An-Najah National University
Faculty of Graduate Studies

Purification of Agricultural Soil from Organic Contaminants by Solar-Driven Photo-degradation with ZnO Nanoparticles: Laboratory and Pilot-Plant Scale Study

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Dedication

I am so glad – at the end of my work- to offer the dedication to each of:

The first teacher of human, Prophet Mohammad (pbuh),

To my beloved husband (Shaher), to my children (Yousuf & Mariam), to my mother and my father, to my sister (Worood), and my brother (Othman), to my mother and my father in law and to my sister in law (Shireen), last but no way least to all my relatives & friends for their continuous support and encouragement with my love.

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الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

Purification of Agricultural Soil from Organic Contaminants by Solar-Driven Photo-degradation with ZnO Nanoparticles: Laboratory and Pilot-Plant Scale Study

تنقية التربة الزراعية من الملوثات العضوية باستخدام الطاقة الشمسية مع دقائق أكسيد الزنك النانوية: دراسة مخبرية وميدانية

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Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degrees or qualifications.

Student's name: اسم الطالبة: رزان احمد علي ضرغم

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Date: التاريخ: ٢٣/٢/٢٠١٥م

List of Abbreviations

Symbol	Abbreviation
3-chlorophenol	3-cp
AOP	Advanced oxidation processes
POPs	Persistent organic pollutants
UV	Ultraviolet light
eV	Electron volt
VB	Valence band
CB	Conduction band
E_bg	Energy band gap
e^-	Electron
h^+	Hole
Abs	Absorbance
λ	Wavelength
nm	Nanometer
W/cm^2	Watt per square centimeter
XRD	X-Ray diffraction
PL	Photoluminescence
ppm	Part per million
TN	Turnover number
TF	Turnover frequency
QY	Quantum yield
HPLC	High Performance Liquid Chromatography

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Purification of Agricultural Soil from Organic Contaminants by Solar-Driven Photo-degradation with ZnO Nanoparticles: Laboratory and Pilot-Plant Scale Study

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Abstract

Purification of the agricultural soil from toxic organic contaminants using solar-driven photo-degradation was studied in the present research. This type of degradation was based on the availability of sunlight as a major source of power, low cost catalyst and possible photochemical degradation process.

The aim of this research is to find an effective and a low cost method for mineralization of chlorinated hydrocarbons contaminating agricultural soils. The compound 3-cp, which is a hazardous compound resulting from pesticides use and certain factories residues and pollutes the water and the soil, was chosen here.

The present study involved two types of experiments: The laboratory scale study and the pilot-plant scale study. Two forms of catalyst were used: the lab-prepared ZnO and the commercial ZnO.

The effect of certain factors such as, concentration of the contaminant, irradiation time, pH value, catalyst loading and application method on the contaminant's degradation had been studied. The results showed an increase in the percent photo-degradation when the amount of catalyst and irradiation time were increased. Value of percent photo-degradation was influenced by the concentration of contaminant as it showed a decrease. Acidic medium was found to be more suitable for the contaminant degradation than the basic medium. There were no significant differences between the powder form and spray form of the catalyst. Pilot-plant scale results were consistent with the lab-scale results, as the percent photo-degradation increased as a function of time of time overall 4 days of irradiation. Finally, this method appears to be efficient for the degradation of 3-cp in the lab-scale & in the pilot-plant scale, and by using either of the two forms of ZnO catalyst, lab-prepared and commercial form.

Chapter One

Introduction

Chapter One

Introduction

1.1. Background

Rapid development of science and technology has increased significantly during the last few decades. This development improved human life, industry, agriculture, and transportation. Within this context, large amounts of wastes and hazardous types of pollutants are introduced into the environment as a result of these activities, causing a serious danger which threatens not only human, plant and animal lives, but also the surrounding eco-system [1-3]. Large amounts of chemical products, detergents, pharmaceuticals, pesticides and fertilizers are being produced and consumed with a significant percentage is being released into the air, water and soil resulting in a serious environmental problem[4]. For instance, contamination of groundwater and surface-water sources by industrial effluents and organic pollutants is a growing problem. For example, recent research showed 80% contamination of streams with organic pollutants in USA [5]. Contamination of soil resulting from hazardous chemicals has gained significant attention due to the toxicity and mutagenicity of such pollutants[3, 6]. Most of these organic pollutants are highly toxic and resistant to natural degradation processes. Such pollutants are called; persistent organic pollutants, POPs. They are considered as a global environmental issue that needs to be addressed. Much of the conducted research has focused on solving the pollution problem, definitely, by degradation methods. Physical, chemical and biological remediation methods have been proposed and applied. Photo-catalytic degradation is one of the advanced oxidation processes (AOPs) which proved to be an efficient way in the degradation of various pollutants especially the Chlorophenols [7-20].

1.2 Motivation

As previously mentioned, POPs are considered as a global environmental problem that needs to be addressed due to their harmful properties and environmental effects, among the highly toxic POPs are chlorophenols. Chlorophenols have low biodegradability and have been extensively used in both agricultural and industrial fields. Therefore, there is a need to conduct an efficient process for the degradation and mineralization. One method of choice is to use a suitable photo-catalytic semiconductor like nanoparticle ZnO, which utilizes clean solar light source.

1.3. Objectives

1.3.1. Strategic Objective:

The strategic objective of this work is to purify the agricultural soil from 3-cp contaminant due to its toxicological effects on human and environment and due to its persistence to degradation, as they are considered one of the metabolites of many insecticides and fungicides. Purification includes degradation of the contaminant that could be done by using nanoparticles of Zinc oxide (ZnO) catalyst. ZnO was prepared at An-

Najah University Laboratory and compared with the available commercial form. This catalyst is characterized by its low cost and efficiency under direct sunlight.

