, Sardo, Ferrara, Guida, Nappi, Zullo, & Di Carlo, 2015).

Drinking water and having access to it is a very important issue for the human population. Water gets contaminated before getting to its consumers through different ways; the source, purification process, leakages, and distribution system (Shaikh, Al Suhaimi, Hanafiah, Ashraf, & Harun, 2018). Different materials are used

in lining the distribution system for water which could further contaminate water through corrosion or leaching, before getting to the consumer. Organic polymers such as epoxy resins and polyurethane are used in lining the pipes to prevent corrosion. Epoxy resins contain BPA and epichlorhydrin; these two components react to form different polymers that leach into drinking water (Rajasärkkä, Pernica, Kuta, Lašňák, Šimek, & Bláha, 2016).

1.2.4 Advanced Oxidation Processes for BPA Removal

Since BPA is highly soluble in water (300 mg L^{-1} at 25 °C), it has been found in natural water and wastewater at concentrations ranging from 1.3 to 370 mg L^{-1}, inland fill leachates as high as 17 mg L^{-1}, and sewage sludges, sediment, and biosolids as high as 95 mg kg^{-1} (Jhones dos Santos, Sirés, & Brillas, 2021). It is then essential to build technologies to remove BPA in aqueous effluents in order to prevent its harmful effects.

Physical and chemical technologies for pretreatment and treatment of BPA removal have recently been offered. Adsorption, membrane filtration, and a variety of other useful methods for BPA oxidation are among the choices currently available in the removal process. While it is still debatable if these technologies are cost-effective for full-scale plants, their effectiveness is high (Zielinska, Wojnowska-Baryla, & Cydzik-Kwiatkowska, 2018). Significant attempts have been made in recent years to improve advanced treatment to allow for the effective treatment of wastewater to meet strict discharge quality requirements (X. Tian, Song, Shen, Zhou, Wang, Jin, Han, & Liu, 2020). Therefore, advanced oxidation processes (AOPs) such as photocatalysis, will oxidize BPA since various researchers have also looked into it (Kang, Kim, Kim, & Zoh, 2020).

Advanced oxidation processes (AOPs) are water and wastewater treatment methods that use in-situ generated hydroxyl to degrade organic contaminants in the aqueous medium. Because of the superior oxidation capacity of the hydroxyl radical high redox potential ($E°(^{\bullet}OH/H_2O)$= 2.8 V), hydroxyl radical-based AOPs are the most popular and commonly accepted (Kang et al., 2020); thus AOPs have been commonly used for the degradation of recalcitrant organic pollutants. Hydroxyl radicals are the most common reactive species and a non-selective strong oxidant that is produced in traditional AOPs. They are crucial in the decomposition of organic pollutants that are resistant to degradation. Other reactive species, such as superoxide radicals, can be formed in AOPs in addition to hydroxyl radicals (J. Wang & Wang, 2018). Once generated, hydroxyl radicals can attack organic chemicals through electron transfer, hydrogen abstraction, and radical combination (Mayyahi & Al-asadi, 2018).

Some reactive species, such as singlet oxygen and superoxide radicals, have a lower redox potential than hydroxyl radicals, but they can still degrade certain stubborn organic pollutants (Cai, Li, Xie, Huang, Zeng, Zhang, Liu, Lv, & Liu, 2019). Since reactive species are in charge of degrading organic pollutants in AOPs, understanding the formation, detection, and reaction mechanism of reactive species in various AOPs is critical for understanding the concepts of AOPs and the degradation mechanism of recalcitrant organic contaminants (J. Wang & Wang, 2020). One of the possible classifications for AOPs is dependent on the source of oxidizing species generation, or the process for producing hydroxyl radicals. These are Fenton oxidation, photocatalysis oxidation, electrochemical oxidation, ozonation, gamma-ray/electron beam emission, persulfate-based oxidation, wet air oxidation,