UNIVERSITY OF CAPE COAST

PHOTOCONVERSION OF ENDOCRINE DISRUPTORS (PARABENS) USING ZINC OXIDE PHOTOCATALYST

SETH DONKOR

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BY

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Thesis submitted to the Department of Chemistry of the School of Physical Sciences, College of Agricultural and Natural Sciences, University of Cape Coast, in partial fulfilment of the requirements for the award of Master of Philosophy degree in Chemistry

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DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original research and that no part of it has been presented for another degree in this university or elsewhere.

Candidate's Signature ………..………………….   Date ………………

Name: Seth Donkor

Supervisor's Declaration

I hereby declare that the preparation and presentation of this thesis were supervised in accordance with guidelines on supervision of thesis laid down by the University of Cape Coast.

Supervisor's Signature …………………   Date………………

Name: Prof. Ruphino Zugle

ABSTRACT

Parabens are widely used as preservatives in drugs, cosmetic products, and foodstuffs. They are found in water bodies, food stuffs, cosmetics, pharmaceutical and personal care products. These parabens cause breast cancer and reproductive issues due to their absorption through the skin. Safety concerns have recently increased due to their potential health risks associated with exposure to these parabens. The purpose of this study is to photoconvert ethylparaben, a member of the paraben's family, and a potential endocrine disruptor into less toxic substances using cost effective and efficient methods involving light. Photocatalytic degradation experiments were carried out in the sunlight and UV light irradiation under magnetic stirring conditions. HPLC analysis was done and it was found out that the ethylparaben used was pure. UV-Visible absorption spectra analysis was done to monitor the degradation pattern and the maximum absorption wavelength was =256 nm for different concentrations. Kinetic study conducted gave the apparent rate constant to be 0.0041014 molL^{-1}min^{-1}, the absorption coefficient was 0.56874 mol^{-1} and $R^2 = 0.9959$ using the Langmuir–Hinshelwood (L–H) kinetic model. The photocatalytic reaction obeys the first order kinetics as R^2 was greater than 0.96. The degradation % of the Sunlight/ZnO was 63.16 % and that of the UV-Vis/ZnO was 82.2 % for a concentration of 0.0361 mM. The degradation of ethylparaben was less efficient in acidic medium and highly efficient in basic medium. At pH 10.4 (basic), the degradation percentage was 73.9 % and at pH 3.3 (acidic), the degradation percentage was 4.87%. The natural solution pH was 6.7, gave a degradation % of 63.16%. GC-MS analysis was done and some of the products and their mass to charge ratio (m/z) were obtained.

KEY WORDS

Endocrine disruptors

Ethylparaben

Gas Chromatography-Mass Spectroscopy

Photoconversion / Photodegradation

UV-Visible Spectrophotometry

Zinc Oxide Photocatalyst

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DEDICATION

To my uncle, Rev. Dr. John Poku

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LIST OF CONSTANTS AND SYMBOLS

m	Meter
mm	Millimeter
mL	Milliliter
mM	Millimolar
Mins	Minutes
mg	Milligram
R^2	Correlation Coefficient
nm	Nanometer

LIST OF ACRONYMS

EDCs	Endocrine Disruption Chemicals
EP	Ethylparaben
GC-MS	Gas Chromatography-Mass Spectrometry.
UV-Vis	Ultra-Violet Visible
SAICM	Strategic Approach to International Chemical Management
HPLC	High Performance Liquid Chromatography
US	United States
WHO	World Health Organization
UNEP	United Nations Environmental Programme
NOEL	No Observed Effect Levels
NOAEL	No Observed Adverse Effect Levels
MP	Methylparaben
PP	Propylparaben
ER	Estrogenic Receptor
LOELs	Lowest Observed Effect Levels
DES	Diethyl Stilbestoral
HBMOS	Hygiene Based Margin Of Safety
EACs	Endocrine Active Chemicals
IBP	Isobutylparaben
HBA	Hydroxybenzoic Acid
BA	Benzoic Acid
BCHE	Bicyclo Heptan-2-ol, Exo
DCH	Dihydrocatechol
DEHP	Di (EthylHexyl) Phthalate

DEP	Di Ethyl Phthalate
VB	Valence Band
CB	Conduction Band
eVB	Electron at valence band
eCB	Electron at conduction band
BPA	Bisphenol A
MB	Methyl blue
ZPC	Point Charge
IR	Infrared
GC	Gas Chromatography
MS	Mass spectrometry
M/Z	Mass to charge ratio
EI	Electron Impact
AOP	Advanced Oxidation Process
SPE	Solid Phase Extraction
USA	United States of America
L-H	Langmuir- Hinshelwood
NIST	National Institute of Standard and Technology
EEB	Epoxy Ethyl Benzene
BAC	Benzeneacetaldehyde

CHAPTER ONE

INTRODUCTION

Background to the Study

Parabens are commonly used as antimicrobial preservatives in cosmetics, pharmaceuticals, food and beverages processing. Widespread human exposure to parabens by dermal penetration or by ingestion has been recently documented. Some parabens have demonstrated adverse effects on male reproductive system in animal studies. However, according to Canosa et al. (2006), human epidemiologic studies are lacking. Since Harvey & Darbre (2004) suggested, that the exposure of the male foetus to environmental estrogens could be the cause of subsequent reproductive and developmental effects in men and also breast cancer in women. There has been little definitive research to provide conclusions to their hypothesis. This issue has been challenged by reviewing several researches on scientific databases. The basis is that parabens are used as preservatives in food, drugs, cosmetics, pharmaceutical and personal care products (PPCPs). It is therefore tempting to think that these parabens or preservatives are safe to use. Several health risks have been reported with the use of these parabens as preservatives. (Neidig & Burrell, 1944; Harvey & Darbre, 2004; Haman, Dauchy, Rosin, & Munoz, 2015; & Frontitis et. al, 2016). Government and advocacy groups such as the Centre for Science, seeks to ban all these products because of limited evidence about their safety in the public interest.

There is the need to remove pollutants from the environment because they may have negative impacts pollutants both on ecosystem and on humans such as toxicity, carcinogenic and mutagenic properties (Busca et al., 2008).

Pollutants may cause imbalances in the ecosystem and may cause algal infestation in waters which leads to production of cyanobacterial toxins, taste and odour compounds (Juttner & Watson, 2007; Bamuza-Pemu, 2014). Pollutants may endanger the aquatic ecosystem and human health with possible health disorders such as kidney, reproductive system, liver, brain and central nervous system (CNS) damage and ulceration of skin and mucous membranes (Hung et al., 2012). Some methods or processes of removing pollutants from the environment involve adsorption processes, chemical processes, physical processes, biological processes, advance oxidation processes such as photolytic, photochemical, and photocatalysis. This study seeks to remove ethyl paraben from aqueous solution by degrading it with a photo –catalyst.

The endocrine system is a complex system, comprising glands that produce hormones in the body. These glands create hormones, which promote growth, metabolism, and how humans develop and function sexually. Hormones are natural chemicals produced in cells within endocrine glands, which are located throughout the body. The endocrine system reins many of the bodies' processes, from conception to old age. The endocrine system particularly regulates the development of the brain and nervous system (Raven, Losos, & Johnson , 2005).

However, certain environmental chemicals affect the proper function of these hormones. They are generally referred to us Endocrine Disruptive Chemicals (EDCs).

Scientific knowledge about Endocrine Disruptive Chemicals (EDCs) has been increasing rapidly in recent years. They are defined by the Endocrine Society as: “an exogenous (non-natural) chemical, or mixture of chemicals, that interferes with any aspect of hormone action.” Endocrine-disruptive chemicals (EDCs) are either man-made or naturally occurring chemicals that interfere with the body’s ability to regulate its growth, development, metabolism and other functions.(Gore, Crews, Doan, & Merrill, 2014).

EDCs are sometimes referred to as hormone mimics. There are hundreds of EDCs in the environment, in food, and in consumer products. They include components of plastics and plasticizers including bisphenol A, phthalates, dioxins, pesticides, heavy metals, industrial chemicals and fuels, preservatives including parabens, in cosmetics and pharmaceuticals and fragrances in cosmetics (Diamanti-Kandarakis et al., 2009).

Hormones work in the body in very tiny amounts, so even small exposures to EDCs can affect development and function of hormones. Unlike most other toxic substances, low doses of EDCs may be more dangerous than higher doses. Higher exposures may overwhelm the endocrine system and cause less response to the chemical. This is a concern because safety testing of chemicals assumes that low doses are not harmful if higher doses do not show effects. Most EDCs have not been thoroughly tested for health effects at very low exposures.

Hormones coordinate the development of every individual from a single fertilized cell to the many millions of specialized cells that make up the blood, bones, brain, and other tissues. As a whole, the endocrine system is one of the body’s major interfaces with the environment, allowing for development, adaptation and maintenance of bodily processes and health. In other words, hormones play key roles in determining the quality of life, and many hormones are absolutely essential for survival.

The role of the endocrine system is critical in so many important biological and physiological functions, and so any impairments in any part of the endocrine system can lead to diseases or even death. By interfering with the body’s endocrine systems, EDC exposure can therefore perturb many functions. EDCs competes with natural hormones such as binding to cells and causing changes that natural hormones would otherwise initiate. As a result, the body responds as though the hormones are sending signals for cells to grow, die, turn genes on or off, reproduce and so on. This can cause particularly devastating and lifelong health problems if the wrong signals are received by cells, starting at conception and going through adolescence when organs and tissues are developing. As a result, fetuses and children are at high risk of harm from exposures to EDCs, though adults can also be affected either from exposures early in life or from cumulative exposures over a lifetime. EDCs can contribute to a wide range of diseases and disabilities including obesity, diabetes, cancer, heart disease, reproductive health problems and neurodevelopmental and neurodegenerative disorders.

According to Diamanti-Kandarakis et al., (2009), EDCs are a global and universal problem. Exposure occurs at home, in the office, on the farm, in the air, the food, and the water. In addition to the known EDCs, there are countless suspected EDCs or chemicals that have never been tested.

Exposures to known EDCs are relatively high in contaminated environments in which industrial chemicals leach into soil and water. EDCs are finally taken up by microorganisms, algae, and plants; and it goes through the food chain. Animals at the top of the food chain, including humans, have the highest concentrations of such environmental chemicals in their tissues. The prevailing dogma applied to chemical risk assessment is that "the dose makes the poison." These testing protocols are based on the idea that there is always a simple, linear relationship between dose and toxicity, with higher doses being more toxic, and lower doses less toxic. This strategy is used to establish a dose below which a chemical is considered "safe," and experiments are conducted to determine that threshold for safety. Traditional testing involves chemicals being tested one at a time on adult animals, and are presumed safe if not result in cancer or death (Gore, Crews, Doan, & Merrill, 2014)

Like natural hormones, EDCs exist in the body in combination due to prolonged or continual environmental exposures, and also EDCs have effects at extremely low doses (typically in the part-per-trillion to part-per-billion range) to regulate bodily functions. EDCs are described as contaminants of emergent concern and so parabens have been classified as emerging environmental pollutant by the US Environmental Protection Agency.

Parabens are also designated as esters of p-hydroxybenzoic acid. The most commonly found parabens are methyl-, ethyl-, propyl- and butylparaben. Parabens are extensively used as antimicrobial preservatives in food, cosmetics and pharmaceutical products due to their broad spectrum of activity, inertness and low cost. Parabens are ideal as preservative for several reasons. Parabens are stable and effective over an extensive pH range, sufficiently soluble in water to produce an effective concentration in aqueous phase, have no perceptible odor or taste, no induction of discoloration and stability over broad pH and heat ranges (Neidig, & Burrell, 1944)

Man is daily exposed to these substances from a large array of consumer products, and they are considered to be safe. Several toxicity studies of these compounds have been carried out in animals and in man. No marked toxicity was found as they are rapidly absorbed, metabolized and excreted from the body (Neidig & Burrell, 1944). However, recent reports indicated that parabens could act as endocrine modulators or disruptors with a moderate estrogenic activity which could lead to possible undesirable effects on human health. Moreover, parabens-containing antiperspirants have been suspected of increasing breast cancer incidence.

This work involved the degradation of paraben (ethyl paraben) under solar light and ultra violet light irradiation with Zinc Oxide as photo-catalyst. The degradation process was monitored by using UV-Vis Spectrophotometry for the absorption spectrum of the paraben. The degraded products were determined by Gas Chromatography Mass Spectrometry (GC-MS).

Statement of the Problem

Significant advances in research into endocrine-disruptive chemicals (EDCs) and their health effects have elevated concerns in recent years among a number of international scientific and health organizations. The Endocrine Society was the first to take a public stance on the state of endocrine-disrupting chemical (EDC) science with the 2009 publication of its Scientific Statement on endocrine-disruptive chemicals (EDCs) (Diamanti-Kandarakis et al., 2009). The Endocrine society asserted that there was evidence to conclude that endocrine-disruptive chemicals (EDCs) pose a public health risk.

In recent years and given the rapid growth of analytical techniques, the scientific community has shown a special interest in “contaminants of emerging concern” which include; endocrine disruptive compounds (EDCs), pharmaceuticals and personal care products (PPCPs) (Frontitis et al., 2016). According to Frontitis et al. (2016), parabens are considered as parts of the contaminants of emerging concerns. They are esters of 4-hydroxybenzoic acid with an alkyl or benzyl group and have been used as preservatives in foodstuff, cosmetics and pharmaceuticals and personal care products (PPCPs) for a century (Frontitis et al, 2016).

Parabens just like most pollutants are mostly removed from the environment by adsorption processes. This method is quite deficient in the sense that it leads to the production of secondary pollution involving the absorbent and the pollutant. On the other hand, parabens can be degraded relatively easily in conventional wastewater treatment plants by chemical means. However, they are continuously still released due to their high usage and, therefore, frequently met in the aquatic environment (including freshwater, marine water and sediments) (Frontitis et al, 2016).

Current Research efforts have been focused on photodegradation of pollutants particularly organic pollutants. The method is cost effective and efficient involving light. Various photosensitizers have been applied in the degradation of a wide range of organic pollutants using advance oxidation processes. In particular, inorganic photosensitizers have been applied with considerable success in the degradation of some organic compounds. However, few organic pollutants such as dichlorodiphenyltrichloroethane (DDT) and its derivatives dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane

(DDD) remain quite resistant to degradation using inorganic photosensitizers (Gusain et al., 2019; Melchionna et al., 2016; Zugle & Nyokong, 2012).

This current study sought to investigate the possibility of using an inorganic photosensitizer, zinc oxide to degrade ethylparaben in the presence of solar and ultra violet light. It is also intended to identify the degraded products.

Purpose of the Study

The purpose of this study is to convert ethylparaben, a potential endocrine disrupting chemical (EDC) into less toxic substances using cost effective and efficient methods involving light.

Objectives

1 To investigate the feasibility of degrading ethyl paraben using zinc oxide photo-catalyst in the presence of light (solar light and ultra violet light)

2 To examine the effect of operation parameters such as initial concentration and solution pH of sample solution on the degradation efficiency.

3 To study the kinetics of the degradation process based on the Langmuir-Hinshelwood (L-H) first-order kinetic model.

4 To identify the degraded products of ethyl paraben using gas chromatography mass spectrometry (GC-MS).

Significance of the Study

Parabens are esters of p-hydroxybenzoic acid. Parabens have broad antimicrobial spectrum with good stability and non-volatility. Parabens have been extensively used as preservatives for cosmetics in restricted concentration levels. In 1990s, parabens were deemed xenoestrogens (Haman, Dauchy, Rosin, & Munoz, 2015) while they have been linked to breast cancer and reproductive issues due to their absorption through the skin (Lin, Ferronato, Deng, & Chovelon, 2011). In view of the above, parabens have been classified as emerging environmental pollutants by the US Environmental Protection Agency. (Harvey & Darbre, 2004; Naidu et al., 2016).

Several health risks have been reported with the use of these parabens as preservatives. Government and advocacy groups such as the center for science in the public interest seeks to ban all these products because of limited evidence about their safety. This work therefore sought to find a cost effective and appropriate method to degrade ethyl paraben as a representative paraben to less harmful products.

Delimitations

The zinc oxide was able to degrade the ethyl paraben in the sun and in the ultra violet light. The ultraviolet visible spectrophotometer was able to monitor the absorption spectra of the ethyl paraben.

Limitations

It was difficult to maintain a stable and a reliable light source and there was no control over the intensity of the sun light source.

Definition of Terms

Endocrine disruptive chemicals or endocrine disruptors are defined by the Endocrine Society as: “an exogenous (non-natural) chemical, or mixture of chemicals, that interferes with any aspect of hormone action.” Endocrine-disruptive chemicals (EDCs) are either man-made or naturally occurring chemicals that interfere with the body's ability to regulate its growth, development, metabolism and other functions. (Frontitis et al., 2016; Gore, Crews, Doan, & Merrill, 2014).

Photocatalysis is a reaction which uses light to activate the substance which increases the rate of a reaction without being involved itself.

Photocatalyst is the substance which increase the rate of a chemical reaction using light irradiation.

Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed in the end. This substance is known as a catalyst which increases the rate of a reaction by reducing the activation energy (Sakthivel et al, 2003; Bamuza-Pemu, 2014).

Organization of the Study

This thesis consists of the following chapters:

Chapter 1 presents an introduction to the study: it explains the main aims and objectives, the significance of the study, highlighting the importance of the research. It also gives the organizational structure of the thesis.

Chapter 2 provides a detailed report of literature relevant to the present research, with some technical information on the background of photocatalysis and some examples of application. It also provides advances in research and the status of the implementation of technology.

Chapter 3 presents technical details of the laboratory reaction setup, the materials used, analytical equipment, and reaction conditions, as well as experimental methods and analytical methods used during the course of the study.

Chapter 4 presents the results and discusses the outcome of the studies, such as photocatalytic degradation of ethyl paraben and gas chromatographic analysis of the degraded samples of ethyl paraben. It gives degradative pathway analysis and some kinetic analysis of ethyl paraben degradation.

Chapter 5 gives a summary of the key findings of the research and conclusions drawn from the findings, and also some few recommendations for further studies.

A listing of all citing reference materials is included at the end of the report.

Chapter Summary

In this chapter, a general overview of the study has been described. This chapter gives the general background to the issues concerning ethyl paraben. The purpose behind this research, the significance of the study, the limitations and delimitations with this study has also been clearly stated in the chapter.

CHAPTER TWO

LITERATURE REVIEW

Introduction

This chapter presents the literature of the study of this work. It includes the following, endocrine disruptors or endocrine disruptive chemicals, structure and general properties of parabens, exposure routes of parabens to human, effect of exposure to human health, effect of exposure on animal health. This chapter also discusses, advanced oxidation process (AOP), basic principles of heterogeneous photocatalysis, zinc oxide (ZnO) as a photocalyst, operating parameters of photocatalytic processes and kinetic studies such as Langmuir-Hinshelwood (L-H) first order kinetic model have been described.