1.3.2 Technical Objectives:

The technical objectives of this work include:

1- To prepare the nanoparticle ZnO catalyst: lab-prepared and commercial forms to be used for degradation of chlorophenol and soil purification.

2- To characterize the two forms of catalysts using XRD, UV/Visible spectra, and other techniques.

3- To compare the characteristics of the two forms of the catalyst in terms of their efficiency in degradation of the contaminant under the laboratory conditions (laboratory scale study).

4- To study the effect of certain parameters on photo-degradation of the contaminant such as the concentration, irradiation time, pH value, catalyst concentration and its form.

5- To apply the results obtained from the laboratory scale study for the pilot plant scale study to optimize the best conditions for degradation of the contaminant.

1.4. Hypothesis

The following hypotheses need to be investigated through the experimental part:

1- The present research offers an efficient degradation and mineralization process of 3-cp using sun light source.

2- 3-cp which is a widespread pesticide metabolite in agricultural soil that needs to be degraded and removed from the soil.

3- ZnO is known to be cheap and serves as a good catalyst for the photo-degradation of the contaminant due to its efficiency in absorbing UV light.

4- No adsorption of contaminant molecules usually occurs on the soil surface.

1.5. Novelty of the Present Study

The stability of chlorophenols results in accumulation in the environment and poses a threat to human due to their toxicity. Degradation of chlorophenols is an active area of research and is considered as one of the most important challenges for the researchers and scientists because of their stability. The novelty of this work is relying on using ZnO semiconductor as a catalyst in the degradation of 3-cp contaminant. The choice of this method was based on the relatively high efficiency of ZnO, its low cost, and its advantage of being a fertilizer, which supports this work. On the other hand, solar light is a cheap and available source of energy. Moreover, novelty appears in the application of pilot-plant scale study to simulate the field conditions for the degradation of the contaminant.

1.6. Thesis Overview

The general outline of this thesis could be summarized as follows:

Chapter 1 involves a brief background about water, air and soil pollution as a result of human activities, motivation for establishing this work, strategic and technical objectives, hypotheses to be investigated and novelty of the research work.

Chapter 2 covers the literature review about organic compounds, their properties in general, and some examples of organic compounds that have been officially banned. It highlights on chlorophenols as the primary focus of this research, their uses, sources, toxicity and health effect and exposure routes. It also focuses on 3-cp as a contaminant model and its properties. The remaining sections of this Chapter are related to the studies about photo-catalytic degradation of chlorophenols, photo-catalytic process and its mechanism and ZnO as a photo-catalyst.

Chapter 3 describes the whole methodology used during experimentation, including materials and equipment used, solutions and catalyst preparation and finally the catalytic process and its mechanism.

Chapter 4 presents the results of the catalytic experiments and their analysis where the first section represents the characterization results of catalyst including UV-spectrophotometry, XRD and PL. The second section investigates the photo-degradation process by presenting results and analysis of parameters studied during the experiment at a laboratory scale and pilot-plant scale.

Chapter 5 offers a general discussion of the results obtained and compares them with previous literature done in this respect.

Chapter 6 gives general conclusions and recommendations for the future research. References and appendices are placed in the latest pages of this thesis

Chapter Two

Literature Review

Chapter Two
Literature Review

Preface

This Chapter starts with a general introduction on persistent organic pollutants, their characteristics and some of these pollutants that have been officially banned. It focuses mainly on chlorophenols and their properties, then it focuses on 3-cp as a contaminant model. The subsequent sections are related to studies about photo-catalytic degradation of chlorophenols, photo-catalytic process and its mechanism and ZnO as a photo-catalyst.

2.1. Persistent Organic Pollutants (POPs)

POPs are synthetic organic chemical substances that persist and accumulate in the environment. They are incorporated into the environment either a direct way by producing these chemicals and using them in agriculture, or an indirect way, which results from industrial processes and combustion of dioxins [21]. Direct incorporation of POPs into the environment is a result of the successful achievements of beneficial results in crop production and pest control, whereas indirect incorporation is done through a variety of industrial applications like, electrical transformers and large capacitors, hydraulic and heat exchange fluids, and additives to paints and lubricants. However, these compounds are characterized by high toxicity and having adverse effects on human health and the whole surrounding environment [22]. And thus, they are considered as a complex environmental problem which needs to be addressed on a global scale. In the recent years, a number of international agreements were signed outlining the disposal, restriction, use and release of POPs [22, 23]. The United Nations Economic Commission for Europe, for example, has adopted a protocol about the POPs in June 1998 in Denmark. The protocol banned the production and use of eight products of these compounds which are aldrin chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene. The protocol severely restricted the use of other products such as dichlorodiphenyltrichloroethane (DDT), Hexachlorocyclohexane (HCH) and polychlorinated biphenyls (PCBs). And by December 2009, an amendment of the protocol was adopted to include other new seven substances which are hexachlorobutadiene, octabromodiphenyl ether, pentachlorobenzene, pentabromodiphenyl ether, perfluorooctanesulfonates, polychlorinated naphthalenes and short-chain chlorinated paraffins [24-27]. The Stockholm Convention on POPs was adopted in 2001 in which the participant parties agreed to stop the production, use, and release of 12 POPs called "Dirty Dozen" shown in table (2.1) .The convention came into implementation by 2004 [28-30].

Table (2.1): Dirty dozen of POPs adopted by the Stockholm Convention, adapted from [31].

POP and CAS no.	Global Historical Use/Source	Overview of U.S. Status
Aldrin, dieldrin 309-00-2, 60-57-1	✓ Insecticides for corn and cotton; ✓ Control termite.	✓ No U.S. registrations; most uses canceled in 1969; all uses by 1987. ✓ All applications on food crops cancelled in 1986. ✓ No production, import, or export.
Chlordane 57-74-9	✓ Insecticide for vegetables, small grains, potatoes, sugar beets, fruits, citrus, and cotton. ✓ Home lawn and garden pests. ✓ Control termites.	✓ No U.S. registrations; most uses canceled in 1978; all uses by 1988. ✓ All applications on food crops cancelled in 1986. ✓ No production (stopped 1997), import, or export. ✓ Regulated as a hazardous air pollutant.
Dioxins, furans 118-74-1, 110-00-9	✓ Unintentionally produced during combustion. ✓ Trace contaminants in certain herbicides, wood preservatives, and in PCB mixtures.	✓ Regulated as hazardous air pollutants (CAA). ✓ Dioxin in the form of 2,3,7,8-TCDD is a priority toxic pollutant (CWA).
DDT 50-29-3	✓ Insecticide for cotton, and insects that carry diseases such as malaria and typhus.	✓ No U.S. registrations; most uses canceled in1972; all uses by 1989. ✓ Applications on food crops cancelled in 1986. ✓ No U.S. production, import, or export. ✓ Priority toxic pollutant (CWA).
Endrin 72-20-8	✓ Insecticide for cotton and grains ✓ Control rodents.	✓ No U.S. registrations; most uses canceled in 1979; all uses by 1984 ✓ No production, import, or export. ✓ Priority toxic pollutant (CWA).

POP and CAS no.	Global Historical Use/Source	Overview of U.S. Status
Heptachlor 76-44-8	✓ Insecticide of soil insects and termites, crop pests and malaria.	✓ Most uses canceled by 1978 ✓ All pesticide applications on food crops cancelled in 1989. ✓ No production, import, or export.
Hexachloro benzene 118-74-1	✓ Fungicide for seed treatment. ✓ An industrial chemical in fireworks, ammunition, synthetic rubber, and other substances. ✓ Unintentionally produced during combustion and manufacturing of certain chemicals. ✓ An impurity in certain pesticides.	✓ No U.S. registrations; all uses canceled by 1985. ✓ No production, import, or export as a pesticide. ✓ Manufacture and use for chemical intermediate (as allowed under the Convention). ✓ Regulated as a hazardous air pollutant (CAA). ✓ Priority toxic pollutant (CWA).
Mirex 2385-85-5	✓ Insecticide of fire ants, termites, and mearly bugs. ✓ Fire retardant in plastics, rubber, and electrical products.	✓ No U.S. registrations; all uses canceled in 1977. ✓ No production, import, or export.
PCBs 1336-36-3	✓ Used in industrial processes and purposes, including in electrical transformers, capacitors, as heat exchange fluids ✓ As paint additives, plastics. ✓ Unintentionally produced during combustion.	✓ Manufacture and new use prohibited in 1978 (TSCA). ✓ Regulated as a hazardous air pollutant (CAA). ✓ Priority toxic pollutant (CWA).
Toxaphene 8001-35-2	✓ Insecticide on crops and pests. ✓ Kill unwanted fish in lakes.	✓ No U.S. registrations; most uses canceled in 1982;all uses by 1990. ✓ All applications on food crops cancelled in1993 ✓ No production, import, or export. ✓ Regulated as a hazardous air pollutant (CAA).

2.2. Chlorophenols

Chlorophenols are synthetic organic chemicals in which one or more hydrogen atoms are replaced by one or more chlorine atoms. They can be classified into mono- , di- , tri- , tetra- and penta- chlorinated phenols. They are good representatives of POPs due to their persistency in the environment and their high toxicity.

2.2.1. Uses of Chlorophenols

Chlorophenols have wide applications in the fields of agriculture and industry. They are used as intermediates in manufacturing of agricultural chemicals, pharmaceuticals, biocides, and dyes [32, 33]. They are also used in synthesis of pigments, phenolic resins, herbicides, pesticides, fungicides, mold inhibitors, disinfectants and wood preservatives [34, 35].

2.2.2. Sources of Chlorophenols

Chlorophenols get into the environment through various sources such as: wastes of industries which produce domestic preservatives, textiles, leather products, petroleum effluents, plastics, resins, iron, steel and forestry industries[32, 36-38]. The widespread utilization of pesticides and herbicides constitute a significant source [39], and they also could result from partial degradation of phenoxy herbicides [40], chlorobenzene and chlorinated hydrocarbons[32].

2.2.3. Toxicity and Health Effect of Chlorophenols

Chlorophenols are well known to be toxic and resistant to degradation. The presence of such contaminants in the environment may affect the quality of air, soil, water, human and animal health and may cause public health hazards. They may cause histopathological alterations, health genotoxicity, mutagenicity, carcinogenicity and other abnormalities in humans and animals. Workers in phenoxy fungicide factories tend to have higher morbidity and mortality percentage due to cancer of respiratory system, lymphoma, and myocardial ischaemia [32].

2.2.4. Exposure to Chlorophenols

Human exposure to chlorophenols can be either through eating or drinking contaminated food and water [39]. Workers' exposure was reported in factories manufacturing chlorinated pesticides or fungicides as well as in industrial incinerator and waste plants through inhalation and direct dermal contact of chlorophenols as they penetrate the skin easily [32].

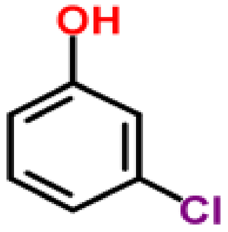
2.2.5. Acute Toxicity of Chlorophenols

There are many ways to measure the acute toxicity of toxic compounds, such as, the lethal dose $_{50}$, LD_{50}, which represents the amount of a substance that causes the death of 50% of a group of test animals, e.g. LD_{50} of 3-cp is 570 mg/Kg rat. The lethal concentration, LC_{50}, which refers to the concentration of the chemical in the air that kills 50% of the test animals during the observation period, is another used parameter. It is also used to measure the concentration of a chemical in water. It is commonly used for toxic pollutants, for example, the LC_{50} values of pentachlorophenol (PCP) and trichlorophenol (TCP), were estimated to be 53 ppm and 19 ppm, respectively in crayfish, in the eighth day at pH of 7.5 & 13°C.