Endocrine Disrupters or Endocrine Disrupting Chemicals

Significant advances in research into endocrine-disrupting chemicals (EDCs) and their health effects have elevated concerns in recent years about these chemicals among a number of international scientific and health organizations. The Endocrine Society was the first to take a public stance on the state of the endocrine disruption chemical (EDC) science with the 2009 publication of its Scientific Statement on endocrine disruption chemicals (EDCs) (Endocrine et al., 2009). At that time, the Society's membership asserted that there was sufficient evidence to conclude that endocrine disruption chemicals (EDCs) pose a public health risk. The Society's 2012 Statement of Principles on endocrine disruption chemicals (EDCs) and Public Health Protection, letters to the European Commission (March 2013), and to the Secretariat of the Strategic Approach to International Chemicals Management (SAICM, June 2013) encouraging science-based action on endocrine disruption chemicals (EDCs) further advanced awareness and understanding of endocrine disruption chemicals (EDCs).

Since the Endocrine Society's inaugural statement in 2009, the number of medical societies voicing concern over endocrine disruption chemicals (EDCs) globally has grown in parallel with the body of literature revealing negative health effects of chemicals that interfere with hormone action. In the United States, the American Medical Association, the largest organization of US medical professionals, adopted a policy in November 2009 (Regulation of Endocrine-Disrupting Chemicals) calling for improved regulatory oversight of endocrine disruption chemicals (EDCs) based on comprehensive data covering both low level and high-level exposures. In the same month, the American Public Health Association called for a precautionary approach to reducing American exposure to endocrine-disrupting chemicals. The American Chemical Society issued a 2012-2015 policy statement on testing for endocrine disruption, recommending expanded education and research, updated testing protocols, and the development of safer alternatives to endocrine disruption chemicals (EDCs).

A number of international and global health organizations also have taken up the call for improved endocrine disruption chemical (EDC) policies. In February 2013, the World Health Organization (WHO) and United Nations Environment Programme (UNEP) launched their joint 2012 report on the state of the science of endocrine disruption chemicals (EDCs) (World Health Organization, 2012). The report outlines the current understanding of endocrine disruption chemicals (EDCs) and their effects on human health. It also recommends improved testing and reduced exposures to endocrine disruption chemicals (EDCs). Also, in 2013, the Collegium Ramazzini, an international academy of renowned occupational and environmental health experts, issued a statement on endocrine-disrupting chemicals (EDCs) in the European Union calling for the expansion of the scope of the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) legislation and more inclusive assessment of the totality of scientific evidence in regulatory decision-making.

Again in 2013, a large group of independent scientists issued the Berlaymont Declaration expressing concern over endocrine disruption chemicals (EDCs) and calling on the European Commission to improve its regulatory regime governing these chemicals. The Declaration has been signed by nearly 100 scientists from 19 countries, including Chile, China, Czech Republic, Mexico, South Africa, and several European Union member states.

The above examples are not an exhaustive list and do not include statements by large medical associations that address endocrine disruption chemicals (EDCs) in the context of the larger universe of toxic chemicals. As the global scientific and medical community continues to express concern over endocrine disruption chemicals (EDCs) and their harmful effects on human health, public policies should be grounded in the latest available scientific evidence (Bellingham, & Sharpe, 2013).

People and animals come into contact with endocrine disruption chemicals (EDCs) by a variety of routes, including consumption of food and water, through the skin, by inhalation, and by transfer from mother to fetus across the placenta or mother to infant lactation if a woman has endocrine disruption chemicals (EDCs) in her body.

To understand how endocrine disruption chemicals (EDCs), perturb the endocrine system, it is necessary to have some basic understanding of how natural hormones work in the body. The chemical composition and three-dimensional shape of each endocrine hormone is unique. Every hormone in turn has a corresponding receptor (or receptors) localized on the target cells. A receptor's shape is complementary to its hormone, similar to the way in which one key (hormone) is specific to a lock (receptor). The response of a given tissue or organ to a hormone is determined by the presence of receptors on target cells and receptor activation by hormone binding. The ability of a hormone to activate its receptor depends upon several factors, including how much hormone is synthesized and released by the endocrine gland, how it is transported through the circulation, how much reaches the target organ, and how potently and for how long the hormone can activate its receptor.

Endocrine disruption chemicals (EDCs) often disrupt endocrine systems by mimicking or blocking a natural hormone. In the case of hormone mimics, an endocrine disruption chemical (EDC) can "trick" that hormone's receptor into thinking that the endocrine disruption chemical (EDC) is the hormone, and this can inappropriately activate the receptor and trigger processes normally activated only by a natural hormone.

In the case of hormone blockers, an endocrine disruption chemical (EDC) can bind to a hormone's receptor, but in this case, the receptor is blocked and cannot be activated, even if the natural hormone is present.

The best-known example is endocrine disruption of estrogenic hormones, which act upon the body's estrogen receptors (ERs). In both males and females, estrogen receptors (ERs) are present in many cells in the brain, in bone, in vascular tissues, and in reproductive tissues. While estrogens are best understood for their roles in female and male reproduction systems, and are also involved in neurobiological functions, bone development and maintenance, cardiovascular functions, and many other functions. Natural estrogens exert these actions, after being released from the gonad (ovary-female or testis-male), by binding to estrogen receptors (ERs) in the target tissues.

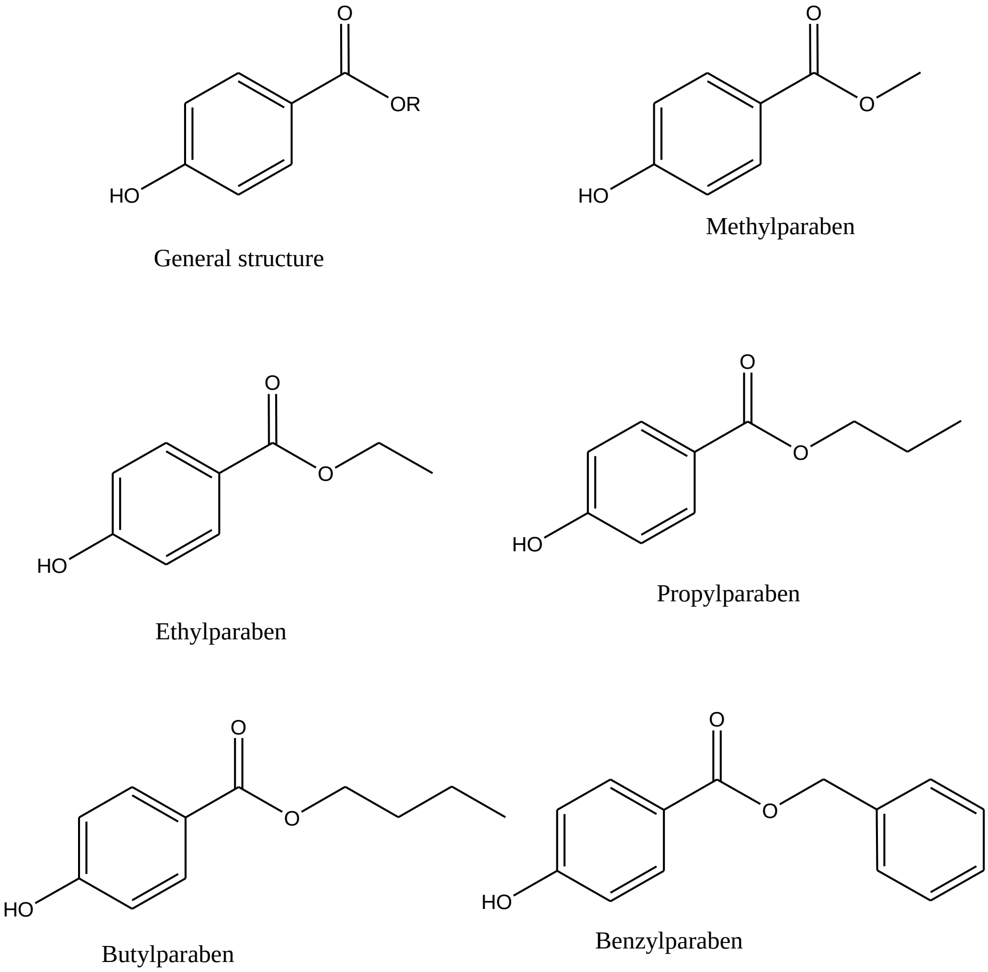
Estrogen receptors are not the only receptors that are attacked in this manner by endocrine disruption chemicals (EDCs), although they are the best studied. Receptors for androgens (testosterone), progesterone, thyroid hormones, and many others, are interfered in their functioning by endocrine disruption chemicals (EDCs). In addition, because endocrine disruption chemicals (EDCs) are not natural hormones, a single endocrine disruption chemical (EDC) may have the ability to affect multiple hormonal signaling pathways. Thus, it is quite likely that one type of endocrine disruption chemical (EDC) can disrupt two, three, or more endocrine functions, with widespread consequences on the biological processes that are controlled by those vulnerable endocrine glands.

Structure and Health Effect of Parabens

Paraben is a generic name for a wide range of compounds. Paraben often exert adverse health effect on animals and humans.

Structure of Parabens

Figure 1 shows the general structure and structures of some derivatives of paraben. Parabens are designated as esters of p-hydroxybenzoic acid. The most commonly found parabens are methyl-, ethyl-, propyl- and butylparaben.



General structure

Methylparaben

Ethylparaben

Propylparaben

Butylparaben

Benzylparaben

Figure 1: Structures of Parabens and its Derivatives

Propylparaben is a stable, non-volatile compound used as an antimicrobial preservative in foods, drugs and cosmetics for over 50 years. It is an ester of p-hydroxybenzoate. Propylparaben is readily absorbed through the gastrointestinal tract and dermis. It is hydrolyzed to p-hydroxybenzoic acid, and then conjugated. The conjugates are rapidly excreted in the urine. There is no evidence of accumulation. Acute toxicity studies in animals indicate that propyl paraben is relatively non-toxic by both oral and parenteral routes, although it is mildly irritating to the skin. Chronic administrations of, no-observed-effect levels (NOEL) as high as 1200–4000 mg/kg have been reported in rat and a no-observed-effect level (NOEL) of 5500 mg/kg is posited. Propylparaben is not carcinogenic, mutagenic or clastogenic. It is not cytogenic *in-vitro* in the absence of carboxyesterase inhibitors. The mechanism of hydrolyzing and conjugation of propylparaben may be linked to mitochondrial failure, dependent on induction of membrane permeability transition accompanied by the mitochondrial depolarization and depletion of cellular adenosine triphosphate (ATP) through uncoupling of oxidative (Soni, Carabin, & Burdock, 2005).

Methylparaben is a methyl ester of p-hydroxybenzoic acid. As well as Propylparaben, it is a stable, non-volatile compound used as an antimicrobial preservative in foods, drugs and cosmetics for over 50 years. Methylparaben is readily and completely absorbed through the skin and from the gastrointestinal tract. It is hydrolyzed to p-hydroxybenzoic acid which then form conjugate. Parabens are extensively used as antimicrobial preservatives in food, cosmetics and pharmaceutical products due to their broad spectrum of activity, inertness and low cost. Parabens also congregate several criteria for an ideal preservative: they are stable and effective over an extensive pH range, sufficiently soluble in water to produce an effective concentration in aqueous phase, have no perceptible odor or taste, no induction of discoloration and stability over broad pH and heat range (Harvey & Darbre, 2004). Parabens are lipophilic compounds with increasing octanol/water partition coefficients (expressed as log K_{ow}) as the carbon number of the alkyl chain of parabens increases. Antimicrobial activity of parabens increases with the length of alkyl grouping from methyl to n-butyl (Han, & Washington, 2005). Since microbial replication generally occurs in the water phase of oil/water bases, the amount of paraben dissolved in the water phase generally determines the preservative efficiency; for such reason, in order to increase the ability of the system to withstand microbial contamination, it is common to find combinations of two or more paraben homologues within a single product (Pozzo, & Pastori, 1996).

Several toxicity studies of these compounds have been carried out in animals and in man. No marked toxicity was found as they are rapidly absorbed, metabolized and excreted from the body (Soni, Carabin, & Burdock, 2005). However, recent reports indicated that parabens could act as endocrine modulators or disruptors with a moderate estrogenic activity which could lead to possible undesirable effects on human health. Moreover, parabens-containing antiperspirants have been suspected of increasing breast cancer incidence. The detection in small quantities of non-metabolized parabens in human breast tumors (Harvey & Darbre, 2004) may suggest that the substances could accumulate over time in tissues and induce toxic effects (Golden, Gandy, & Vollmer, 2005; Terasaka, Inoue, Tanji, & Kiyama,). The routes of exposure for parabens are ingestion, dermal absorption, and inhalation from contaminated air and dust.

Parabens are extensively metabolized. They are mainly hydrolyzed to 4- hydroxybenzoic acid in mammals, which is thereafter conjugated with sulfate, glucuronide or glycine prior to being excreted in urine (Tsukamoto, & Terada, 1964). Esterases are efficient in the hydrolysis of parabens to 4-hydroxybenzoic acid (Jewell et al., 2007). In man, parabens can also be excreted as glucuronides and sulfate conjugates (Soni, Carabin, & Burdock, 2005). The metabolic profile is strongly dependent on the exposure route. Indeed, paraben glucuronides have been used as urinary biomarkers of exposure in man, rather than 4-hydroxybenzoic acid, which is a nonspecific metabolite of all parabens (Ye, Bishop, Reidy, Needham, & Calafat, 2006).

Human exposure to Parabens

In humans, the metabolism of parabens may include the formation of conjugated species such as glucuronides and sulfates. The free species, non-conjugated forms are considered biologically active. Therefore, information on the concentration of these free species in blood or urine could be helpful for risk assessment. The conjugates could hydrolyze to their corresponding free forms during collection, handling, and storage of biological specimens.

Therefore, information on the temporal stability of the conjugates is of interest. In the study which was done by (Ye et al. 2009), the stability of the conjugates (glucuronides and sulphides) of four phenols; bisphenol A, benzophenone-3, triclosan, and 2,5-dichlorophenol (methylparaben and propylparaben). In 16 human serum samples for 30 days at above-freezing temperature storage conditions (4 °C, room temperature, and 37 °C) were investigated, it found that the percentage of the conjugated species of the four detected compounds (2.5-dichlorophenol, triclosan, and methyl and propyl parabens) in these serum specimens even when stored at 37 °C for at least 30 days did not vary significantly. These preliminary data suggest that the phenols' serum conjugates appear to be more stable than their corresponding urinary conjugates.

Recently, (Calafat et al. 2010) have assessed exposure to methyl, ethyl, propyl, and butyl parabens in a representative sample of persons above or of 6 years of age in the U.S. general population from the 2005-2006 National Health and Nutrition Examination Survey. The analysis of 2,548 urine samples by using online solid-phase extraction coupled to isotope dilution-high-performance liquid chromatography/tandem mass spectrometry. The study detected methylparaben (MP) and propylparaben (PP) in 99.1 % and 92.7 % of the samples, respectively. They also detected ethyl (42.4 %) and butyl (47 %) parabens less frequently and at median concentrations at least one order of magnitude lower than methylparaben (MP) (63.5 ng L^{-1}) and PP (8.7 ng L^{-1}). Least-square geometric mean (LSGM) concentrations of methylparaben (MP) were significantly higher among non-Hispanic blacks than among non-Hispanic whites except at older ages greater than or equal to 60 years. Adolescent and adult females had significantly higher least-square geometric mean (LSGM) concentrations of methylparaben (MP) and propylparaben (PP) than did adolescent and adult males. Females were more likely than males and non-Hispanic blacks were more likely than nonHispanic whites to have concentrations above the 95th percentile. The general U.S. population was exposed to several parabens during 2005-2006. Differences in the urinary concentrations of methylparaben (MP) and propylparaben (PP) by sex and race/ethnicity likely reflect the use of personal care products containing these compounds.

Darbre & Harvey, (2008) have reported that the presence of intact paraben esters (free parabens) in human body tissues has been confirmed by independent measurements in human urine, and the ability of parabens to penetrate human skin intact without breakdown by esterases and to be absorbed systemically has been demonstrated through studies not only in-vitro but also in-vivo using healthy human subjects.

Ye Xiaoyun et al., (2006), assessed human exposure to parabens by measuring in urine the conjugated or free species of parabens or their metabolites. They evaluated the use of free and conjugated parent parabens as new biomarkers for human exposure to these compounds. They detected methyl and n-propylparabens at the highest median concentrations (43.9 ng $(mL)^{-1}$ and 9.05 ng $(mL)^{-1}$, respectively) in nearly all (greater than 96 %) of the samples. The results, demonstrating the presence of urinary conjugates of parabens in humans, suggest that such conjugated parabens could be used as exposure biomarkers and finally this fact that conjugates appear to be the main urinary products of parabens and may be important for risk assessment.

Effect of Parabens on Human Health

Okubo et al., (2001) examined Estrogenic activities of the phenolic preservatives methylparaben, ethylparaben, propylparaben, butylparaben, isopropylparaben and isobutylparaben by assaying estrogen-receptor (ER)-dependent proliferation of cells. In conclusion, it was observed that parabens have estrogen-receptor (ER)-dependent estrogenic activities, and their effects on the intracellular signalling pathway might be different from that of 17 beta-estradiol.

Harvey and Darbre, (2004) have verified two hypotheses. The first was that human exposure and low potency of environmental estrogens might have reduced concerns and the second was that chemicals applied in body care cosmetics including moisturizers, creams, sprays or lotions applied to axilla, chest or breast areas affecting breast cancer incidence in women presents a different case scenario, not least in the consideration of the exposure issues. The hypothesis for a link between estrogenic ingredients in underarm and body care cosmetics and breast cancer was forwarded and reviewed in terms of: data on exposure to body care cosmetics and parabens. These include dermal absorption; paraben estrogenicity; the role of estrogen in breast cancer; detection of parabens in breast tumours; recent epidemiology studies of underarm cosmetics use and breast cancer; the toxicology database; the current regulatory status of parabens and regulatory toxicology data uncertainties.

It was called for further research to provide the first evidence that, environmental factors may be adversely affecting human health by endocrine disruption, because exposure to estrogenic chemicals through application of body care products, unlike diffuse environmental chemical exposures, should be amenable to evaluation, quantification and control. The exposure issues are clear and the exposed population is large, and these factors should provide the necessary impetus to investigate this potential issue of public health.

Pugazhendhi, Pope, and Darbre, (2005) addressed the question of whether p-hydroxybenzoic acid, the common metabolite of the alkyl esters of p-hydroxybenzoic acid (parabens), possesses estrogenic activity in human breast cancer cell lines. It was reported that p-hydroxybenzoic acid possessed oestrogenic activity in a panel of assays in human breast cancer cell lines. It was concluded that removal of the ester group from parabens did not abrogate its estrogenic activity and that p-hydroxybenzoic acid could give oestrogenic responses in human breast cancer cells.

Golden, Gandy and Vollmer, (2005) has revealed some test of parabens to varying degrees that individual paraben compounds have weakly estrogenic activity in some in vitro screening tests. In this research, a comparative approach involving both dose and potency was used to assess whether in uterus or adult exposure to parabens might be associated with adverse effects mediated via an estrogen-modulating mode of action. Based on these comparisons using worst-case assumptions pertaining to total daily exposures to parabens and dose/potency comparisons with both human and animal no-observed-effect levels (NOELs) and lowest-observed-effect levels (LOELs) for estrogen or diethylstilbestoral (DES), it is biologically implausible that parabens could increase the risk of any estrogen-mediated endpoint, including effects on the male reproductive tract or breast cancer.