2.3 Contaminant Identification

The target contaminant model in this research is 3- chlorophenol. Table (2.2) summarizes its characteristics.

Table (2.2) : Properties of 3- chlorophenol[41-43].

Structural formula of 3-cp	
Systematic name	3-cp
CAS number	108-43-0
Chemspider ID	13875432
Molecular Formula	C_6H_5ClO
Molecular weight	128.556
SMILES	C1=CC(=CC(=C1)Cl)O
Experimental Melting Point	30-34 °C
Experimental Boiling Point	214 °C
Experimental Gravity	1.245 g/mL
Appearance	yellow solid or liquid crystalline with an unpleasant smell
Stability	Stable. Combustible. Incompatible with acid chlorides, oxidizing agents, acid anhydrides. Discolours in air
Toxicity on human	• Transformed either by breathing or by direct touch • Corrosive chemical and contact can irritate and burn the skin and eyes. • Breathing can irritate the nose, throat and lungs causing coughing, wheezing and shortness of breath. • High exposure can cause headache, dizziness, fatigue, restlessness, muscle weakness, tremors, seizures, coma andeven death. • May damage the liver and kidneys.

2.4. Studies Related to Photo-catalytic Degradation of Chlorophenols

A promising method for the degradation of Chlorophenols is the photo-catalytic oxidation. It is one of the advanced oxidation processes

(AOPs) that proved to be efficient in the degradation of numerous pollutants. The heterogeneous photo-catalysis process has gained wide interest in the purification of water and soil from organic pollutants due to its efficient role in the degradation and mineralization of organic compounds by utilizing solar UV and visible light spectrum and by using semiconductors of suitable band gaps. The derivatives of phenols and their azo dyes are known to be organic contaminants which are continuously introduced into the environment as pesticides and fertilizers and by industrial wastes [44]. Many semiconductor materials have been used as heterogeneous photo-catalysts. ZnO and TiO_2 have been extensively investigated in such processes due to their high capacity of degrading and mineralizing toxic pollutants with fairly simple procedures and due to non-toxic effects and low costs [11, 45-52]. The following studies are examples of related research works about photo-catalytic degradation of organic pollutants by applying zinc oxide and other catalysts. For example, commercial ZnO was used for the degradation and mineralization of aqueous 2-chlorophenol and 2,4-dichlorophenol after 2 hours of irradiation with solar energy and slightly acidic solution [53]. The catalyst proved its efficiency combined with TiO_2 (Degussa P-25 form) in complete degradation of fluorophenol contaminant in 90 minutes[54]. In fact, photo-catalytic activity of ZnO was reported to be higher than TiO_2 in the degradation of phenols and 2-phenylphenol under UV-vis light [55]. Various semiconductor catalysts (ZnO, TiO_2 anatase, ZnS, SnO_2, Fe_2O_3 and CdS) were compared in their efficiencies for the degradation of Acid red 18 under UV irradiation. Higher degradation was achieved by ZnO over TiO_2 anatase and other catalysts[56]. However, it has been reported that ZnO nanostructures doped with silver (Ag), lead (Pb), cobalt (Co) and manganese (Mn) have shown enhanced visible light absorption and photo-catalytic activity [55]. Coupled oxide photo-catalyst was proved to have higher degrading capacity than pure ones. For example, the efficiency of coupled oxide ZnO-SnO_2 has shown significantly higher degrading efficiency of methyl orange (MO) compared to ZnO or SnO_2 alone [57]. There are still many examples of applications of zinc oxide as a photo-catalyst.

2.5. Proposed Photo-catalytic Mechanism

It is well known that the electronic structure of a semiconductor material comprises a highest occupied band filled with electrons called valence band (V.B.) and a lowest unoccupied band called conduction band (C.B.). The two bands are separated from each other by a region called band gap. When a photon of appropriate wavelength owns energy larger than band gap energy, electrons in the V.B. are excited to high energy states in the C.B. leaving positively charged holes in V.B. These electrons and holes make their separate ways towards the surface of the semiconductor for the possibility of interaction with contaminant molecules adsorbed on the catalyst surface and degrade them [58]. Electrons in the C.B. reduce the oxygen into superoxide $\bullet O_2^-$ anion, or the superoxide H_2O_2 which subsequently produce hydroxyl radicals $OH\bullet$. On the other hand the positive holes in the V.B. with a high oxidizing potential, oxidize the contaminant molecules. This occurs either directly, or by reaction with water or hydroxyl anion OH^- producing hydroxyl radicals OH• which in turn react with contaminant molecules causing complete or partial decomposition and mineralization [51, 55, 59-61].

The basic reactions of the above-mentioned process can be summarized as follows[55]:

The photo-excitation of ZnO semiconductor by proper UV light irradiation, resulting in the formation of electron-hole pairs which can be presented by:

$$ZnO + h_v \rightarrow h^+ + e^-$$

The photo-reduction reaction happening in the C.B by electrons:

$$e^- + O_2 \rightarrow \bullet O_2^-$$

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2$$

$$e^- + H_2O_2 \rightarrow OH\bullet + OH^-$$

The photo-oxidation reaction happening by positive holes:

h^+ + organic pollutant →[organic pollutant$^{\bullet +}$]→ degradation

$$h^+ + H_2O \rightarrow H^+ + HO\bullet$$

$$h^+ + OH^- \rightarrow HO\bullet$$

The hole photo-catalysis reaction is:

Organic pollutant +HO•→ intermediates →$CO_2 + H_2O$

The mechanism of photo-catalysis degradation of the whole reaction is represented schematically in Figure (2.1).