Additional analysis based on the concept of a hygiene-based margin of safety (HBMOS), a comparative approach for assessing the estrogen activities of weakly active endocrine-active chemicals (EACs), demonstrates that worst-case daily exposure to parabens would present substantially less risk relative to exposure to naturally occurring endocrine-active chemicals (EACs) in the diet such as the phytoestrogen daidzein.

Darbre & Harvey, (2008) firstly measured the intact esters of p-hydroxybenzoic acid (parabens) in human breast cancer tissues, and suggested that their presence in the human body might originate from topical application of body care cosmetics. With the continued use of parabens in the majority of body care cosmetics, there is a need to carry out detailed evaluation of the potential for parabens, together with other estrogenic and genotoxic co-formulants of body care cosmetics, to increase female breast cancer incidence, to interfere with male reproductive functions and to influence development of malignant melanoma which has also recently been shown to be influenced by estrogenic stimulation.

Results presented by Darbre & Charles, (2010) and elsewhere demonstrate that in combination, chemicals can give estrogenic responses at lower concentrations, which suggests that in the breast, low doses of many compounds could sum to give a significant estrogenic stimulus. Updated incidence figures show a continued disproportionate incidence of breast cancer in Britain in the upper outer quadrant of the breast which is also the region to which multiple cosmetic chemicals are applied. It was concluded that if exposure to complex mixtures of estrogenic chemicals in consumer products is a factor in breast cancer development, then a strategy for breast cancer prevention could become possible.

Many environmental compounds with estrogenic activity are measurable in the human breast and estrogen is a known factor in breast cancer development. Exposure to environmental estrogens occurs through diet, household products and cosmetics, but concentrations of single compounds in breast tissue are generally lower than needed for assayable estrogenic responses (Darbre & Charles, 2010).

Effect of Parabens on Animal Health

Nakagawa and Moldéus, (1998) studied the relationship between the metabolism and the cytotoxic effects of the alkyl esters of p-hydroxybenzoic acid (parabens) in freshly isolated rathepatocytes. Incubation of hepatocytes with propyl-paraben (0.5 mM to 2.0 mM) elicited a concentration- and time-dependent cell death that was enhanced when enzymatic hydrolysis of propyl-paraben to p-hydroxybenzoic acid was inhibited by a carboxylesterase inhibitor, diazinon. In the comparative toxic effects based on cell viability, adenosine triphosphate (ATP) level, and rhodamine 123 retention, butyl and isobutyl-parabens were more toxic than propyl- and isopropyl-parabens, and ethyl- and methyl parabens and p-hydroxybenzoic acid were less toxic than propyl-paraben. These results indicate that

1 propylparaben-induced cytotoxicity mediated by the parent compound rather than by its metabolite p-hydroxybenzoic acid;

2 the toxicity is associated with adenosine triphosphate (ATP) depletion through impairment of mitochondrial function related to membrane potential and/or oxidative phosphorylation; and

3 the toxic potency of parabens to hepatocytes or mitochondria depends on the relative elongation of alkyl side-chains esterified to the carboxyl group of p-hydroxybenzoic acid.

The estrogenic activity of the parabens, methyl-, ethyl- and propyl p-hydroxybenzoate, widely used as antimicrobials in food, and butyl p-hydroxybenzoate, which is used in cosmetic products, and their shared main metabolite p-hydroxybenzoic acid was investigated by (Hossaini, Larsen & Larsen, 2000) in a mouse uterotrophic assay. P-Hydroxybenzoic acid and butyl p-hydroxybenzoate were also tested by the subcutaneous route in a rat uterotrophic assay. A significant increase in the uterus weight at day 4 was considered an estrogenic effect. In the mouse assay, none of the compounds tested produced any estrogenic response at dose levels up to 100 mg $(kg)^{-1}$ body weight per day, for ethyl p-hydroxybenzoate even at a dose level of 1000 mg $(kg)^{-1}$ body weight per day. In immature Wistar rats, subcutaneous administration of butyl p-hydroxybenzoate produced a weak estrogenic response at 600 mg $(kg)^{-1}$ body weight per day. From the last studies of (Kawaguchi et al. 2009b), isobutyl-paraben (IBP), a widely used preservative, exhibits estrogenic activity. The effects of exposure to isobutyl-paraben (IBP) during gestation and lactation via dam on social recognition behavior in ovariectomized offspring of Sprague-Dawley rats was analysed by (Kawaguchi et al. 2009a). Offspring were ovariectomized at 7 weeks of age, and were used in a social recognition test at 16 weeks of age. Each offspring was exposed to a novel ovariectomized rat four times and to a second novel rat in a fifth exposure. The isobutyl-paraben, IBP-exposed rats showed impaired social behaviour compared with controls. These data imply that early exposure to isobutyl-paraben (IBP) may have an effect on adult social behaviour, which is reported to be an autism spectrum disorders in humans. Canosa et al. (2006) investigated chemical transformations of four alkyl esters of phydroxybenzoic acid, parabens, in chlorinated water samples. Quantification limits of parent species and their possible transformation products were at the low ng L^{-1} level. By employing ultrapure water solutions, for the first type of sample, only two by-products were detected for each paraben.

It was corresponded to chlorination of the aromatic ring in one or two carbons situated in ortho positions to the hydroxyl group. Both species were also generated after the addition of parabens to chlorinated tap water. Moreover, three new transformation products were noticed for each parent compound and were identified as bromo- and bromochloro-parabens, formed due to the existence of traces of bromide in tap water sources. In addition, the presence of the di-chlorinated forms of methyl and propylparaben has been detected in raw sewage water samples.

Guadarrama et al., (2008) by using a mathematical model studied four parabens (methyl, n-butyl, benzyl and isobutylparaben) in order to evaluate their estrogenic activity through simplified models.

According to the calculated results, methylparaben is the paraben with higher estrogenic activity. The antibacterial activity of parabens was also explored considering the formation of potassium salts in the phenolic (OH) groups. From the obtained relative energy values, methylparaben was the most active preservative.

Nicotinamide is a hydrophilic molecule, freely soluble in water, used as cosmetic active ingredient for its moisturizing and depigmenting properties. Moreover, it has the ability to augment the solubility of poorly water-soluble molecules acting as a hydrotrope (Nicoli et al. 2008). The aim of this work was to study the effect of nicotinamide on the transdermal permeation of methyl, ethyl, propyl and butyl paraben. Parabens flux was measured *in-vitro* in the presence and absence of different amounts of nicotinamide. From solubility studies it was found that nicotinamide forms one or more complexes with methyl, propyl and butyl paraben in water, even though with low stability constants. The association of nicotinamide with parabens causes a significant reduction of the permeability coefficients of these preservatives through rabbit ear skin, caused by a reduction of the stratum corneum/vehicle partition coefficient. The effects of nicotinamide on parabens solubility, permeation and partitioning are potentially very interesting because nicotinamide can facilitate paraben dissolution in aqueous media (solutions, gels), reduce parabens partitioning in the oily phase thus guaranteeing an effective concentration in the water phase in emulsion and reduce transdermal penetration, thus reducing the toxicological risk.

Rudel and Perovich, (2009) summarized reported indoor and outdoor air concentrations, chemical use and sources, and toxicity data for some chemical classes. These products include polychlorinated biphenyls (PCBs), chlorinated and brominated flame retardants, pesticides; used to control insects, weeds and other pests in agriculture, lawn maintenance, and the built environment; phthalates, plastics, fragrances, and also alkylphenols and parabens; used to preserve products like lotions and sunscreens. The median indoor air concentration of methyl paraben was 2.9 ng m^{-3} and the maximum was 21 ng m^{-3}. Small on-site greywater treatment and reuse plants are susceptible to high short-term variation in flow and pollutant concentrations and the flow ranges from no-flow periods to high-flow periods.

Brausch and Rand, (2011) examined the acute and chronic toxicity data available for personal care products (PCPs) and highlights areas of concern. Personal care products (PCPs) including triclosan, paraben preservatives, and UV filters have evidence suggesting endocrine effects in aquatic organisms and thus need to be investigated and incorporated in definitive risk assessments. Finally, it was noticed that published literature for environmental concentrations is fairly substantial for some personal care products (PCPs) compounds (diethyltoluamide (DEET), fragrances) but relatively little is available for others (UV filters, preservatives). Additional research for surface water concentrations of personal care product (PCP) compounds and uptake into biota needs to be conducted in order to develop aquatic risk assessments for personal care products (PCPs) released in wastewater treatment plant (WWTP) effluent. There are also substantial data gaps in published literature addressing potential toxicity of personal care products (PCPs) to aquatic organisms.

Tay, Rahman and Abas, (2010) investigated the reaction kinetics and degradation mechanism of parabens (methylparaben, ethylparaben, propylparaben and butylparaben) during ozonation. Hydroxylation has been found to be the major reaction formation. Through the hydroxylation reaction, a variety of hydroxylated parabens were formed.

Advanced Oxidation Process (AOP)

Advanced Oxidation Process (AOP) has been widely applied as an alternative to conventional treatment methods in treating wastewater especially those from textile industry owing to its effectiveness in dye degradation and mineralization (Singh & Arora, 2011; Karthik, et al., 2014). Advance oxidation processes (AOPs) possesses advantages as reported by Daghrir, Drogui & Robert (2013) and Gupta et al., (2015). These include;

1 Generation of highly reactive species. They react with wide ranges of organic pollutants.

2 Possible complete mineralization of organic pollutants into benign substances.

3 No residual sludge disposal/ treatment required.

Among AOPs, heterogeneous photocatalysis has shown possibility in degrading dye compounds completely into harmless compounds such as carbon dioxide (CO_2), water (H_2O) and organic acids. (Priyanka & Srivastava, 2013; Ong et al., 2012; Akpan & Hameed, 2009).

Basic Principles of Heterogeneous Photocatalysis

Heterogeneous photocatalysis is a type of advance oxidation process (AOP) that has shown prominent ability in degrading wide ranges of organic pollutants in wastewater including azo dyes.

Heterogeneous photocatalysis utilizes a solid photocatalyst with reactions occurring at the surface of the catalyst. Solid semiconductors such as TiO_2 and ZnO are most employed as photocatalysts which are photoactive and can absorb photon energy (hv) to initiate a series of reactions which generate reactive free radicals to destruct target pollutants (Prinyanka & Srivastava, 2013; Lam et al.,

2012).

Semiconductors have distinct energy difference between their valence band (VB) and conduction band (CB), which is known as the band gap energy. For instance, titanium dioxide (TiO_2) and zinc oxide (ZnO) both have a band gap energy of 3.2 eV (Daghrir, Drogui &Robert, 2013). When photons of energy higher than the band gap energy is absorbed by the photocatalyst, localized electrons at the valence band (VB), (eVB) would be brought to excited state and promoted to the conduction band (CB) and the electrons are now referred to as photo-excited conduction band electrons, eCB. Simultaneously, positive holes (h^+) are formed at the valence band, VB. This was known as the formation of the electron/hole (e^-/h^+) pair as shown in Equation (1). Subsequently, localized electrons at the conduction band (eCB) and holes, h^+ migrate separately to the surface of the photocatalyst for subsequent redox reactions with the reactants. The basic mechanism of excitation of photocatalyst is illustrated in the equations below (Coronado & Hernández-Alonso 2013; Klan & Wirz, 2009; Pichat, 2013).

Photocatalyst + hv → Photocatalyst + e-CB + h+VB (1)

Photocatalyst (e-CB) + O_2 → Photocatalyst + $O^{2\bullet-}$ (2)

$O^{2\bullet-} + 2H^+$ + e-CB → H_2O_2 (3)

$H_2O_2 + 2H^+$ + e-CB → $\bullet OH + H_2O$ (4)

$\bullet OH + H^+ \rightarrow HO_2\bullet$ (5)

Photocatalyst (h^+_{VB}) + H_2O → Photocatalyst + H^+ + •OH (6)

Photocatalyst (h^+_{VB}) + OH^- → Photocatalyst + •OH (7)

Organics (pollutants) + •OH, $O^{2\bullet-}$, $HO_2\bullet$ → Degradation Product (8)

Redox reactions between the electron/hole (e-/h+) pair with the reactants occur in the presence of oxygen and can take place through two pathways which are:

1 Direct electron transfer with electron/hole (e-/h+) pair,

2 Reactive radicals mediated pat

hway (Pichat, 2013).

In the first pathway, reactants adsorbed on the surface of the photocatalyst and directly reduced/oxidized by electron/hole (e-/h+) pair to form reduction/ oxidation products, which can be further broken down by radicals formed in the second pathway.

In contrast, the second pathway involves generation of reactive species followed by reaction with the target pollutants. Oxygen molecules (O_2 molecules) are first reduced by the localized electrons at the conduction band (eCB) into superoxide radicals ($O^{2\bullet-}$) as shown in Equation (2). Superoxide radicals ($O^{2\bullet-}$) then can be further reduced to hydrogen peroxide, H_2O_2 as shown in Equation (3) which are reduced subsequently into hydroxyl radicals (•OH), which have a high oxidizing potential of 2.8 eV as shown in Equation (4). Hydroperoxyl radicals, (HO_2•) can be generated as shown in Equation (5). The hole (h^+) contributed in generating hydroxyl radicals (•OH radical) as well, as shown in Equations (6) and (7). These generated active species then react with the organic compounds to produce intermediates and eventually complete mineralization occurs as represented in Equations (8). According to Sharma & Sanghi (2012), hydroxide radical (•OH radical) is effective in degrading refractory organics due to its high reactivity and nonselectivity.

Zinc Oxide (ZnO) as Photocatalyst

Zinc oxide (ZnO) is a common photocatalyst employed in heterogeneous photocatalysis next to titanium dioxide (TiO_2). According to Di Paola, et al. (2012), zinc oxide (ZnO) has good photocatalytic properties and a wide band gap of 3.2 eV. Furthermore, zinc oxide (ZnO) is low cost which makes it considerable in commercial applications (Coronado, et al., 2013). Zinc oxide (ZnO) has an absorption spectrum that consists of a single, broad intense absorption band of about 370 nm, which lie in the UV light wavelength range.

Zinc oxide (ZnO) generally occur in three crystal structures which are rocksalt, zinc blende and wurzite structures, where both rocksalt and zinc blende are cubic while wurzite is hexagonal (Johar, et al., 2015). Zinc oxide (ZnO) wurzite structure is the most common structure which exist as white hexagonal crystal (white powder) at ambient temperature and pressure and the most common form employed in photocatalysis (Lee, et al., 2016, Lam et al., 2012).

Fascinating results have been shown in many studies on zinc oxide (ZnO) photodegradation of dyes under optimized operational parameters (Lee, et al., 2016; Jia et al., 2016). Zinc oxide (ZnO) catalyst was employed in a study conducted by Sobana & Swaminathan (2007) and resulted in 88 % Acid Red dye degradation under UV irradiation. Danwittayakul et al., (2015) has shown methylene blue (MB) degradation of 80 % using zinc oxide (ZnO) composite after 180 minutes of UV irradiation time. It was therefore evident that zinc oxide (ZnO) can be applied effectively in removing recalcitrant dyes from the wastewater and to be further studied on its usage in commercial scale.

Parameter Studies/ Photocatalytic Processes

There are many factors such as initial organic pollutant concentration, catalyst loading, and the pH of the solution that influenced the photocatalytic reaction. The rate and efficiency of a photocatalytic reaction depends on a number of operating parameters that govern the degradation of organic pollutants in wastewater. These are light intensity and wavelength, initial substrate concentration, catalyst loading, the pH of solution, reaction temperature, and dissolved oxygen. Two different operating parameters namely initial ethylparaben concentration and the pH of solution were examined in this study.

Effect of Initial Substrate Concentration of Photodegradation Process

Due to the fact that, as the concentration of model pollutant increases, more and more molecules of the organic compound get adsorbed on the surface of the photocatalyst, the initial substrate concentration can influence the extent of reaction rate at the surface of the photocatalyst. Tsai et al., (2009) found that the degradation efficiency of bisphenol A (BPA) was strongly dependent on the initial substrate concentration. The degradation efficiency of bisphenol A (BPA) over titanium dioxide, TiO_2 suspension decreased gradually, ranging from 100 % to 97 % as the initial substrate concentration increased from 1 to 20 mg L^{-1}. Nevertheless, the bisphenol A (BPA) concentration increased from 20 to 50 mg L^{-1}; the degradation efficiency showed a significant decreasing trend, ranging from 97 % to 67 %. Jung et al., (2001) investigated the effect of initial concentration in the range of 2.5 to 10 mg L^{-1} on the photocatalytic degradation of pentachlorophenol (PCP) using titanium dioxide (TiO_2) thin films coated on stainless steel cloth.

Maximum pentachlorophenol (PCP) degradation was observed at 2.5 mg L^{-1}. Chung, & Chen, (2009) conducted the titanium dioxide (TiO_2) photocatalytic experiment at different di (2-ethylhexyl) phthalate (DEHP) concentrations ranged from 25 to 300 µg L^{-1}. Their results showed that the degradation efficiency decreased with the increased concentration of di (2-ethylhexyl) phthalate (DEHP). This was attributed to the rise of internal optical density, which caused the solution become impermeable to UV light.

High initial concentration on dye solution has been reported to have adverse effects on dye degradation efficiency (Jia, et al., 2016; Lee, et al., 2016). Increase in dye concentration refers to the increase in number of substrates which would be adsorbed to the photocatalyst while the number of active sites present on the catalyst remains constant for a fixed catalyst loading, light intensity and time of irradiation. This resulted in competition between dye molecules and other molecules involved in generation of radicals such as oxygen molecules (O_2) leading to ineffective radicals' generation for dye degradation and lower dye degradation efficiency.

Increased amount of dye also increases the colour intensity of the solution which leads to interception of photons before reaching the surface of catalyst. The lower light penetration causes ineffective irradiation of photocatalyst which resulted in lower dye degradation efficiency (Luk, 2016, Lee, et al., 2016).

In (Luk, 2016) study on the degradation of methylene blue (MB) dye with zinc oxide (ZnO) nanoparticles, dye degradation rate has decreased from 0.1268 min^{-1} to 0.0459 min^{-1} with increasing initial concentration of methylene blue (MB) solution from 8×10^{-6} to 2.4×10^{-6} M. In addition, (Jia, et al.,) has found that degradation efficiency of brilliant yellow dye has decreased from (95.1 to 53.1) % when initial dye concentration was increased from (50 to 200) mg L^{-1} after 60 minutes of irradiation time using UV-Vis light source. It is evident that increased dye concentration resulted in increased competition of molecules on adsorbing on photocatalyst surface.

The Effect of pH of the sample solution

The pH of an aqueous solution significantly affects all metal oxide semiconductors including the surface charge on the semiconductor particles and the size of the aggregates formed (Lam, Sin, & Mohamed, 2010; Modirshahla et al., 2011). Due to amphoteric behavior of TiO_2 particle suspended in aqueous solution, the effect of pH of the solution on degradation rate depends on the acid-base properties of the semiconductor surface and can be explained on the basis of zero-point charge. In addition, the pH of the solution can affect the formation of hydroxide radicals (•OH radicals) by the reaction between hydroxide ions, OH^{-} ions and the positive holes. The positive holes are favored as major oxidation species at low pH, whereas hydroxide radicals (•OH radicals) are favored as principal oxidizing species responsible for the degradation process at neutral or high pH levels (Konstantinou, & Albanis, 2004). It is important to note that, the photocatalytic degradation of some organic pollutants is more efficient in alkaline solution (Subagio et al., 2010) and others at about neutral pH (Zu et al., 2009). It has earlier been reported that, in alkaline solution, there is a higher concentration of hydroxide ions, OH^{-} ions, which can lead to the photo-generation of much of the reactive hydroxide radicals (•OH radicals) and, thus, increasing the rate of bisphenol A (BPA) degradation. In summary, different organic pollutants have different activities in photocatalytic reaction. Some are degraded effectively at lower pH, while others degraded effectively at higher pH. All these may be attributed to the type of catalyst used and the nature of the organic pollutant to be degraded. Therefore, appropriate pH control strategies should be implemented for an efficient photocatalytic water treatment process.

The pH of solution affects the surface charge of the photocatalyst thus affecting the adsorption of substrates to its surface. The studies related to influence of the pH of solution on dye degradation.

The zero-point charge pH of zinc oxide (ZnO) was reported to be about 9 by many literatures (Luk, 2016; Lam, et al., 2012; Sobana & Swaminathan, 2007). Surface of zinc oxide (ZnO) is positively charged at pH below zero-point charge (ZPC) with presence of more hydrogen ions, H^{+} ions and negatively-charged at pH above zero-point charge (ZPC) by means of adsorbed hydroxide ions, OH^- ions (Sobana & Swaminathan, 2007).

In general, alkaline condition favors the formation of hydroxide radicals (•OH) as presence of more hydroxide ions, OH^- ions can react with photo-generated positive holes to generate more hydroxide radicals (•OH) for photocatalytic degradation of dyes (Akpan & Hameed, 2009). However, charges of dye particle under treatment must be taken into consideration as well. In a study conducted by Sanatgar-Delshade, Habibi-Yangjeh & Kohahadi-Moghaddam (2011), they have found that degradation of cationic dye, Methylene Blue (MB) was remarkable in zinc oxide (ZnO) mediated photocatalysis at pH above 9. At pH above 9, surface of zinc oxide (ZnO) was negatively-charged and cationic methylene blue (MB) molecules were attracted to zinc oxide (ZnO) surface due to electrostatic attraction. On the other hand, Jia, et al. (2015) has found that degradation of anionic dye, brilliant yellow dye using zinc oxide (ZnO) photocatalyst decreasaed in alkaline condition due to electrostatic repulsion between negatively-charged surface of zinc oxide (ZnO) and brilliant yellow dye molecules. pH of solution is also crucial in zinc oxide, ZnO-based photocatalysis due to instability of zinc oxide (ZnO) in acidic solution. Zinc oxide (ZnO) tends to dissolve by its reaction with increased amount of hydroxide ions, H^+ ions in acidic condition as shown in Equation (9) (Sangatar-Delshade, Habibi-Yangjeh & Kohahadi-Moghaddam, 2011).

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \qquad (9)$$

Effect of Light Intensity and Wavelength of Photodegradation Process

Light irradiation plays a significantly important role in all of photocatalytic reactions and generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst. The energy of a photon is related to its wavelength, and the overall energy input to the photocatalytic process is dependent on the light intensity. Therefore, the effects of both intensity and wavelength have been studied in numerous investigations for various organic pollutants including phthalates, bisphenol A, and chlorophenols. It has been reported that at low light intensity (catalyst dependent, surface reaction limited) the rate was linearly proportional to the light intensity, while at medium-high intensity, the rate became proportional to the square root of the light intensity, and, at higher light intensity, the rate was independent of the light intensity (Ollis et al., 1991; Konstantinou et al., 2004; Mehrotra et al., 2005). This variation is likely due to the recombination of photogenerated electron-hole pairs under different irradiation intensities. Huang and Chen (2010) examined the effect of light intensity on the photocatalytic degradation of diethyl phthalate (DEP) using TiO_2 as catalyst. The degradation efficiency of diethyl phthalate (DEP) was observed to increase linearly with UV radiation intensity up to (2.50×10^{-6}) $\mu Em^{-2}s^{-1}$ and then only smaller changes when the light intensity increased from 2.50×10^{-6} $\mu Em^{-2}s^{-1}$ to 4.00×10^{-6} $\mu Em^{-2}s^{-1}$. The study explained that, at lower UV intensity, the photocatalytic degradation was limited. As the UV intensity increased, more hydroxide radicals (•OH radicals) were formed, thus, resulted in the increase of diethyl phthalate (DEP) degradation.

Effect of Catalyst Loading of Photodegradation Process

It is well documented that the rate and efficiency of photocatalytic degradation would increase with catalyst loading. The increase in the efficiency seems to be due to the effective surface area of catalyst and the absorption of light. At lower catalyst loading, the absorption of light controlled the photocatalytic process due to the limited catalyst surface area. However, as the catalyst loading increased, an increase in the active surface area of TiO_2 is obtained. The enlarged number of photons absorbed and the amount of organic pollutants adsorbed on the TiO_2 surface improved the photocatalytic degradation. When the TiO_2 loading is overloaded nevertheless, owing to an increase in the particle’s aggregation, the surface that absorbed the photons is not increasing in a geometrical ratio (Wang et al, 2009). In addition, the number of active sites on the TiO_2 surface also decreased because of the decrease in light penetration due to light-scattering effect with an increase of the turbidity of the suspension and leading to the shrinking of the effective photoactivated volume of suspension. The integration of these two reasons resulted in a reduced performance of photocatalytic activity rather than the linearly increased with the overloaded catalyst. Hence, many researchers have verified that there was an optimum amount of catalyst loading in the photocatalysis studies (Akpan, & Hameed, 2009; Konstantinou, & Albanis, 2004; Yao, & Wang, 2010). In any given application, the optimum catalyst loading has to be determined in order to avoid an ineffective excess of catalyst and to ensure total absorption of efficient photons.

Effect of Reaction Temperature of Photodegradation Process

A number of studies have been indicated on the dependence of the photocatalytic reaction rate of degradation of organic pollutants on the reaction temperature. Such dependency could be realized when operating the photocatalytic process under natural sunlight, where the reaction temperature of stream may increase as the solar irradiation contains a considerable infrared (IR) factor (Bhatkhande et al., 2002). Generally, as the photocatalytic process proceeds on the surface of the TiO_2, higher reaction temperatures would promote collision frequency between the organic pollutants and the catalyst, leading to higher reaction rates (Yawalkar et al., 2002).

Nevertheless, several researchers have reported that, while an increase in photocatalytic reaction temperature may enhance the reaction rate of organic pollutants, reaction temperature would also lower the adsorption of organic pollutants and could reduce the oxygen concentration in the solution (Thiruvenkatachari et al., 2005; Malato et al., 2009). In addition, as the irradiation energy simply serves to overcome the energy barrier for the process, it is often found the apparent activation energy is very small (a few $KJmol^{-1}$) (Rajeshwar, 1995). Hence, the photocatalytic process does not appear to be particularly temperature sensitive. In sum, the optimum temperature is generally in the medium temperature range ($20^\circ C \leq \theta \leq 80^\circ C$). This absence of heating is attractive for photocatalytic reactions carried out in aqueous media and in particular for photocatalytic water purification (Herrmann, 1999).

Kinetics of Photodegradation

Langmuir-Hinshelwood (L-H) model is frequently used in studying the kinetics of heterogeneous photocatalysis and was reported to be compatible with the actual experimental findings in many studies (Luk, 2016; & Lam, et al., 2012). The rate of degradation of reactant, r can be expressed in Equation (10) where it is expressed in the units of mgL^{-1} min^{-1}, C represents the concentration of reactant in mgL^{-1}, t refers to the irradiation time, kn represents the rate constant of photocatalytic reaction in mgL^{-1}min^{-1} and K represents the adsorption constant of the reactant in L (mg)$^{-1}$ (Kumar, Porkodi & Selvaganapathi, 2007).

$$r = -dC \,/\, dt = \frac{knKC}{1+KC} \qquad (10)$$

The equation can then be simplified into linear form when C is considered as much lesser than 1 (C << 1). The simplified first order reaction is as shown in Equation (11) where k_{app} (min^{-1}) is the apparent first order rate constant obtained from the slope of ln (Co/C) vs. t graph, Co is the initial concentration of reactant. The theoretical data can then be computed using the simple first-order law (Asenjo et al, 2013).

$$ln\left(\frac{Co}{C}\right) = kapp\ t \qquad (11)$$

Instrumental Techniques Used in this Study.

Three instrumental techniques were employed in this work. These include one spectroscopic, Ultra-Violet Visible Spectrophotometry and two separation techniques namely High-performance liquid chromatography (HPLC) and Gas chromatography mass spectrometry (GC-MS).

Ultra Violet- Visible Spectrophotometry

The UV-Visible spectrophotometer is used to determine the absorption spectra of compounds. It measures the amount of light absorbed by the dissolved substance. It can be used for both qualitative and quantitative purposes. It is based on the Beer Lamberts law, which states that, the absorbance is directly proportional to the concentration of a solution. The higher the concentration, the higher the absorbance. A UV-Visible spectrum consists of broad absorption bands over a wide range of wavelengths. The shape of the graph is due to different kinds of atoms and bonds present in a molecule of a compound. The UV-Visible absorption spectrum ranges from 100nm (ultra violet) to 750 nm (visible). The visible spectrum spans from about 350 nm to 700 nm while the ultra violet (UV) spectrum ranges from 200 to 400 nm. The 100-200 nm region is usually not scanned because absorption by the atmospheric carbon dioxide becomes significant below 200 nm. The wavelength (λ) of absorption is reported as λmax, the wavelength at the highest point of the curve. The absorption energy is recorded as absorbance and not transmittance as in infrared spectra (Fessenden & Fessenden, 1990; Harris, 2010; Skoog et al., 2014).

High Performance Liquid Chromatography (HPLC)

High performance liquid chromatography (HPLC) is the most widely used type of elution chromatography. This technique is used by scientist for separating and determining species in a variety of organic, inorganic and biological material. It is used to check the purity and authenticity of a compound. Pumping pressures of several hundred atmospheres are required to achieve reasonable flow rates with packings in the 3 to 10 mm size range, which are common in modern liquid chromatography. Because of these high pressures, the equipment for high-performance liquid chromatography tends to be considerably more elaborate and expensive than that encountered in other types of chromatography (Skoog et al., 2014).

Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography-mass spectrometry (GC-MS) consists of two analytical techniques: gas chromatography (GC), a separation technique, and mass spectrometry (MS), an identification technique. Combination of gas chromatography with mass spectrometer has several advantages which includes the ability of the method to separate components of a complex mixture so that mass spectra of individual compounds can be obtained for qualitative purposes.

The method also provides quantitative information on these same compounds (Sparkman & Watson, 2007). Gas chromatography is one of the most widely used techniques for qualitative and quantitative studies. In gas chromatography, the components of a vaporized sample are separated by being distributed between a mobile gaseous phase and a liquid or a solid stationary phase held in a column (Skoog, Holler, & Crouch, 2007). In the mass spectrometer, analyte molecules are converted to ions when energy is applied to them. The ions formed are then separated on the basis of their mass-to-charge-ratios (m/z) and then further directed to a transducer that converts the number of ions (abundance) into an electrical signal. The ion abundance is then plotted against mass-to-charge-ratio yielding what is known as the “mass spectrum” (Skoog et al., 2007; Skoog et al., 2014). Samples may be introduced as solids, liquids or gases depending on the type of ionization to be employed. The inlet system introduces a micro amount of sample into the ion source where the components of the samples are converted to gaseous ions by bombardment with electrons, photons, ions or molecules. This results in a stream of positive ions which are then accelerated into the mass analyzer where the ions are then separated based on the mass-to charge-ratios. The ions of particular m/z values are then collected and converted into an electrical signal by the ion transducer. The data handling system processes the results to produce the mass spectrums (Harris, 2010; Skoog et al., 2014).

Electron ionization (EI) is the most widely used method for generating ions for mass spectrometry. Electron ionization produces molecular ions from gas phase analytes. These molecular ions then fragment in a reproducible way, which results in a “fingerprint” of the analyte. Because of the uniqueness of these “chemical fingerprints”, commercially available libraries containing hundreds of thousands of standard electron ionization (EI) mass spectra can be used to facilitate identification of unknown compounds (Silverstein, Webster, & Kiemle, 2005; Sparkman & Watson, 2007).

Some structural features of the analyte molecule can be deduced from the fragmentation pattern of the molecular ion which is designated as $M^{+\bullet}$. Based on the knowledge gained from advanced organic chemistry structural elucidation can be deduced. (Fessenden & Fessenden, 1990; Pavia, Lampman, & Kriz, 2001).

Chapter Summary

In this chapter, a discussion is made on endocrine disruptors, parabens, advanced oxidation process (AOP), basic principles of heterogeneous photocatalysis, zinc oxide (ZnO) as photocatalyst, parameter studies/photocatalytic processes such as initial concentration of ethylparaben solution, the pH of solution and kinetics of photodegradation. Also, extensive review is provided on paraben, photocatalytic degradation processes, reactions, mechanisms, and kinetic studies of zinc oxide (ZnO) photocatalyst.

CHAPTER THREE

RESEARCH METHODOLOGY

Introduction

In this chapter, the experimental procedures, chemicals, materials and instruments or equipment used in present study are discussed.

Materials and Chemicals

All chemicals used were of analytical grade and no further purification was performed.

Ethylparaben (model paraben) was obtained from the British Drug House Ltd., and employed in this study as the pollutant of which solution of various concentrations were prepared. Zinc oxide (99 %), the inorganic photocatalyst was obtained from Central Drug house(P) Ltd. Hydrochloric acid, HCl (37 %) was from Vwr Prolabo Chemicals and was used to adjust the pH of the sample solution. Sodium hydroxide pellets (99.7 %) was used to adjust the pH of the solution to the alkaline region. Acetonitrile (99.5 %) was obtain from the Kosdaq Listed Company and was used to extract the ethylparaben and its degradation products from aqueous solution. Ethanol (99.8 %) was obtained from VWR Prolabo Chemicals and was used as a solvent.

Instrumentation

All weighings were done using Sartorius CP124S with a capacity of 120g and uncertainty of 0.1mg. A CHROM O-VUE® C-70G UV-VIEWING SYSTEM from UVP Upland, U.S.A was used as the ultra-violet light source. A High-Performance Liquid Chromatography (HPLC) from Shimadzu LC 20AD couple with UV-Visible detector was used to confirm the purity of the ethyl paraben. A T70 UV-VIS Spectrophotometer from Mettler Toledo was used to obtain the UV-Visible spectra of sample solution during the degradation process. A QP2020 Gas Chromatography-Mass Spectrometer (GC-MS) from Shimadzu was used to separate and identify the degraded products of the ethylparaben.

Photocatalytic Reactions

The photocatalyst, Zinc Oxide (ZnO) was used to degrade ethylparaben solution in the presence sunlight and ultra-violet light using a UV-Lamp source. Sample solutions were magnetically stirred. Photocatalytic experiments were performed to examine the catalytic activity of Zinc Oxide (ZnO) towards the degradation in the presence of the various light sources.

A Sartorius balance CP124S with a capacity of 120 g and uncertainty of 0.1 mg was used to measure the masses of ethylparaben and Zinc Oxide. Ethanol was used as a solvent to dissolve the ethylparaben powder in the preparation of the various standard solutions of ethylparaben. UV-visible absorption spectra of the various solutions were obtain using a spectrophotometer. The absorption maxima for each standard solution was obtained at 256 nm. A calibration curve was then plotted, that is, absorbance against standard concentration.

For the photocatalytic reactions, the mass of the zinc oxide (ZnO) photocatalyst used was kept constant. An 85 mL volume of ethylparaben solution of each standard solution was poured into 120 mL beakers and 71.5 mg of ZnO was weighed and added to the solution and then first placed in a dark. The sample was then stirred using a magnetic stirrer for 90 minutes. Afterwards the suspension was filtered to remove the solid zinc oxide. The

UV-Visible spectrum was then taken. These experiments served as control to demonstrate the role of the importance of the presence of light in photocatalytic reactions.

Subsequently, the photocatalytic reactions were conducted in batch reactions in the presence of either ultra violet or sunlight for various time intervals; 30 min, 60 min, 90 min, 120 min, 150, and 180 min as shown in plates 1 and 2. At the end of each run, the sample was filtered and the absorption spectrum taken. This was to help detect any degradation of the ethylparaben by monitoring the degradation profile from the resulting absorption spectra.

The role of the photocatlyst, zinc oxide was also demonstrated by using a blank solution in which no zinc oxide was present and irradiation with the various light sources conducted.

Finally, Gas Chromatography-Mass Spectrometry (GC-MS) analysis was then conducted on the samples to determine the degraded products as described below.

Plate 1: A Typical Setup for the Batch Reaction Under Sunlight Irradiation

Plate 2: A Typical Setup for the Batch Reaction Under UV Light Irradiation

High Performance Liquid Chromatography (HPLC) Analysis of the Parent Ethylparaben

The purity of ethylparaben was analyzed by using HPLC (Shimadzu). The mobile phase comprised methanol (60 %) and high purity water (40 %) in a ratio of 3:2. The analysis was carried out at 40 ^{o}C, coupled with the total flow rate of 0.5 mL/min and the detector wavelength at 254 nm. The instrument used is shown in plate 3.

Plate 3: The HPLC Instrument Used in this Work

UV-Visible Spectrophotometer Analysis

UV-Vis spectrophotometer analysis was conducted to determine the character and absorption spectra of the ethylparaben. The wavelength range was 400-200 nm (ultraviolet region). Blank solutions were prepared and used to calibrate the T70 UV-Vis spectrophotometer. Quartz cuvette was used. The UV-Vis spectrometer was switched on and allowed to stand for about 30minutes to ensure its readiness. The cuvette was properly rinsed with distilled water and the outer surfaces were cleaned with a tissue before it was inserted into the UV-Vis spectrophotometer. The blank solutions were run before the various solutions to determine the character and the absorption spectra of the solutions.

A T70 UV-Vis spectrophotometer was used to generate a standard calibration curve for ethylparaben solutions and to measure the absorbance of the various samples of degraded ethylparaben solutions.

The mode used in this spectrophotometer was the single wavelength mode where light of wavelength, $\lambda = 256$ nm was used in light of λmax of ethyl paraben.

Standard calibration curve for ethylparaben solutions were obtained by determining the absorbance values of several ethylparaben standard solutions of known concentrations where the spectrophotometer generated the graph of concentration, C (mg L^{-1}) versus absorbance value, A (abs). The strong linear correlation between the two parameters was represented by a correlation coefficient, R^2 of larger than 0.9.

Absorbance values of ethylparaben sample were measured and also the degree of degradation of ethylparaben, D_{abs} can be computed using the A values obtained as shown in Equation (12).

$$Dabs = \frac{Ao-At}{Ao} \times 100\% \qquad (12)$$

Where A_0= Initial absorbance of sample at t=0 minute of reaction time, abs.

A_t= Absorbance of sample at a given time (t) minutes of reaction time, abs.

$$\text{Ethylparaben degradation efficiency (\%)} = \frac{Do-Df}{Do} \times 100\% \qquad (13)$$

Where D_o is the initial concentration of the ethyl paraben at t=o (mg L^{-1}), D_f is the concentration at a given time (mg L^{-1}).