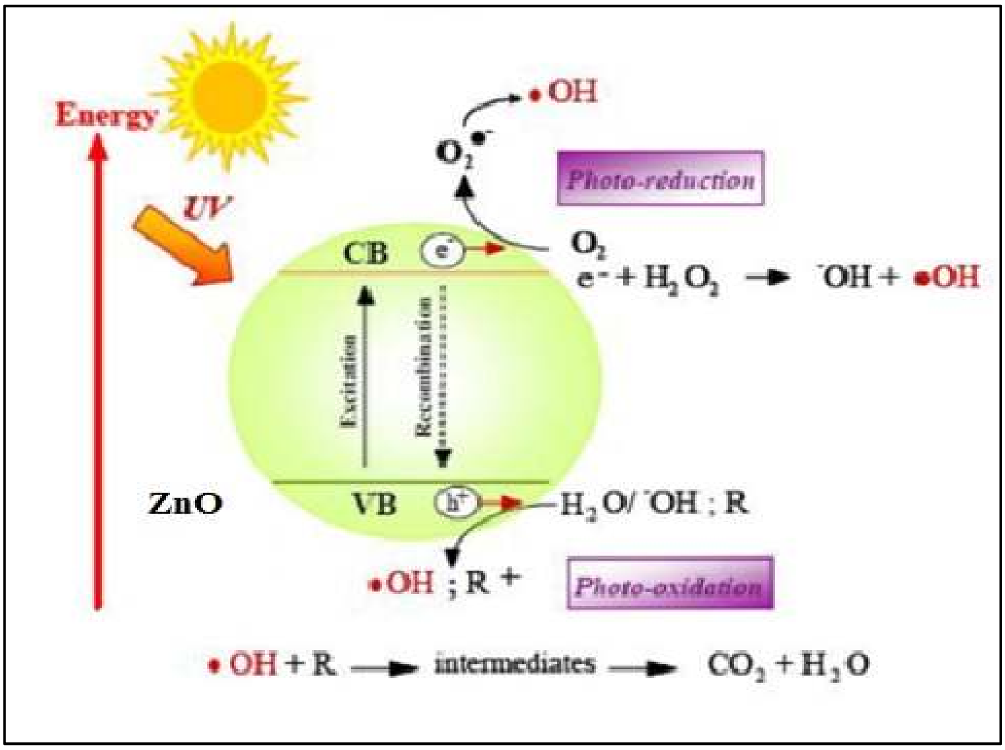


Figure (2.1): Mechanism of photo-catalysis degradation of the whole reaction. Adapted from[59].

The proposed mechanism of the degradation of 3-chlorophenol and the complete mineralization into carbon dioxide and water is shown in **Figure (2.2)** as the hydroxide radicals react with the contaminant molecule forming unstable intermediates, which ends with ring opening and bond breaking that results in forming of carbon dioxide and water. Chlorine radicals may react with each other or with hydrogen radical to form Chlorine or hydrochloric acid, respectively.

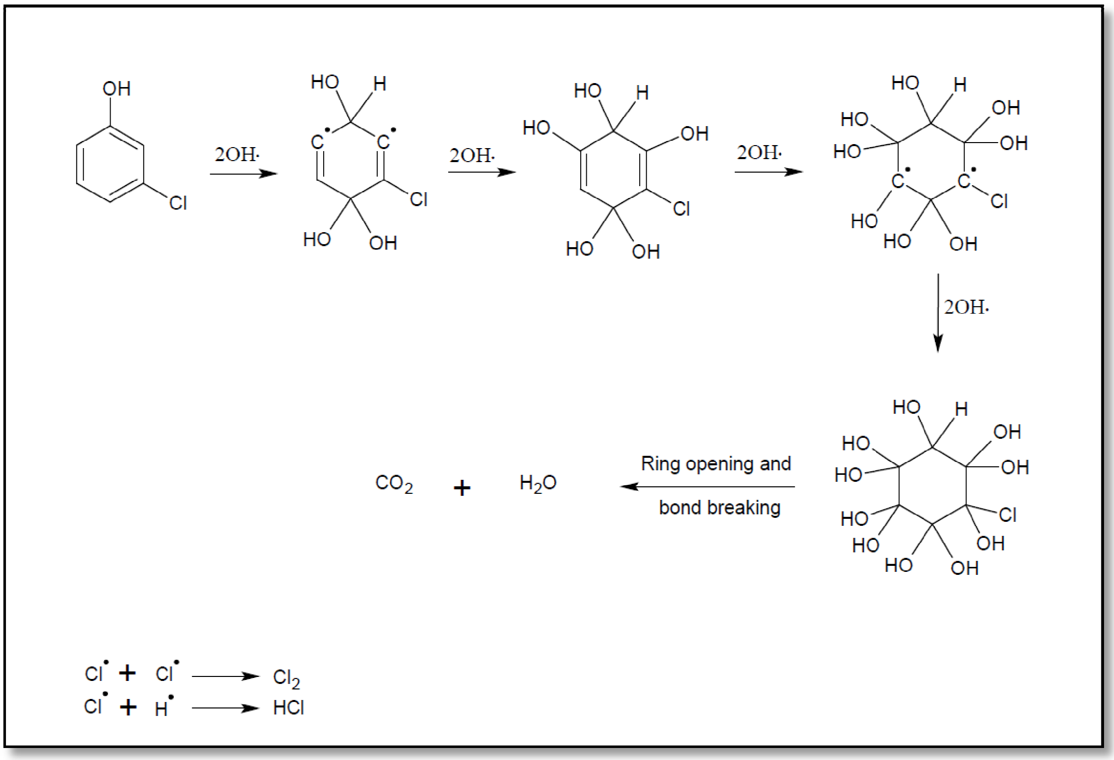


Figure (2.2): Proposed mechanism of the photo-catalysis degradation of 3-chlorophenol contaminant.

2.5.1. Zinc Oxide Photo-catalyst

Several years ago, semiconductors have been extensively introduced in optical and electrical devices. Zinc oxide is one of the promising semiconductors which attracted intensive research efforts due to its considerable features.