Investigation of Some Factors that Affect Photodegradation Efficiency

There are many factors that affects photodegradation efficiency such as initial ethylparaben concentration, catalyst loading and solution pH that influenced the photocatalytic reaction. Two different operating parameters namely initial ethylparaben concentration and solution pH were examined in this study.

Initial Ethylparaben Concentration

The effect of initial ethylparaben concentration on ethylparaben degradation efficiency was studied by varying the initial ethylparaben concentration in ethylparaben samples prepared. The selected initial ethyl paraben concentrations under study were 0.0361 mM, 0.0602 mM, 0.0723 mM and 0.12 mM.

The experiment was carried out at natural pH of 6.7 and the mass of catalyst loaded was 71.5 mg.

The pH of Ethylparaben Solution

Under optimum condition of 0.0361 mM of ethylparaben with mass of catalyst loading, effect of ethylparaben solution pH on ethylparaben degradation efficiency at pH 3.3 and 10.4 was studied. pH of solution was adjusted using 1.0 M HCl and 1.0 M NaOH. pH value was measured using a pH MESSGERAT/pH meter which was calibrated with buffer solution of pH 4, 7, and 10.

Kinetic Study

A Langmuir-Hinshelwood (L-H) first order kinetic model was used to determine the initial degradation rate, k_{app} of ethylparaben mediated by ZnO at distinct initial ethylparaben concentrations, C_o. k_{app} can be obtained from the slope of ln (C_o/C) vs. time, (t) graph as represented in Equation (14) where

Co is the initial concentration of ethylparaben solution, C is concentration of ethylparaben solxution in mg L^{-1}, at a time, (t) in minutes and k_{app} in min^{-1}.

$$ln\left(\frac{Co}{C}\right) = kapp.t \qquad (14)$$

By determining the k_{app} at different initial ethylparaben concentrations, the optimum initial ethylparaben concentration that rendered fastest ethylparaben degradation can be determined in this study. The L-H expression in its first-order Equation (14) can then be employed to determine the kn, the photocatalytic reaction rate constant (mg (L min)$^{-1}$) and K, the adsorption equilibrium constant (L (mg)$^{-1}$) by plotting a plot 1/r (L min (mg)$^{-1}$) vs. 1/C (L (mg)$^{-1}$) through the relationship expressed in Equation (16).

$$ln\frac{Co}{C} = kn\,Kt = kapp.t \quad (15)$$

$$\frac{1}{r} = \frac{1}{knKC} + \frac{1}{kn} \quad (16)$$

Plate 4: The UV-Visible Spectrophotometer Used in this Work

Gas Chromatography Mass spectrometry (GC-MS) Analysis

The identification of the degraded products were carried out on a gas chromatography-mass spectrometry (GC-MS) QP2020. The solid phase extraction (SPE) cartridge was conditioned with the extracting solvent acetonitrile and then the sample was loaded unto the cartridge and eluted by applying pressure to the top of the cartridge using a syringe pump fitted with glass filter.

The solid phase extraction (SPE) cartridge was conditioned with 1 mL of distilled water and 0.5 mL of acetonitrile. The sample was loaded unto the column and the cartridge was washed with 1 mL of distilled water and 1 mL of acetonitrile and the cartridge was left to dry for 2 mins by applying vacuum at the top using a syringe pump and the analytes of interest were eluted with 2 mL acetonitrile and collected and transferred into auto-sampler vials for Gas Chromatography-Mass Spectrometry (GC-MS) analysis.

Plate 5: The GC-MS QP2020 Used in this Work

The gas chromatograph-mass spectrometer used was the GC-MS QP2020 model.

Helium gas was used as the carrier gas. The pressure was 100.00 kPa. The instrument was operated in splitless mode. Injection port temperature was 250^{o}C with a sampling time of 1 min using a linear velocity flow mode with a total flow of 50.0 mL min^{-1} and a column flow of 1.69 mL min^{-1}. Chromatographic separation was achieved on a 30 m × 0.25 mm ID, 0.25 μm restek column from Shimadzu technologies (USA). The initial oven temperature was 50^{o}C which was held for 1 min before ramping to a final temperature of 280^{o}C and held at that temperature for 6 mins. The total run time of 25 mins was used for the separation.

Electron impact ionization mode was employed for the mass selective detector. The ion source temperature was held at 230^{o}C and the interface temperature was 250^{o}C whereas an electron voltage of 70 eV was used. The instrument was operated in a scan mode from start m/z of 29 to m/z of 200. The solvent cut time was 2 mins.

Chapter Summary

This chapter presents and outlines the chemicals, materials or apparatus, instruments and all instrumental procedures employed for analyzing the samples. The instruments such as UV-Visible spectrophotometer, high pressure liquid chromatography and gas chromatography-mass spectrometer.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

Introduction

This chapter consists of results and discussions of the present study. The first section of this chapter presents and discusses the VU- Visible spectral features of the ethylparaben as well as its purity assessment using high performance liquid chromatographic (HPLC) analysis. The second section deals with the performance of photocatalytic removal of the ethylparaben using zinc oxide (ZnO) at varied initial concentrations and pH under sunlight and UV-Visible ligth irradiation. The third section deals with gas chromatography- mass spectrometry (GC-MS) analysis of the degraded product of ethylparaben. The fourth section consists of the kinetic study on the photocatalytic reaction based on a Langmuir-Hinshelwood (L-H) kinetic model.

This study was about photocatalytic degradation of ethylparaben. The zinc oxide was used as photocatalyst to remove or degrade a chemical compound (ethylparaben) in the presence of light. In this study, zinc oxide (ZnO) as photocatalyst was used to remove or degrade ethylparaben in the presence of sunlight (solar) and ultra violet lamp light irradiation under magnetic stirring condition. The absorption of light by zinc oxide (ZnO) in the visible region was more compared to titanium dioxide, TiO_2. Consequently, it was concluded that the zinc oxide (ZnO) was more active than other photocatalysts when sunlight was used as energy sources (Sakthivel et al, 2003).The ultra violet rays from the sun and the uv lamp light were allowed to settle on the reaction surface and the kinetics (rates of reactions) of these two conditions were analyzed using UV-Visible Spectrophotometer. High performance liquid chromatography (HPLC) was used to check the purity of the sample ethylparaben used and Gas chromatography-mass spectrometry (GC-MS) was used to identify the products of the degraded sample solutions of ethylparaben.

Absorption Spectral Features of EthylParaben

UV-Visible spectra of ethylparaben solutions were obtained to establish the maximum absorbance wavelength. The absorption spectrum of the ethyl paraben solutions of different concentrations were studied in the wavelength range of 200-350 nm. A maximum absorbance wavelength of 256 nm was found for all the ethylparaben solutions of different concentrations. It was also realized that the absorbance of the various solutions changes with the concentrations of the solutions. The absorbance decreases with decreasing concentration of ethyl paraben as shown in figure 2.

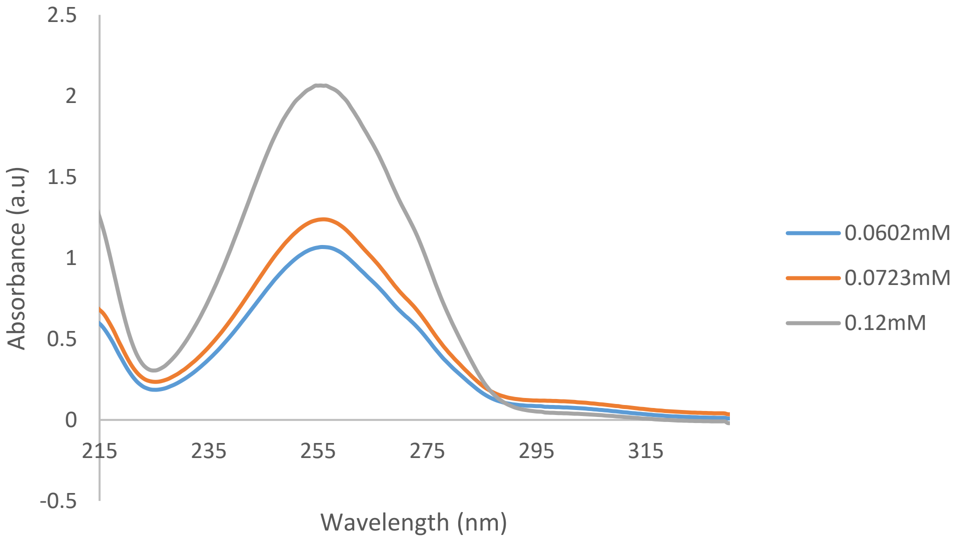


Figure 2: Variation of the Absorbance of Ethylparaben with Concentration

Figure 2 suggests, that, the degradation of a sample of ethylparaben can be monitored using UV-Visible spectral analysis. The variation of the absorbance with concentration was also examined to find out whether it fits the Beer Lambert's law, as shown in figure 3.

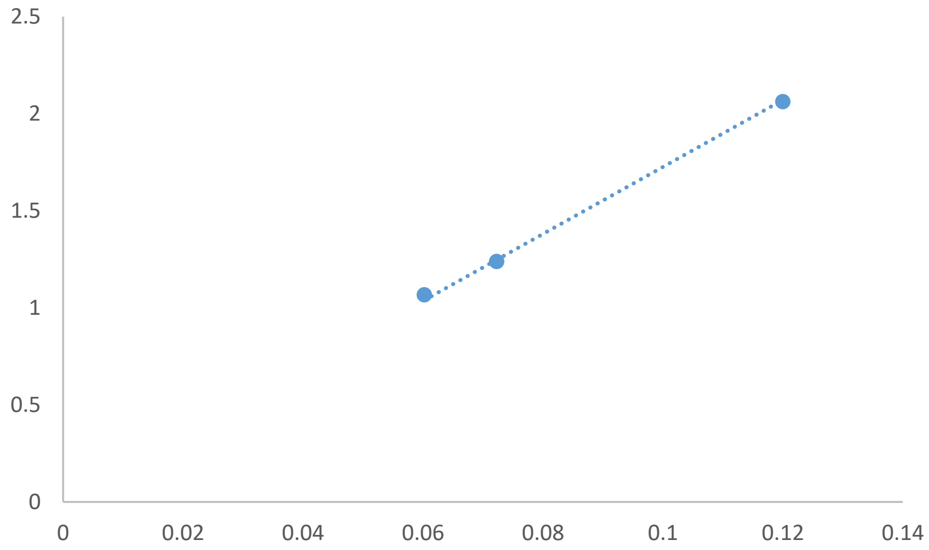


Figure 3: A Plot of Absorbance with Standard Solutions (0.0602, 0.0723 and 0.12 mM) Ethylparaben

From figure 3, there is a good linear fit with $R^2 = 0.9983$ suggesting that Beer Lambert's law is obeyed within these concentration range. This suggest that quantitative analysis for the content of ethylparaben can be done within these concentration range using the Beer Lambert's law. Therefore, the initial concentration solutions of ethylparaben for the photodegradation of ethylparaben were within these range.

HPLC Analysis for the Purity of Sample Ethylparaben Solution Concentration

The HPLC analysis was done to confirm and ascertain the purity of the sample of paraben used. From the spectrum, the maximum absorbance for the least ethylparaben solution concentration was chosen for the high-performance liquid chromatographic (HPLC) analysis**.** The optimum condition recommended in the experimental part for the HPLC analysis were applied to obtain the retention time for the ethylparaben.

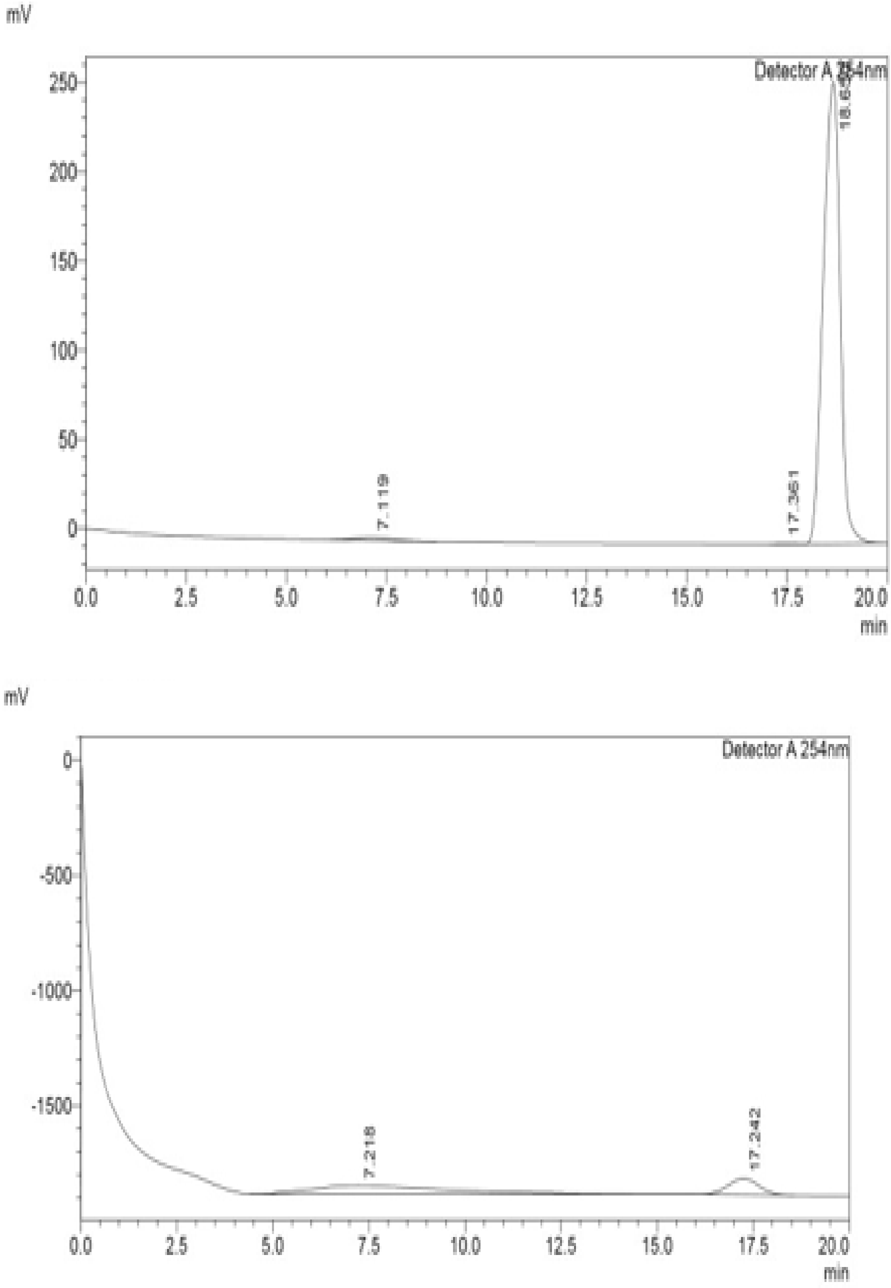


Figure 4: HPLC Chromatogram for Ethylparaben Using Methanol
(Conditions: Detection = 254 nm, Temperature 40 ^{o}C,
pH 6.7, Mobile Phase: 60 % Methanol and 40 % Water,
Flow rate 0.5 mL/min and using SPD-20AV UV/VIS Detector).

As in figure 4, the retention time for the ethylparaben was found to be 18.650 min. The other peaks obtained were originated from the solvent, methanol used as the peaks at the retention times 7.119 min and 17.361 min correspond to the peaks of the solvent's chromatogram. A single clear peak was obtained for the ethylparaben showing that, the ethylparaben was pure.

Degradation of Ethylparaben Using Zinc Oxide Photocatalyst Under Sun Light/ Solar Irradiation

Photocatalytic experiments were performed to examine the potential of ZnO to Solar or sun light irradiation.

Figure 5, depicts the UV-Visible absorption spectra of Ethylparaben which undergone the Sunlight/ZnO photocatalysis at different time intervals.

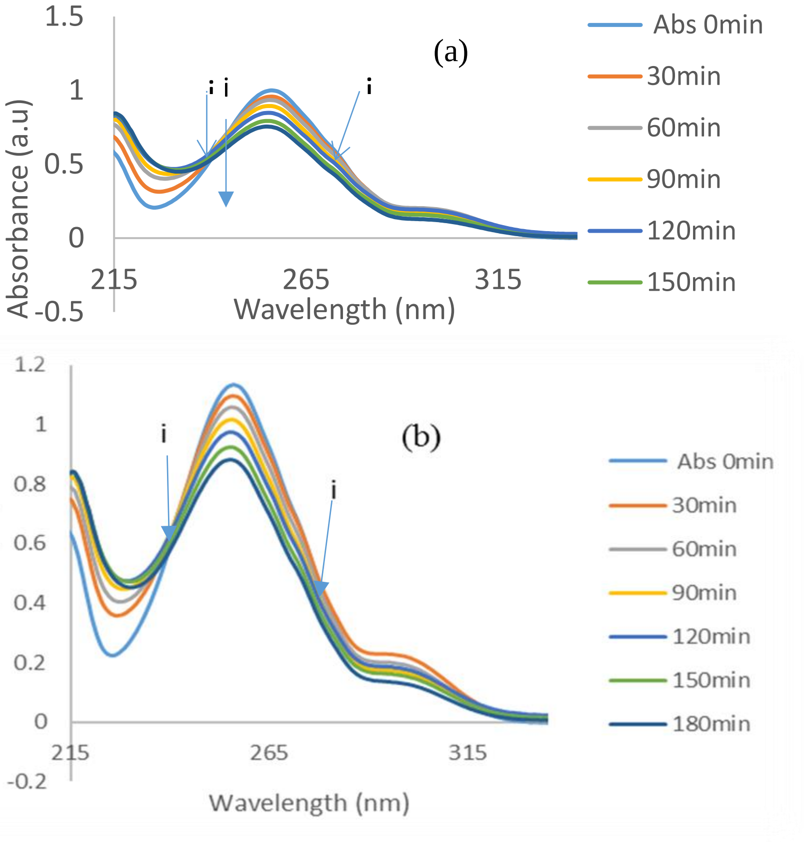


Figure 5: UV –Visible Absorption Spectrum Showing the Degradation Profile of Ethylparaben Various Concentrations (a) 0.0602 Mm and (b)0.0723 mM, Using Sunlight/ZnO at Different Time Intervals. Natural Solution pH= 6.7

Figure 5 indicates that the peak of the spectra occurred consistently at wavelength equal to 256 nm. The absorption peaks at 256 nm corresponding to ethylparaben molecules, decreased gradually as the exposure of time increased and disappeared after 180 minutes of Sunlight/ZnO photocatalysis. The gradual reduction of the peak at wavelength 256 nm indicates the breakage of C-O-C or C=O bonds in ethylparaben which led to its removal. The decrease in absorbance showed the reduction of ethylparaben concentration in the various solutions. The reduction in concentrations was observed where the solutions changed from clear white colorless to deep white colorless solutions.

One striking feature of the degradation profile in figure 5 (a) and (b) was the appearance of an isosbestic point labelled i. This suggest the formation of a degradation product that was UV-active.

The degradation of ethylparaben using zinc oxide photocatalyst was also done under ultra-violet light source irradiation. The corresponding degradation profile is shown in figure 6

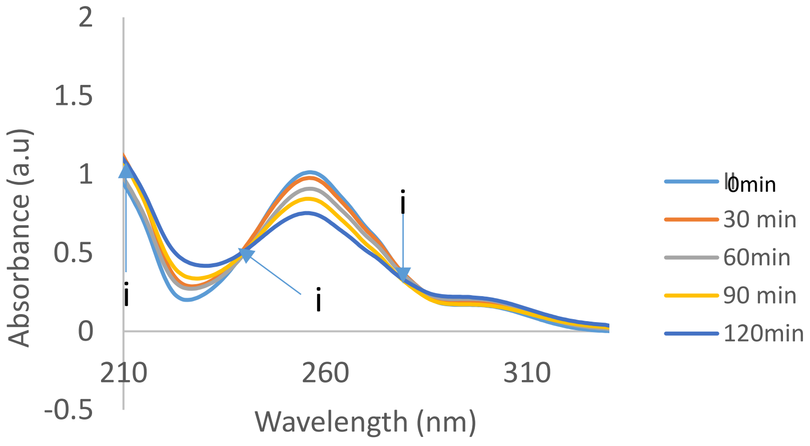


Figure 6: UV –Visible Absorption Spectrum Showing the Degradation Profile of Ethylparaben Concentration of 0.0723 mM Using Ultraviolet Light Source at Different Time Intervals. Natural Solution pH= 6.7

The degradation profile when ultraviolet light source was applied was very similar to figure 6 when only visible light was applied. An isosbestic point was also formed indicating the products formation. The curves in the degradation profile met at a common point called isosbestic point. The isosbestic point labelled (i) in the degradation profile indicates products formation that are UV-active.

Comparative Assessment of the Extent of Degradation of Ethylparaben Under Various Conditions

The comparative degradation percentage (%) of ethylparaben under dark, UV-Visible and Sun light condition using zinc oxide.

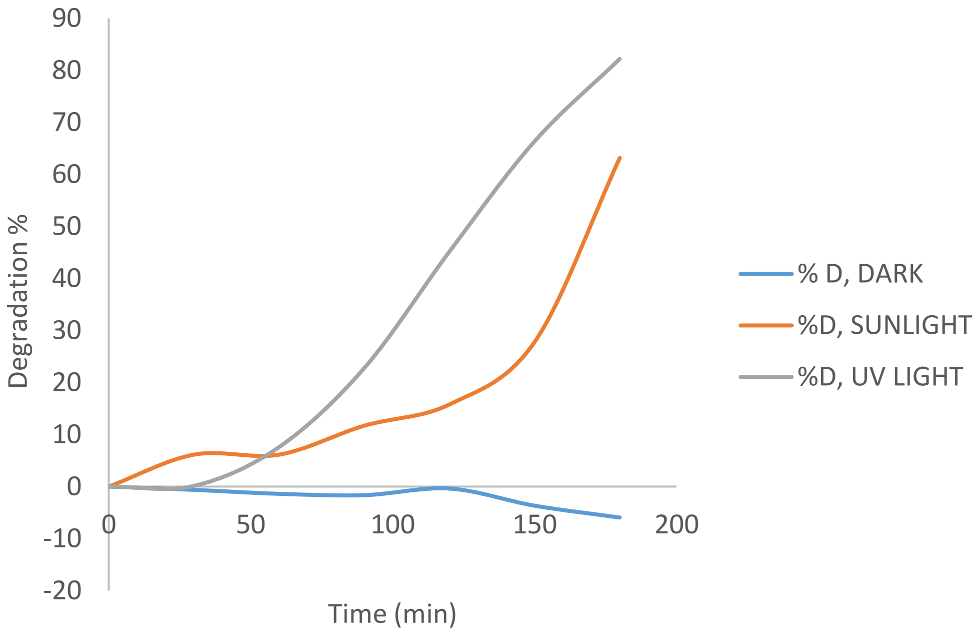


Figure 7: Percentage Degradation of Ethylparaben Degradation Using Dark/ZnO, UV-Vis/ZnO, and Sunlight/ZnO. (Concentration of Ethylparaben =0.0361 mM and Solution pH= 6.7)

The figure 7 above displays the comparative degradation percentage (%) of ethylparaben under Dark/ZnO, UV-Vis/ZnO and Sunlight/ZnO. The experiments were conducted under fixed conditons: Concentration = 0.0361 mM, natural solution pH = 6.7, mass of catalyst (ZnO) used = 0.0715 g.

The Dark/ZnO means the sample solution concentration of 0.0361 mM ethylparaben was kept in the dark without any UV-Vis light or sunlight source under magnetic stirring condition. From the figure, there was no significant ethylparaben degradation in the dark after 180 minutes. This reveals that the ethylparaben was stable in the dark without undergoing significant degradation. There wasn't any degradation in the dark.

The Sunlight/ZnO means that the degradation was carried out using the sunlight as a light source with ZnO as a photocatalyst used under magnetic stirring condition. The ultraviolet rays (radiations) from the sun was used to degrade the ethylparaben by using ZnO as a photocatalyst under magnetic stirring condition. From the figure five above, the degradation percentage (%) of the Sunlight/ZnO was found to be 63.16 %. This means that the ZnO was effective in degrading or removing ethylparaben in the sun under magnetic stirring conditions.

The UV-Vis/ZnO means the degradation of the 0.0361 Mm solution was carried out in the ultraviolet visible light source (UV LAMP) by using ZnO as a photocatalyst under magnetic stirring condition. From the figure above, the degradation percentage (%) of the UV-Vis/ZnO was found to be 82.2 %. This means that the ZnO was more effecient in degrading or removing ethylparaben in the ultraviolet visible lamp light source and this may be due to the fact that all the rays coming out of the ultra violet lamp are ultra violet rays and therefore, there is full exposure of the ultra violet rays from the ultra violet lamp but in the sunlight not all the rays reaching the earth's surface contain ultra violet rays as sunlight consists of components and therefore, it is due very little exposure of ultra violet rays from the sunlight. Also, this may be due the constant supply of the light source and the shorter distance between the light source from the ultra violet lamp and the sample solution.

The comparative degradation % of ethylparaben using Dark/ZnO, Sunlight/ZnO and UV-Vis/ZnO showed that the UV-Vis/ZnO gave the highest degradation 82.2 % than Sunlight/ZnO due to the fact that the sunlight (or white light) consists of other component colours or visible light and therefore not all the rays reaching the earth surface contain ultraviolet light. The maximum light absorption occurs in the ultraviolet portion of the electromagnetic spectrum, which constitute a smaller portion of the spectrum, and thus less available than the visible portion required by other photocatalysts. There is a higher degradation percentage in the ultraviolet light than in the sunlight because in the ultraviolet light, all the rays coming out of the ultraviolet lamp are ultraviolet rays and so there is full exposure of the ultraviolet rays but in the sunlight not all the rays reaching the earth's surface contain ultraviolet rays and therefore, it is due to very little exposure of the ultraviolet rays from the sunlight.

Effect of Initial Ethylparaben Concentration on Percentage Degradation Under Sun Light Irradiation

The influence of initial ethylparaben concentration was determined in this study by varying the initial ethylparaben concentration from 0.0361 mM to 0.12 mM. The experiments were conducted under fixed conditions of photocatalyst loading of 71.5 mg and at natural solution pH of 6.7.

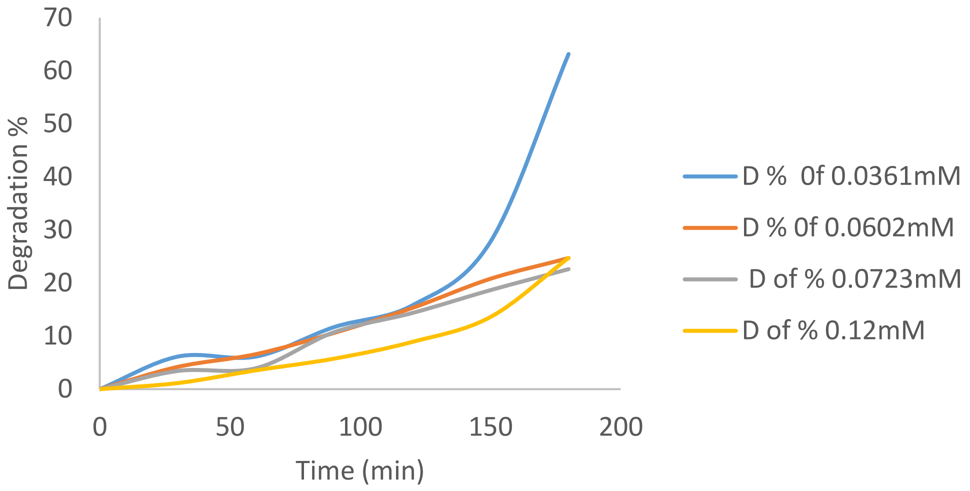


Figure 8: Effect of Initial EthylParaben Concentration on Degradation Percentage (Mass of ZnO = 71.5 mg, Solution pH = 6.7)

From figure 8 above, presents the effect of initial ethyl paraben concentration on degradation percentage of ethylparaben using ZnO photocatalyst. It was observed from the figure that, as the initial ethylparaben concentration increased, the degradation percentage decreased markedly. The best initial ethylparaben concentration determined was 0.0361 mM which achieved the highest degradation percentage of 63.16 % after 180 minutes of sun light irradiation. For higher initial ethylparaben concentration at 0.0602 Mm, 0.0723 Mm, and 0.12 Mm, the achieved degradation percentage were 24.7 %, 22.62 % and 24.74 %, respectively at similar light irradiation time. Thus, the smaller the concentration the higher the degradation percentage. Because as the concentration is increased, more molecules are produced on the ZnO photocatalyst surface thereby reducing or blocking the amount of light reaching on the surface of the ZnO photocatalyst surface and less degradation efficiency.

Effect of Solution pH

The effect of the pH of the sample on the degradation of paraben using ZnO photocatalyst was studied by varying the solution pH from 3.3 to pH 10.4. This was done to analyze the behavior of the ethylparaben to see whether it would degrade under acidic and basic condition or not. The experiments were conducted under fixed conditions of initial ethylparaben concentration of 0.0361 mM.

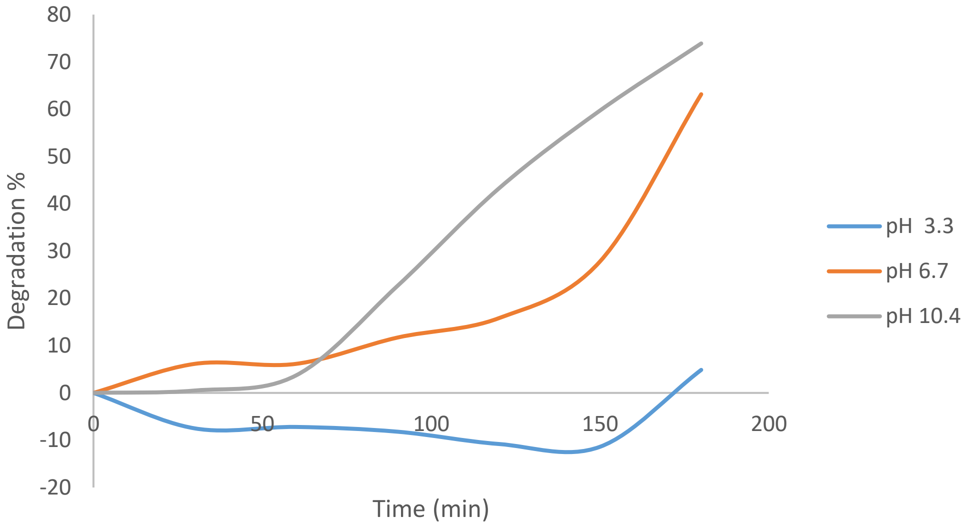


Figure 9: Effect of Solution pH on Ethylparaben (Mass of ZnO = 71.5 mg, Ethylparaben Concentration =0.0361 Mm)

The figure 9 above presents the effect of solution pH on the photocatalytic degradation of ethylparaben in the sun. As exhibited in the figure, the optimum pH which corresponded to the highest degradation percentage of 73.9 % was pH 10.4, which was the basic pH. Additionally, the percentages of degradation at pH 3.3 and pH 6.7 were comparable and gave a value of 4.87 % and 63.16 %, respectively. The ethylparaben degradation was least efficient at pH 3.3 with a degradation percentage of 4.87 %.

Effect of Initial Ethylparaben Concentration on Rate of Degradation

In literature, the photocatalytic degradation reaction of organic pollutants obeys the first-order kinetics (Pung, Lee & Aziz, 2012; Abass, et al., 2016).

Therefore, first-order kinetics was employed in this study to determine the apparent rate constant, k_{app} at different initial ethylparaben concentrations. Knowing the reaction order (n = 1).

$$r = -dC/dt = kapp.C \tag{17}$$

The integrated form of this equation can be used to determine the k_{app} of the reaction at different initial ethylparaben concentrations. Thus, the equation 18, was used to plot a graph of In C_0/C vs t and the slope was found to be equal to $k_{app.}$

$$In\ \frac{C0}{C} = kapp.t \tag{18}$$

A plot of In (C_0/C) versus t gives a straight line with the slope equal to $k_{app.}$

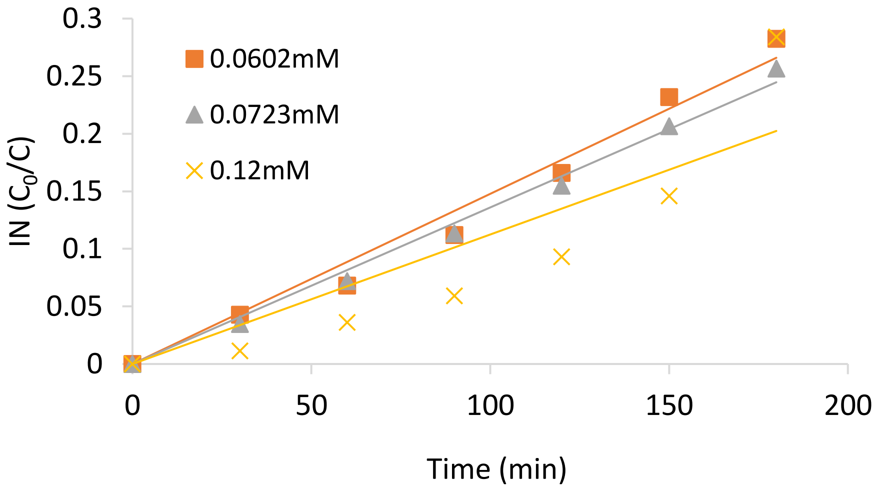


Figure 10: Kinetics of Photocatalytic Degradation of Ethylparaben at Different Initial Ethylparaben Concentrations (Solution pH = 6.7)

From figure 10 above, the plot of In (C_0/C) versus time (t) of different initial ethylparaben concentrations was used to determine k_{app} values and R^2 values.

Table 1**:** The K_{app} and R^2 values at Distinct Initial Ethylparaben

Initial Ethlparaben concentration/mM	k_{app} min^{-1}	R^2
0.0602	0.0015	0.9786
0.0723	0.0014	0.9919
0.12	0.0008	0.8765

Table 1 above shows the k_{app} and R^2 values. From the table, it can be found that as the initial concentration of ethylparaben increases, the k_{app} values also decreases. Thus, the higher the concentration, the smaller the k_{app} value.

The Langmuir-Hinshelwood (L-H) Kinetic Model

The photo-catalytic degradation of various organic compounds by means of illuminated ZnO can be formally described by the Langmuir– Hinshelwood (L–H) kinetics model. This model has been successfully used to describe solid–liquid reactions

In heterogenous catalysis, the reaction rate at the surface of the catalyst is related to the concentration of the reactant covering the surface according to the Langmuir–Hinshelwood (L–H) kinetic model.

$$r = -\frac{dC}{dt} = \frac{knKC}{1+KC} \tag{19}$$

Where r is the initial rate of photocatalytic degradation (mg (L min)$^{-1}$), C is equal to Co when t=0 where Co is the concentration of ethyl paraben after dark adsorption of 90 minutes (mg L^{-1}), kn is the rate constant of photocatalytic reaction (mg (L min)$^{-1}$) and K is the adsorption equilibrium constant (L (mg)$^{-1}$), respectively.

The L-H expression can be simplified into the first-order form as shown in Equation (4) below.

$$In\frac{C0}{C} = knKt = kapp.t \tag{20}$$

It can be further expressed in terms of r as shown in Eq. (5), where 0 concentration was assumed to be very low (KC <<1) (Asenjo, et al., 2013). When KC is very small, the equation becomes;

$$r = -\frac{dC}{dt} = knKC = kapp.C \tag{21}$$

$$\frac{1}{r} = \frac{1}{kn} + \frac{1}{K\,knC} \tag{22}$$

Where r is rate of the reaction, kn is the apparent reaction rate constant, K is the adsorption coefficient and C is the initial concentrations of ethylparaben.

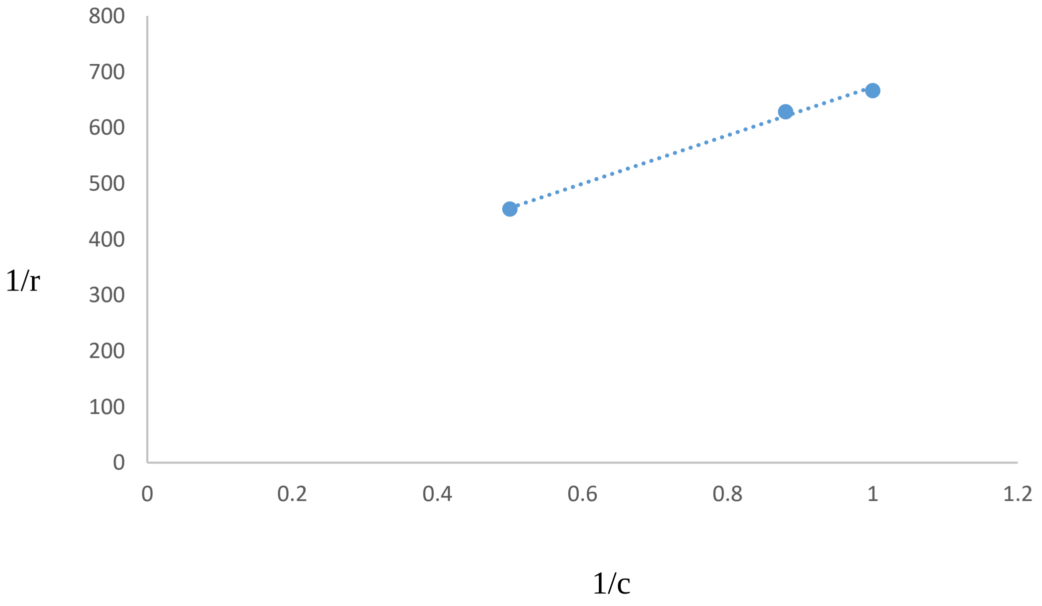


Figure 11: Plot of 1/r versus 1/c of Photocatalytic Degradation of Ethylparaben

From the figure 11 above, Plots of the inverse of initial reaction rate, $(\text{rate})^{-1}$ versus the reciprocal of the initial concentration of ethylparaben, $(\text{C})^{-1}$ was found to be linear with non-zero intercept. The apparent rate constant kn was determined to be 0.0041014 $\text{molL}^{-1}\text{min}^{-1}$ and the absorption coefficient K, was found to be 0.56874 mol^{-1}.