2.5.1.1. Crystal Structure

Three main structures can be crystallized by ZnO. The rock-salt, Figure (2.2) (a) is only stable under high pressure and resembles NaCl crystal structure. The cubic zinc blende structure can only be stabilized by epitaxial growth of zinc oxide on cubic lattice structure of substrate. ZnS is a good representative model of this structure, Figure (2.2) (b).

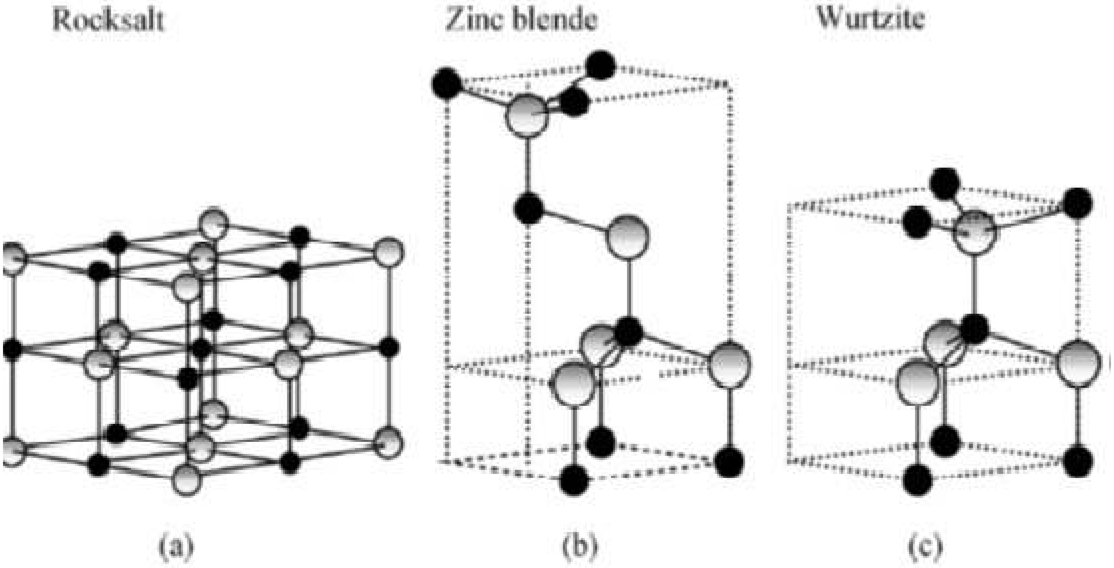


Figure (2.3): Ball and stick representation of ZnO crystal structures, (a) The cubic rock- salt structure, (b) The cubic zinc blende and (c) The hexagonal wurzite ZnO. Where the grey balls represent oxygen, and black balls represent the zinc, respectively, adapted from[62].

The most common and thermodynamically stable crystal structure of ZnO is the hexagonal wurtzite Figure (2.2)(c), with lattice parameters of a = 0.32498 nm, b = 0.32498 nm, c = 0.52066 nm according to JCPS card no. 36-1451 [63]. The corresponding c/a ratio is about 1.6 which is very close to the hexagonal unit cell value (c/a = $\sqrt{8/3}$ =1.633), [64].

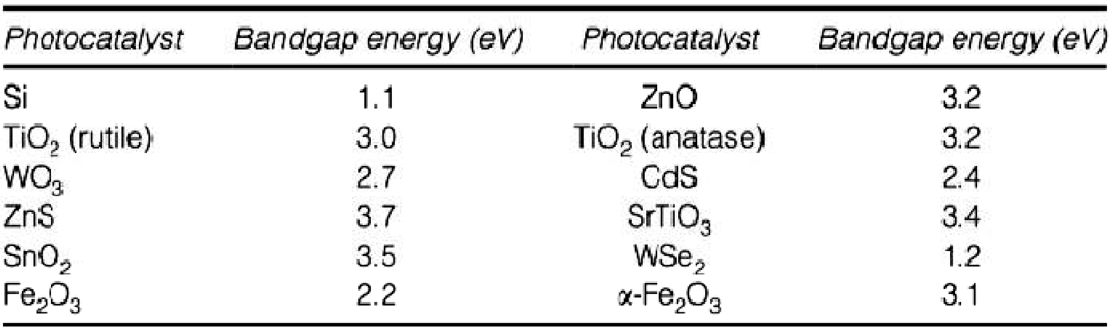
2.5.1.2. Catalyst Applications

ZnO is widely used in microelectronic devices. It can be used as transparent electrodes in solar cells, ultraviolet (UV) light emitters, diode lasers, chemical and gas sensors and room temperature UV LED and laser [65-69]. It can also be used as anti-bacterial agent, anti-reflection coatings and capacitors. Moreover, Zn^{2+} ions are used as fertilizers for some plants [70-73].

2.5.1.3. Catalyst Properties

The vast previously mentioned applications of ZnO may be attributed to its distinguished features, such as, good UV photoconductivity, large band gap energy of about 3.2 eV, Table (2.3), resistance to radiation hardness [74], in addition to its low cost and being environment friendly material [63, 65-69, 74-80].

Table (2.3): Values of band gap energies of some semiconductor photo-catalysts [81].



Photocatalyst	*Bandgap energy (eV)*	*Photocatalyst*	*Bandgap energy (eV)*
Si	1.1	ZnO	3.2
TiO_2 (rutile)	3.0	TiO_2 (anatase)	3.2
WO_3	2.7	CdS	2.4
ZnS	3.7	$SrTiO_3$	3.4
SnO_2	3.5	WSe_2	1.2
Fe_2O_3	2.2	α-Fe_2O_3	3.1

Not all the above semiconductors are stable. For example, n-Si and WO_3 have poor photo oxidation kinetics. CdS is not stable in aqueous media, and metal sulfides and α-Fe_2O_3 may have photo corrosion [55].

In studying catalyst surface charge at different pH values, the zero point charge (pH_{zpc}) of ZnO was found to be 9.0 ± 0.1. Figure (2.3) [53]. This helped in investigating the effect of pH on the photo-catalytic degradation process.

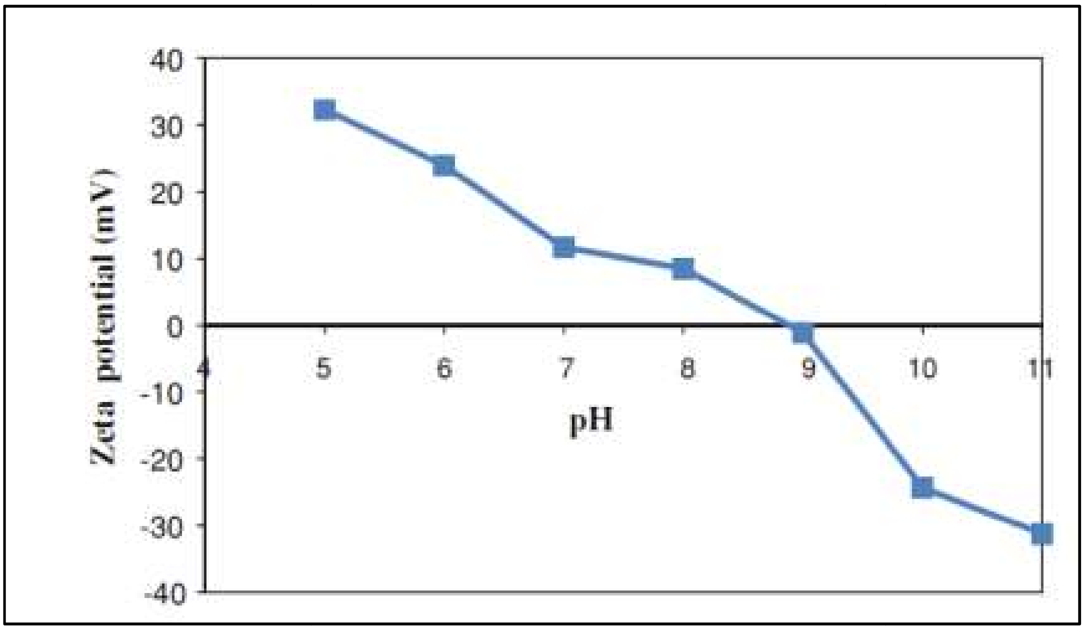


Figure (2.4): Surface charge of ZnO catalyst at various pH values [53].

Chapter Three

Methodology

Chapter Three

Methodology

Preface

This Chapter displays the methodology followed in this research. As it first presents the materials used including chemicals, equipment and devices. Then it describes the experimental part which includes solution and catalyst preparation and the catalytic experiments in its two scales, laboratory and pilot-plant scales.

3.1. Materials

3.1.1. Chemicals

3-chlorophenol (3-cp), corrosive, toxic, M.W. 128.56, b.p. 214 ^{o}C, m.p. 33-35 ^{o}C, Fluka, Catalog no. 25840, Zinc chloride ($ZnCl_2$), commercial powder (ZnO: Catalog no. 205532) were all purchased from Sigma-Aldrich Company. Sodium hydroxide (NaOH), hydrochloric acid (HCl) and ethanol (C_2H_5OH) were purchased from local market.

3.1.2. Petri Dish

Number of petri dishes (of 9 cm diameter) were used as containers for the soil during the lab-scale experiments.

3.1.3. Basins

Five large basins of (50X38 cm^2) were used as containers for soil during the pilot-plant experiment.

3.1.4. The Soil

The agricultural soil for the laboratory and pilot-plant experiments was brought from Qalqilia city and processed as described in Section 3.3.2 below.

3.1.5. Transparent Plastic Sheets

Transparent plastic sheets were used to cover the petri dishes in order to avoid free evaporation, to keep humid conditions during the experiment and to let the solar light penetrate into the soil. The plastic sheets were characterized by using UV-visible absorption & transmittance spectrophotometers as shown in Figure (3.1). The Figure shows that the transparent plastic sheets do not absorb solar energy in the UV region which is suitable for each of ZnO catalyst and the contaminant 3-chlorophenol.

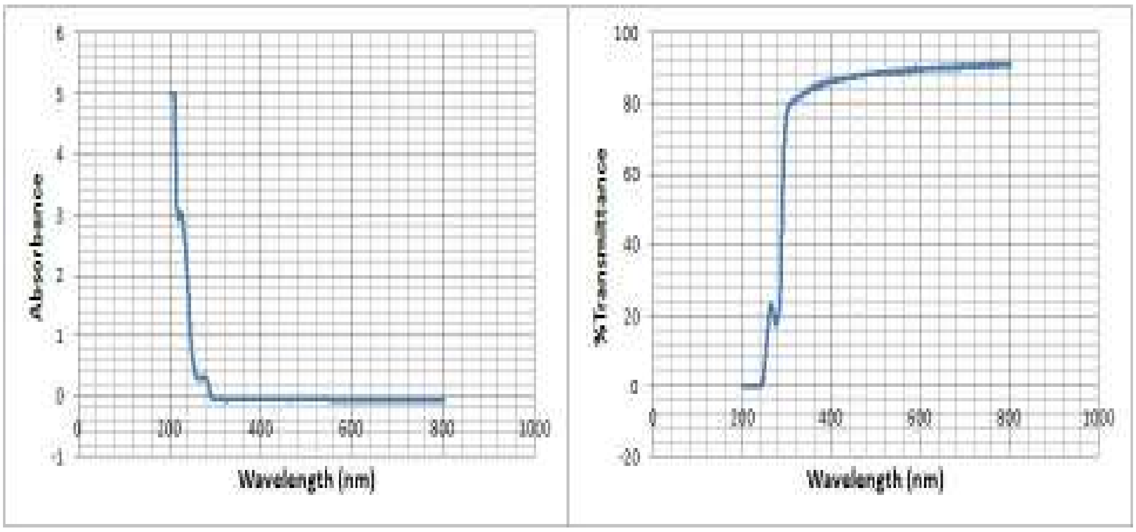


Figure (3.1): Absorbance and transmittance spectra measured for the transparent plastic sheets.