From the graph, kn = 0.0041014 $\text{molL}^{-1}\text{min}^{-1}$, K= 0.56874 mol^{-1} and R^2 = 0.9959. The Langmuir–Hinshelwood (L–H) kinetics model has been successfully used to describe solid–liquid reactions. There is generally a good fit with R^2 values above 0.96 in all cases (Zugle & Nyokong, 2012). The fact that R^2 value is equal to or greater than 0.96 means that the photo catalytic reactions of parabens, ethylparaben and zinc oxide, do follow the first order reaction kinetics and can be used to establish the fact that all organic pollutants do obey the first order kinetics as the data of this study was fitted well to the L-H kinetic model.

GC-MS Analysis of the Degraded Products

The products and the intermediates produced during the photocatalytic degradation of Ethylparaben by ZnO under UV-Visible analysis were detected by GC-MS- QP2020.

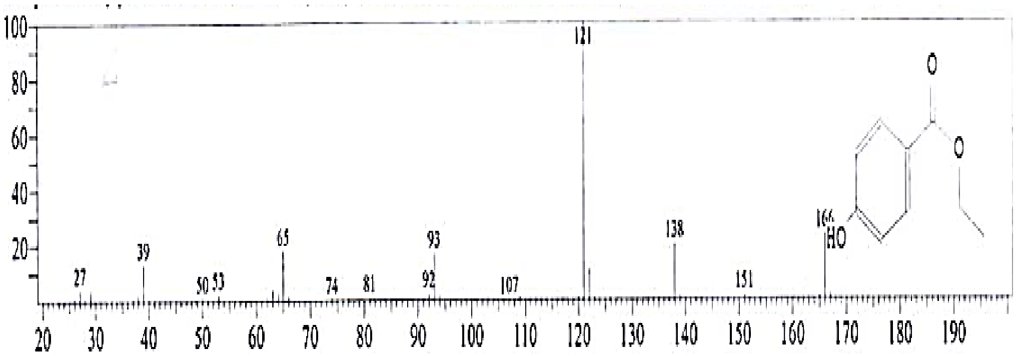


Figure 12: Mass Spectrum of Degradation Products for Ethylparaben

Gas chromatography-mass spectrometry (GC-MS) electron ionization mass spectra was used for the analysis of the degraded extract. The 70-eV high-resolution electron ionization (EI) mass spectra for ethylparaben, was obtained by analysis with gas chromatography-mass spectrometry, GCMS – QP2020. The mass spectrum of ethylparaben in Figure 12 is a spectrum of its free base resulting from thermal dissociation when the compound was vaporized. The positive ion peak at m/z 166 represents the molecular ion peak. This peak was as a result of the loss of an electron from the molecule which was removed by the impacting electron beam. It is commonly referred to as the molecular ion peak ($M^{+\bullet}$), which is highly energetic and thus produced series of fragment ions at, m/z 151, 138, 121, 92, 93, Figure 12. The outstanding feature in this mass spectrum, Figure 17, was the base peak, which was the most intense peak recorded at m/z 121 which was via a heterolytic cleavage. The presence of the peaks at m/z 92, 93 signifies the presence of benzyl cation or tropylium ion in the molecule. The spectra also showed prominent peak at m/z 151 which signifies loss of an ethyl group or radical via a homolytic cleavage. Also, the presence of the peak at m/z 138 signifies loss of an ethyl group via heterolytic cleavage. There were additional prominent peaks at m/z 81, 74, 65, 50, 53 and 39 all resulting from loss of the side chain. The mass spectrum from this analysis matches with the mass spectrum for ethylparaben from the National Institute of Standards and Technology (NIST) Mass Spectra database. The retention index for this analysis which was recorded at the value of 1380 also has satisfactory match with the reference retention index for ethylparaben.

On the basis of gas chromatography-mass spectrometry (GC-MS) findings; Figure 12 above gives the possible degradation pathway for the Ethylparaben photocatalytic degradation. Some of the products and their mass-to-charge ratio obtained were 1-Phenoxypropan-2-ol (152), 2-Phenyloxirane or (1,2-Epoxyethyl)benzene (120), Benzeneacetaldehyde or Phenylacetaldehyde (120), 1,2-Dihydrocatechol(112) or (3,5-Cyclohexadiene-1,2-diol), Bicyclo [2.2.1]heptan-2-ol,exo-(112) or (exo-Norbornyl alcohol), and Bicyclo[2.2.1] heptan-2-ol(112).

Expected Products

Some of the expected products and their mass-to-charge ratio were ethyl paraben (166), phenol (94), benzoic acid (121), methyl paraben (151), 4-hydroxybenzoic acid (137), 3,4-Dihydroxybenzoic acid (154), 2,4-Dihydroxybenzoic acid (154), hydroquinone (112) and ethane (29).

New Products Obtained

Some of the new products and their mass-to-charge ratio obtained were 1-Phenoxypropan-2-ol (152), 2-Phenyloxirane or (1,2-Epoxyethyl)benzene (120), Benzene acetaldehyde or Phenyl acetaldehyde (120), Bicyclo [2.2.1]heptan-2-ol,exo- (112) or (exo-Norbornyl alcohol), and Bicyclo [2.2.1]heptan-2-ol.

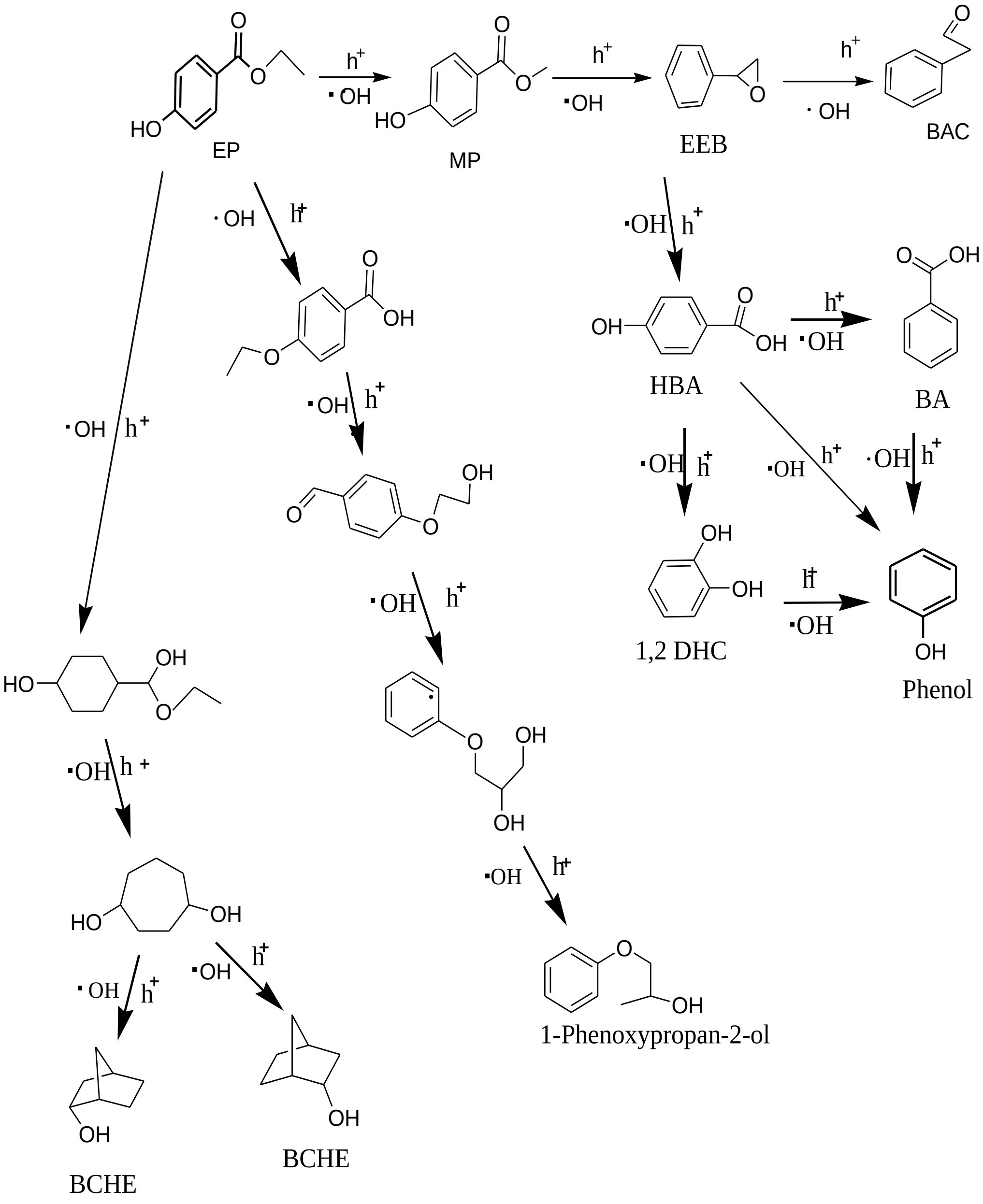


Figure 13: Proposed Photocatalytic Transformation Pathway of Ethylparaben

On the basis of gas chromatography-mass spectrometry (GC-MS) findings; Figure 13 above shows the proposed photocatalytic transformation pathway for the Ethylparaben photocatalytic degradation. Some of the products and their mass-to-charge ratio obtained were 1-Phenoxypropan-2-ol (152), 2-Phenyloxirane or (1,2 Epoxyethyl)benzene (120), Benzeneacetaldehyde or

Phenylacetaldehyde (120), 1,2-Dihydrocatechol(112) or (3,5-Cyclohexadiene-1,2-diol), Bicyclo[2.2.1]heptan-2-ol,exo- (112)or (exo-Norbornyl alcohol) , and Bicyclo[2.2.1]heptan-2-ol(112).

From the figure 13 above: EP = Ethylparaben, MP = methylparaben, EEB = (1, 2-Epoxyethyl) benzene, BAC = Benzeneacetaldehyde, HBA = 4-hydroxybenzoic acid, BA = benzoic acid, BCHE = Bicyclo [2.2.1] heptan-2-ol, exo, 1,2-DHC = 1,2-Dihydrocatechol.

Some of the products such as Bicyclo[2.2.1]heptan-2-ol and Phenylacetaldehyde are not toxic or harmful to the environment. The Phenylacetaldehyde is used in the synthesis of polyesters where it serves as a rate-controlling additive during polymerization reaction. The Bicyclo[2.2.1]heptan-2-ol is used in perfumes. It also aids the digestive system by stimulating the production of gastric juices, improves circulation, relieves pain and reduces swelling.

Chapter Summary

This chapter presents the main points or results of this research. All the findings from conducting of this research has been presented in this Chapter. It includes and discusses the results of the absorption spectral features of the ethyl paraben used for the analysis, the performance of photocatalytic removal of the ethylparaben using zinc oxide (ZnO) at varied initial concentrations and pH under sunlight and UV-Visible light irradiation, the high performance liquid chromatographic (HPLC) analysis of ethylparaben, the kinetic study on the photocatalytic reaction based on a Langmuir-Hinshelwood (L-H) kinetic model, and the gas chromatography-mass spectrometry (GC-MS) analysis of the degraded products.

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Overview

This chapter is the conclusion of the report. It deals with the summary of the entire work. Conclusions and recommendations are also stated in this chapter.

Summary

The main aim of this study was to photo degrade (or photo convert) ethylparaben by using Zinc Oxide photocatalyst under UV-Visible light and sunlight irradiation. UV-Visible absorption and HPLC analyses were conducted to determine the purity of the ethylparaben. From the HPLC analysis, the ethylparaben used was pure. Photocatalytic experiments were carried out and UV-Visible Spectrophotometer was used to monitor the absorption spectra and degradation profile of ethylparaben. Kinetic study was conducted to determine the kinetics of reaction of ethylparaben and GC-MS analysis was conducted to identify some of the degraded products of ethylparaben.

From the photocatalytic degradation experiment, the maximum absorption peak at wavelength 256 nm corresponding to ethylparaben molecules, decreased gradually as the exposure of time increased and almost disappeared after 180 minutes of Sunlight/ZnO photocatalysis. The gradual reduction of the peak at wavelength 256 nm indicates the breakage of bonds in ethylparaben molecules which led to its removal or degradation. The decreased in absorbance showed the reduction of ethylparaben concentration in the various solutions. The reduction in concentrations was observed where the solutions changed from clear white colorless to deep white colorless solutions.

Also, the curves in the degradation profile merged at different wavelengths for different time intervals at a common point called isosbestic point, labelled (i) in the degradation profile indicates products formation that are UV-active.

The degradation percentage (%) of the Sunlight/ZnO was found to be 63.16 %. This means that the ZnO was effective in degrading or removing ethyl paraben in the sun under magnetic stirring conditions.

The degradation percentage (%) of the UV-Vis/ZnO was found to be 82.2 %. This means that the ZnO was more effecient in degrading or removing ethyl paraben in the ultraviolet visible lamp light source and this might be due the constant supply of the light source and the shorter distance between the light source and the sample solution. There was not any degradation in the dark.

The best initial ethylparaben concentration determined was 0.0361 mM which achieved the highest degradation percentage of 82.2 % after 180 minutes of ultra violet lamp light irradiation. For higher initial ethylparaben concentration at 0.0602 Mm, 0.0723 Mm, and 0.12 Mm, the achieved degradation percentage were 24.7 %, 22.62 % and 24.74 %, respectively at similar light irradiation time. Thus, the smaller the concentration the higher the degradation percentage. Because as the concentration is increased, more molecules are produced on the ZnO photocatalyst surface thereby reducing or blocking the amount of light reaching the surface of the ZnO photocatalyst surface and hence less degradation efficiency.

The optimum pH which corresponded to the highest degradation percentage of 73.9 % was pH 10.4, which was the basic pH. Additionally, the percentages of degradation at pH 3.3 and pH 6.7 were comparable and gave a value of 4.87 % and 63.16 %, respectively. The ethylparaben degradation was least efficient at pH 3.3 with a degradation percentage of 4.87 %. The degradation or removal of ethylparaben was less efficient in acidic medium and highly efficient in basic medium.

From the kinetic studies, it was observed that as the initial concentration of ethylparaben increases, the k_{app} values also decreases. Thus, the higher the concentration, the smaller the k_{app} value. The apparent rate constant kn was determined to be 0.0041014 $molL^{-1}min^{-1}$ and the absorption coefficient K, was found to be 0.56874 mol^{-1} and $R^2 = 0.9959$. The Langmuir– Hinshelwood (L–H) kinetics model has been successfully used to describe solid–liquid reactions. There was generally a good fit with R^2 values above 0.96 in all cases. The fact that R^2 value is equal to or greater than 0.96 means that the photo catalytic reactions of parabens, ethylparaben and zinc oxide, do follow the first order reaction kinetics and can be used to establish the fact that all organic pollutants do obey the first order kinetics as the data of this study was fitted well to the L-H kinetic model.

Some of the products obtained are 1-Phenoxypropan-2-ol (152), 2-Phenyloxirane or (1,2-Epoxyethyl)benzene (120), Benzeneacetaldehyde or Phenylacetaldehyde (120), 1,2-Dihydrocatechol(112) or (3,5-Cyclohexadiene-1,2-diol), Bicyclo[2.2.1]heptan-2-ol,exo- (112)or (exo-Norbornyl alcohol) , and Bicyclo[2.2.1]heptan-2-ol(112).

Some of the expected products are ethylparaben (166), phenol (94), benzoic acid (121), methylparaben (151), 4-hydroxybenzoic acid (137), 3,4-

Dihydroxybenzoic acid (154), 2,4-Dihydroxybenzoic acid (154), hydroquinone (112) and ethane (29).

Some of products such as Bicyclo[2.2.1]heptan-2-ol and Phenylacetaldehyde are not toxic or harmful to the environment. Bicyclo[2.2.1]heptan-2-ol is used in perfumes and Phenylacetaldehyde is in the synthesis of polyesters.

The zinc oxide photocatalyst was successfully used to degrade the ethyl paraben. The ethylparaben used was pure as a single clear peak was obtained from the high-performance liquid chromatographic (HPLC) analysis. The degradation percentage (%) of the UV-Vis/ZnO was found to be 82.2 %. The degradation percentage (%) of the Sunlight/ZnO was found to be 63.16 %. This means that the ZnO was more effecient in degrading or removing ethylparaben in the ultraviolet visible lamp light source than in the sunlight irradiation and this may be due the constant supply of the light source from the ultra violet lamp and the shorter distance between the light source and the sample solutions. The pH of the ethylparaben natural solution was slightly acidic (pH 6.7) with a degradation percentage of 63.16 %, the degradation of ethylparaben in a highly acidic medium (pH 3.3) with a degradation percentage of 4.87 % and the degradation of ethylparaben a highly basic medium (pH 10.4) with the degradation percentage of 73.9 %. This means there is a high degradation percentage of ethylparaben in basic medium than in acidic medium or environment.

Conclusions

In conclusions, the ZnO photocatalyst was effective in the degradation of ethylparaben under UV-Visible light as well as sunlight irradiation. The smallest concentration gave the highest degradation percentage and therefore the smaller the initial concentration, the higher the degradation percentage. There is a higher degradation percentage of ethylparaben in the basic medium than in the acidic medium or environment. The kinetic dada of this study was in accordance to the L-H first-order kinetic model. On the basis of GC-MS findings, a possible degradation pathway for the ethylparaben photocatalytic degradation was achieved. This has demonstrated that ZnO photocatalyst is highly suitable to be applied in photocatalytic degradation of organic pollutants such as parabens. Some of the degraded products obtained from the GC-MS analysis are not toxic or harmful to the environment.

Recommendations

For this study, at the start of the reaction, only ethanol was used to dissolve the ethylparaben and to carry out the degradation reaction with zinc oxide in the sun and uv lamp light irradiation under magnetic stirring conditions but there was no degradation for the UV-Visible absorption spectra analysis due to evaporation of ethanol and so it would be recommended that such a path should not be followed, instead distilled water must be added to the solution prepared in order to reduce evaporation of ethanol in the solution.

Also, infrared spectra analysis can be carried out to find the kind of bond that gave rise to the maximum or highest absorption peak.

Again, other catalysts can also be tried and other kinetic models should also be investigated.

Finally, different kinds of parabens family (methylparaben, ethylparaben, propylparaben, butylparaben, and so on) are required in a larger sample size to expand and confirm the generalizability of the study.

REFERENCES

Abass, A. & Raoof, S., (2016). *Photocatalytic removal of alizarin yellow R from water using modified zinc oxide catalyst.* Asian Journal of Chemistry, 28, pp.312-316.

Akpan, U. G., & Hameed, B. H. (2009). *Parameters affecting the photocatalytic degradation of dyes using TiO2-based photocatalysts: a review*. Journal of hazardous materials, 170(2-3), 520-529.

Asenjo, N., Santamaría, R., Blanco, C., Granda, M., Álvarez, P. & Menéndez, R., (2013). *Correct use of the Langmuir–Hinshelwood equation for proving the absence of a synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon*. Carbon, 55, pp.62-69.

Bamuza-Pemu, E. E. (2014). *Photocatalytic degradation of phenolic compounds and algal metabolites in water* (Doctoral dissertation, University of Pretoria).

Bellingham, M., & Sharpe, R. M. (2013). *Chemical exposures during pregnancy: Dealing with potential, but unproven, risks to child health.* Scientific Impact Paper 37.

Bhatkhande, D. S., Pangarkar, V. G., & Beenackers, A. A. C. M. (2002). *Photocatalytic degradation for environmental applications–a review. Journal of Chemical Technology & Biotechnology*: International Research in Process, Environmental & Clean Technology, 77(1), 102-116.

Bhatkhande, D. S., Pangarkar, V. G., & Beenackers, A. A. C. M. (2002). Photocatalytic degradation for environmental applications–a review. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, *77*(1), 102-116.

Brausch, J. M. & G. M. Rand (2011) *A review of personal care products in the aquatic environment:* Environmental concentrations and toxicity. Chemosphere, 82, 1518-1532.

Busca, G., Berardinelli, S., Resini, C., & Arrighi, L. (2008). Technologies for the removal of phenol from fluid streams: a short review of recent developments. *Journal of hazardous materials*, *160*(2-3), 265-288.

Calafat, A. M., Ye, X., Wong, L. Y., Bishop, A. M., & Needham, L. L. (2010). *Urinary concentrations of four parabens in the US population: NHANES 2005–2006*. Environmental health perspectives, 118(5), 679.

Canosa, P., I. Rodríguez, E. Rubí, N. Negreira & R. Cela (2006) *Formation of halogenated byproducts of parabens in chlorinated water*. Analytica Chimica Acta, 575, 106-113.

Chung, Y. C., & Chen, C. Y. (2009). *Degradation of di-(2-ethylhexyl) phthalate (DEHP) by TiO 2 photocatalysis.* Water, air, and soil pollution, 200(1-4), 191-198.

Coronado, J. M., & Hernández-Alonso, M. D. (2013). The Keys of Success: TiO_2 as a Benchmark Photocatalyst. In *Design of Advanced Photocatalytic Materials for Energy and Environmental Applications* (pp. 85-101). Springer, London.

Daghrir, R., Drogui, P., & Robert, D. (2013). Modified TiO_2 for environmental photocatalytic applications: a review. *Industrial & Engineering Chemistry Research*, *52*(10), 3581-3599.

Danwittayakul, S., Jaisai, M., & Dutta, J. (2015). Efficient solar photocatalytic degradation of textile wastewater using ZnO/ZTO composites. *Applied Catalysis B: Environmental*, *163*, 1-8.

Darbre, P. D. & A. K. Charles (2010) *Environmental Oestrogens and Breast Cancer:* Evidence for combined involvement of Dietary, Household and Cosmetic xenoestrogens ANTICANCER RESEARCH, 30, 815-827.

Darbre, P. D., & Harvey, P. W. (2008). *Paraben esters: review of recent studies of endocrine toxicity, absorption, esterase and human exposure, and discussion of potential human health risks.* Journal of applied toxicology, 28(5), 561-578.

Di Paola, A., García-López, E., Marcì, G., & Palmisano, L. (2012). A survey of photocatalytic materials for environmental remediation. *Journal of hazardous materials*, *211*, 3-29.

Diamanti-Kandarakis, E., Bourguignon, J. P., Giudice, L. C., Hauser, R., Prins, G. S., Soto, A. M., ... & Gore, A. C. (2009). Endocrine-disrupting chemicals: an Endocrine Society scientific statement. *Endocrine reviews*, *30*(4), 293-342.

Fessenden, R. J., & Fessenden, J. S. (1990). *Organic Chemistry* (4th ed.). Belmont, California: Wadsworth, Inc.

Frontistis, Z., Antonopoulou, M., Petala, A., Venieri, D., Konstantinou, I., Kondarides, D. I., & Mantzavinos, D. (2016). *Photodegradation of ethyl paraben using simulated solar radiation and Ag3PO4 photocatalyst. Journal of Hazardous Materials*. https://doi.org/10.1016/j.jhazmat. 2016.04.017.

Golden, R., Gandy, J., & Vollmer, G. (2005). *A review of the endocrine activity of parabens and implications for potential risks to human health*. Critical reviews in toxicology, 35(5), 435-458.

Gore, A. C., Crews, D., Doan, L. L., La Merrill, M., Patisaul, H., & Zota, A. (2014). Introduction to endocrine disrupting chemicals (EDCs)—a guide for public interest organizations and policy makers. In *Endocrine Society* (pp. 1-69).

Guadarrama, P., S. Fomine, R. Salcedo & A. Martínez (2008). *Construction of simplified models to simulate estrogenic disruptions by esters of 4-hydroxy benzoic acid (parabens).* Biophysical Chemistry, 137, 1-6.

Gupta, V. K., Khamparia, S., Tyagi, I., Jaspal, D., & Malviya, A. (2015). Decolorization of mixture of dyes: A critical review.

Gusain, R., Gupta, K., Joshi, P., & Khatri, O. P. (2019). Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. *Advances in colloid and interface science*, *272*, 102009.

Haman, C., Dauchy, X., Rosin, C., & Munoz, J. F. (2015). *Occurrence, fate and behavior of parabens in aquatic environments: a review*. Water Research, 68, 1-11.

Han, J., & Washington, C. (2005). *Partition of antimicrobial additives in an intravenous emulsion and their effect on emulsion physical stability*. International journal of pharmaceutics, 288(2), 263-271.

Harris, D. C. (2010). *Quantitative Chemical Analysis (8th ed.).* New York: W.H. Freeman and Company.

Harvey, P. W., & Darbre, P. (2004). Endocrine disrupters and human health: could oestrogenic chemicals in body care cosmetics adversely affect breast cancer incidence in women? A review of evidence and call for further research. *Journal of Applied Toxicology: An International Journal*, *24*(3), 167-176.

Herrmann, J. M. (1999). *Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants*. Catalysis today, 53(1), 115-129.

Hossaini, A., J. J. Larsen & J. C. Larsen (2000). *Lack of oestrogenic effects of food preservatives (parabens) in uterotrophic assays*. Food and Chemical Toxicology, 38, 319-323.

Huang, W. B., & Chen, C. Y. (2010). *Photocatalytic degradation of diethyl phthalate (DEP)* in water using TiO_2. Water, air, and soil pollution, 207(1-4), 349-355.

Hung, L. J., Tsai, S. S., Chen, P. S., Yang, Y. H., Liou, S. H., Wu, T. N., & Yang, C. Y. (2012). Traffic air pollution and risk of death from breast cancer in Taiwan: Fine particulate matter (PM2. 5) as a proxy marker. *Aerosol and Air Quality Research*, *12*(2), 275-282.

Jewell, C., Bennett, P., Mutch, E., Ackermann, C., & Williams, F. M. (2007). *Inter-individual variability in esterases in human liver.* Biochemical pharmacology, 74(6), 932-939.

Jia, T., Fu, F., Long, F., Min, Z., Zhao, J., Chen, J., & Li, J. (2016). Synthesis, characterization and enhanced visible-light photocatalytic activity of Zn2SnO4/C nanocomposites with truncated octahedron morphology. *Ceramics International*, *42*(12), 13893-13899.

Jia, Z., Duan, X., Zhang, W., Wang, W., Sun, H., Wang, S., & Zhang, L. C. (2016). Ultra-sustainable Fe 78 Si 9 B 13 metallic glass as a catalyst for activation of persulfate on methylene blue degradation under UV-Vis light. *Scientific reports*, *6*(1), 1-10.

Johar, M. A., Afzal, R. A., Alazba, A. A., & Manzoor, U. (2015). Photocatalysis and bandgap engineering using ZnO nanocomposites. *Advances in Materials Science and Engineering*, *2015*.

Jung, O. J., Kim, S. H., & Cheong, K. H. (2001). Photocatalytic degradation of pentachlorophenol (pcp) using ti02 thin films prepared by cvD. b Environmental Engineering Research, 6(4), 199-210.

Jüttner, F., & Watson, S. B. (2007). Biochemical and ecological control of geosmin 2-methylisoborneol in source waters. *Applied and environmental microbiology*, *73*(14), 4395-4406.

Karthik, K., Muneeswaran, N. S., Manjunathachar, H. V., Gopi, M., Elamurugan, A., & Kalaiyarasu, S. (2014). Bacteriophages: effective alternative to antibiotics. *Adv Anim Vet Sci*, *2*(3S), 1-7.

Kawaguchi, M., K. Morohoshi, J. Masuda, G. Watanabe, M. Morita, H. Imai, K. Taya & T. Himi (2009b). *Maternal Isobutyl-Paraben Exposure decreases the Plasma Corticosterone Level in ams and Sensitivity to Estrogen in Female Offspring Rats*. Journal of veterinary medical science, 71, 1027-1033.

Klán, P., & Wirz, J. (2009). *Photochemistry of organic compounds: from concepts to practice*. John Wiley & Sons.

Konstantinou, I. K., & Albanis, T. A. (2004). *TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review.* Applied Catalysis B: Environmental, 49(1), 1-14.

Kumar, K. V., Porkodi, K., & Selvaganapathi, A. (2007). Constrain in solving Langmuir–Hinshelwood kinetic expression for the photocatalytic degradation of Auramine O aqueous solutions by ZnO catalyst. *Dyes and Pigments*, *75*(1), 246-249.

Lam, S. M., Sin, J. C., & Mohamed, A. R. (2010). *Parameter effect on photocatalytic degradation of phenol using TiO2-P25/activated carbon (AC).* Korean Journal of Chemical Engineering, 27(4), 1109-1116.

Lee, K. M., Lai, C. W., Ngai, K. S., & Juan, J. C. (2016). Recent developments of zinc oxide based photocatalyst in water treatment technology: a review. *Water research*, *88*, 428-448.

Luk, M. K. (2016). *Photocatalytic Degradation and Chlorination of Azo Dye in Saline Wastewater* (Doctoral dissertation, UTAR).

Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (2009). Catalysis Today, 147(1), 1-59.

Mehrotra, K., Yablonsky, G. S., & Ray, A. K. (2005). *Macro kinetic studies for photocatalytic degradation of benzoic acid in immobilized systems*. Chemosphere, 60(10), 1427-1436.

Melchionna, M., Prato, M., & Fornasiero, P. (2016). Mix and match metal oxides and nanocarbons for new photocatalytic frontiers. *Catalysis Today*, *277*, 202-213.

Modirshahla, N., Hassani, A., Behnajady, M. A., & Rahbarfam, R. (2011). *Effect of operational parameters on decolorization of Acid Yellow 23 from wastewater by UV irradiation using* ZnO and ZnO/SnO2 photocatalysts. Desalination, 271(1-3), 187-192.

Naidu, R., Espana, V. A. A., Liu, Y., & Jit, J. (2016). Emerging contaminants in the environment: risk-based analysis for better management. *Chemosphere*, *154*, 350-357.

Nakagawa, Y. & P. Moldéus (1998). *Mechanism of p-Hydroxybenzoate Ester-induced mitochondrial dysfunction and cytotoxicity in isolated rat hepatocytes. Biochemical pharmacology, 55(11), 1907-1914.*

Nakata, H., Shinohara, R. I., Nakazawa, Y., Isobe, T., Sudaryanto, A., Subramanian, A., ... & Kim, E. Y. (2012). Asia–Pacific mussel watch for emerging pollutants: distribution of synthetic musks and benzotriazole UV stabilizers in Asian and US coastal waters. *Marine Pollution Bulletin*, *64*(10), 2211-2218.

Neidig, C. P., & Burrell, H. (1944). *The esters of p-hydroxybenzoic acids as preservatives.* Drug and Cosmetic Industry, 54(4), 408-410.

Nicoli, S., F. Zani, S. Bilzi, R. Bettini & P. Santi (2008). *Association of nicotinamide with parabens: Effect on solubility, partition and transdermal permeation*. European Journal of Pharmaceutics and Biopharmaceutics, 69, 613-621.

Okubo, T., Yokoyama, Y., Kano, K., & Kano, I. (2001). *ER-dependent estrogenic activity of parabens assessed by proliferation of human breast cancer MCF-7 cells and expression of ERα and PR*. Food and Chemical Toxicology, 39(12), 1225-1232.

Ollis, D. F., Pelizzetti, E., & Serpone, N. (1991). *Photocatalyzed destruction of water contaminants*. Environmental Science & Technology, 25(9), 1522-1529.

Ong, S. A., Min, O. M., Ho, L. N., & Wong, Y. S. (2012). Comparative study on photocatalytic degradation of mono azo dye acid orange 7 and methyl orange under solar light irradiation. *Water, Air, & Soil Pollution*, *223*(8), 5483-5493.

Pavia, D. L., Lampman, G. M., & Kriz, G. S. (2001). Introduction to Spectroscopy (3rd ed.). USA: Thomson Learning, Inc. performance in adult male rats. NEUROSCIENCE RESEARCH, 65, 136-140.

Pichat, P. (2013). Self-cleaning materials based on solar photocatalysis. *New and Future Developments in Catalysis: Solar Photocatalysis*, *7*, 167-190.

Pozzo, A. D., & Pastori, N. (1996). *Percutaneous absorption of parabens from cosmetic formulations.* International journal of cosmetic science, 18(2), 57-66.

Priyanka, N. S., & Srivastava, M. N. (2013). Bandwidth enhancement for microstrip patch antenna using suspended techniques for wireless applications. *International Journal of Advancements in Research & Technology*, *2*(5).

Pugazhendhi, D., Pope, G. S., & Darbre, P. D. (2005). *Oestrogenic activity of p-hydroxybenzoic acid (common metabolite of paraben esters) and methylparaben in human breast cancer cell lines*. Journal of Applied Toxicology, 25(4), 301-309.

Pung, S. Y., Lee, W. P., & Aziz, A. (2012). *Kinetic study of organic dye degradation using ZnO particles with different morphologies as a photocatalyst.* International Journal of Inorganic Chemistry, 2012.

Rajeshwar, K. (1995). *Photoelectrochemistry and the environment*. Journal of applied electrochemistry, 25(12), 1067-1082.

Raven P. H., Losos J.B., Johnson G.B., & Singer S.R. (2005). *Biology. (7th ed). New York, America*. McGraw-Hill Companies, Inc., pp: 993-995.

Rudel, R. A. & L. J. Perovich (2009*) Endocrine disrupting chemicals in indoor and outdoor air.Atmospheric Environment, 43(1), 170-181.*

Sakthivel, S., Neppolian, B., Shankar, M. V., Arabindoo, B., Palanichamy, M., & Murugesan, V. (2003). *Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO*2. *Solar energy materials and solar cells*, *77*(1), 65-82.

Sharma, S. K., & Sanghi, R. (Eds.). (2012). *Advances in water treatment and pollution prevention*. Springer Science & Business Media.

Silverstein, R. M., Webster, F. X., & Kiemle, D. J. (2005). *Spectrometric Identification of Organic Compounds (7th ed.).* New York: John Wiley & Sons, Inc.

Singh, K., & Arora, S. (2011). Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. *Critical reviews in environmental science and technology*, *41*(9), 807-878.

Skoog, D. A., Holler, J. F., & Crouch, S. R. (2007). *Principles of Instrumental Analysis (sixth ed.).* UAS: Thomson BrooksCode.

Skoog, D. A., West, D. M., Holler, J. F., & Crouch, S. R. (2014). *Skoog and West's Fundamental of Analytical Chemistry (9th ed.).* United Kingdom: Cengage Learning, Inc.

Sobana, N., & Swaminathan, M. (2007). The effect of operational parameters on the photocatalytic degradation of acid red 18 by ZnO. *Separation and purification technology*, *56*(1), 101-107.

Soni, M. G., Carabin, I. G., & Burdock, G. A. (2005). *Safety assessment of esters of p-hydroxybenzoic acid (parabens).* Food and chemical toxicology. Food and Chemical Toxicology, 43(7), 985–1015.

Soni, M. G., Carabin, I. G., & Burdock, G. A. (2005). Safety assessment of esters of p-hydroxybenzoic acid (parabens). *Food and chemical toxicology*, *43*(7), 985-1015.

Subagio, D. P., Srinivasan, M., Lim, M., & Lim, T. T. (2010). Photocatalytic degradation of bisphenol-A by nitrogen-doped TiO2 hollow sphere in a vis-LED photoreactor. Applied Catalysis B: Environmental, 95(3-4), 414-422.

Tasukamoto, H., & Terada, S. (1964). *Metabolism of drugs. XLVII. Metabolic fate of p-hydroxybenzoic acid and its derivatives in rabbit*s. Chemical and Pharmaceutical Bulletin, 12, 765-769.

Tay, K. S., N. A. Rahman & M. R. B. Abas (2010) *Ozonation of parabens in aqueous solution: Kinetics and mechanism of degradation*. Chemosphere, 81, 1446-1453.

Terasaka, S., Inoue, A., Tanji, M., & Kiyama, R. (2006). *Expression profiling of estrogen-responsive genes in breast cancer cells treated with alkylphenols, chlorinated phenols, parabens, or bis-and benzoylphenols for evaluation of estrogenic activity*. Toxicology letters, 163(2), 130-141.

Terasaka, S., Inoue, A., Tanji, M., & Kiyama, R. (2006). Expression profiling of estrogen-responsive genes in breast cancer cells treated with alkylphenols, chlorinated phenols, parabens, or bis-and benzoylphenols for evaluation of estrogenic activity. *Toxicology letters*, *163*(2), 130-141.

Thiruvenkatachari, R., Kwon, T. O., & Moon, I. S. (2005). *A total solution for simultaneous organic degradation and particle separation using photocatalytic oxidation and submerged microfiltration membrane hybrid process*. Korean Journal of Chemical Engineering, 22(6), 938-944.

Tsai, W. T., Lee, M. K., Su, T. Y., & Chang, Y. M. (2009). *Photodegradation of bisphenol-A in a batch TiO_2 suspension reactor*. Journal of Hazardous Materials, 168(1), 269-275.

Watson, J. T., & Sparkman, O. D. (2007). *Introduction to mass spectrometry: instrumentation, applications, and strategies for data interpretation*. John Wiley & Sons.

Yao, J., & Wang, C. (2010). *Decolorization of methylene blue with sol via UV irradiation photocatalytic degradation. International Journal of Photoenergy, 2010.*

Yawalkar, A. A., Bhatkhande, D. S., Pangarkar, V. G., & Beenackers, A. A. C. M. (2001). Solar-assisted photochemical and photocatalytic degradation of phenol. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, *76*(4), 363-370.

Ye, X., Bishop, A. M., Reidy, J. A., Needham, L. L., & Calafat, A. M. (2006). *Parabens as urinary biomarkers of exposure in humans*. Environmental health perspectives, 114(12), 1843.

Ye, X., Wong, L. Y., Jia, L. T., Needham, L. L., & Calafat, A. M. (2009). *Stability of the conjugated species of environmental phenols and parabens in human serum*. Environment international, 35(8), 1160-1163.

Zu, S. Z., & Han, B. H. (2009). Aqueous dispersion of graphene sheets stabilized by pluronic copolymers: formation of supramolecular hydrogel. *The Journal of Physical Chemistry C*, *113*(31), 13651-13657.

Zugle, R., & Nyokong, T. (2012). *Journal of Molecular Catalysis A : Chemical Physico-chemical properties of lutetium phthalocyanine complexes in solution and in solid polystyrene polymer fibers and their* *application in photoconversion of 4-nitrophenol.* “Journal of Molecular Catalysis. A, Chemical,” 358, 49–57. https://doi.org/10.1016/j.molcata.2012.02.010.