3.2. Equipment

3.2.1. High Performance Liquid Chromatography (HPLC)

HPLC device (SHIMADZU, Diode Array Detector UV, manual, C18 column) was used for the purpose of investigation of photo-degradation of 3-cp contaminant.

3.2.2. UV/Vis Spectrophotometer

Electronic absorption spectra were measured for the remaining concentrations of 3-cp contaminant after the catalytic experiment. A Shimadzu UV-1601 spectrophotometer was used. It was equipped with thermal printer Model DPU-411-040, type 20BE.

3.2.3. Fluorescence Spectrophotometer

Emission fluorescence spectra were measured for ZnO nanoparticle catalyst in its two forms, lab-prepared & commercial in aqueous phase, for their band gaps. Perkin-Elmer LS50 Luminescence Spectrophotometer was used for this purpose.

3.2.4. X-Ray Diffraction

XRD technique was used for the purpose of characterization for both forms of nanoparticle ZnO, (XRD) patterns were measured by using Philips XRD XPERT PRO diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) as a source at laboratories of ICMCB , Bordeaux University.

3.2.5. pH Meter

The effect of pH medium on the photo-degradation process was studied through this research. Values of pH were measured by using Jenway-3510 pH meter.

3.2.6. Lux Meter

Light intensity was measured periodically during the catalytic experiment by using Lux-102 Light Meter. Online convertor was used to convert the resulted values into W/cm^2 unit.

3.2.7. Ultrasound Sonicator

Nanoparticle zinc oxide was prepared in the laboratory and it was continuously sonicated by using "D Lab Tech-LUC465" Ultrasound Sonicator for more than 6 hours.

3.2.8 Centrifuge

A Scientific Ltd-1020 D.E Centrifuge was used for the extraction of 3-cp contaminant from pre-contaminated soil to be ready for UV/Vis spectrophotometric testing.

3.3. Experimental part

3.3.1. Preparation of Solutions

3.3.1.1. Stock Solution of 3-Chlorophenol

Stock solution was prepared by dissolving 1.00 g of 3-cp contaminant in distilled water and dilution to 1.00 L to get 1000 ppm solution of 3-cp. A series of diluted solutions of 100, 200, 300 and 400 ppm were prepared using the stock solution.

3.3.1.2. Other Solutions

Solutions of NaOH and HCl were prepared and used to control the value of pH of the solutions, according to the following procedure:

1. HCl (10.50 mL of 32% V/V) was diluted to 500 mL with distilled water to get a 0.20 M HCl solution.
2. NaOH (4.00g) was dissolved in distilled water. The solution was then diluted to 0.50 L to prepare a 0.20 M solution of NaOH.

3.3.2. Preparation of the Soil

The soil for lab-scale tests was brought from agricultural fields in Qalqilia city. The soil was air dried at 120 ^{o}C for 4 hours and then sieved with the particle size range (600-1180 μm) taken for further use. The soil for pilot-plant scale study was air dried without sieving to simulate the natural field conditions.

3.3.3. Preparation of Catalysts

3.3.3.1. Commercial ZnO Catalyst

Commercial ZnO catalyst was prepared by adding commercial ZnO powder (5.00 g) into distilled water (100 mL) with continuous stirring and then pouring into a jet sprayer

3.3.3.2. Laboratory-Scale ZnO Catalyst

Laboratory-scale ZnO catalyst was prepared by precipitation method at room temperature as follows:

Sodium hydroxide NaOH (25 mL, 9.00 M) was diluted with distilled water, to get 0.9 M aqueous solution of NaOH in a 250-mL volumetric fask. The final solution was then poured into a 500-mL beaker and heated at ~55^{o}C.

Zinc Chloride $ZnCl_2$ (15.25 g) was dissolved in distilled water (200 mL), and then diluted to 250 mL to get an aqueous solution of 0.45 M $ZnCl_2$. The aqueous solution was added slowly drop wise within a 60-minute period to the heated NaOH solution under vigorous magnetic stirring in a beaker. The precipitated white fine nanoparticle of ZnO was rinsed with deionized water 4 times. The precipitate was then made like slurry as a result of the addition of water and was sonicated for more than 6 hours by using ultrasound sonicator. Finally, it was placed in a jet sprayer to spray specific amounts directly on the surface of the soil for further use.

3.3.4. Photo Catalytic Experiment

3.3.4.1. Laboratory Scale Study

In the laboratory scale study, an experiment was carried out by mixing 3-cp solution (5.00 mL) with known concentration into a petri dish with 10.00 g of soil. ZnO catalyst (0.10 g) was spread out on the surface of the soil. The dish was then covered with plastic transparent sheet to avoid evaporation and keep it under humid conditions during the catalytic process. It was kept first in the dark for 60 min. in order to reach equilibrium, then under direct sun light for 1-hour period. The intensity of the solar light and average rate of temperature were measured periodically every 20 min. Effects of 3-cp concentration, solar irradiation time, pH value, catalyst amount and application method were studied during the experiment. After the specific period, distilled water (45 mL) was added to the petri dish then shaked well for about 20 min, and centrifuged twice at 5000 r/p/m for 10 min each. Finally the absorbance for the remaining 3-cp contaminant was measured using spectrophotometer. Figure (3.2) summarizes the photo-catalytic experiment in the laboratory scale study.

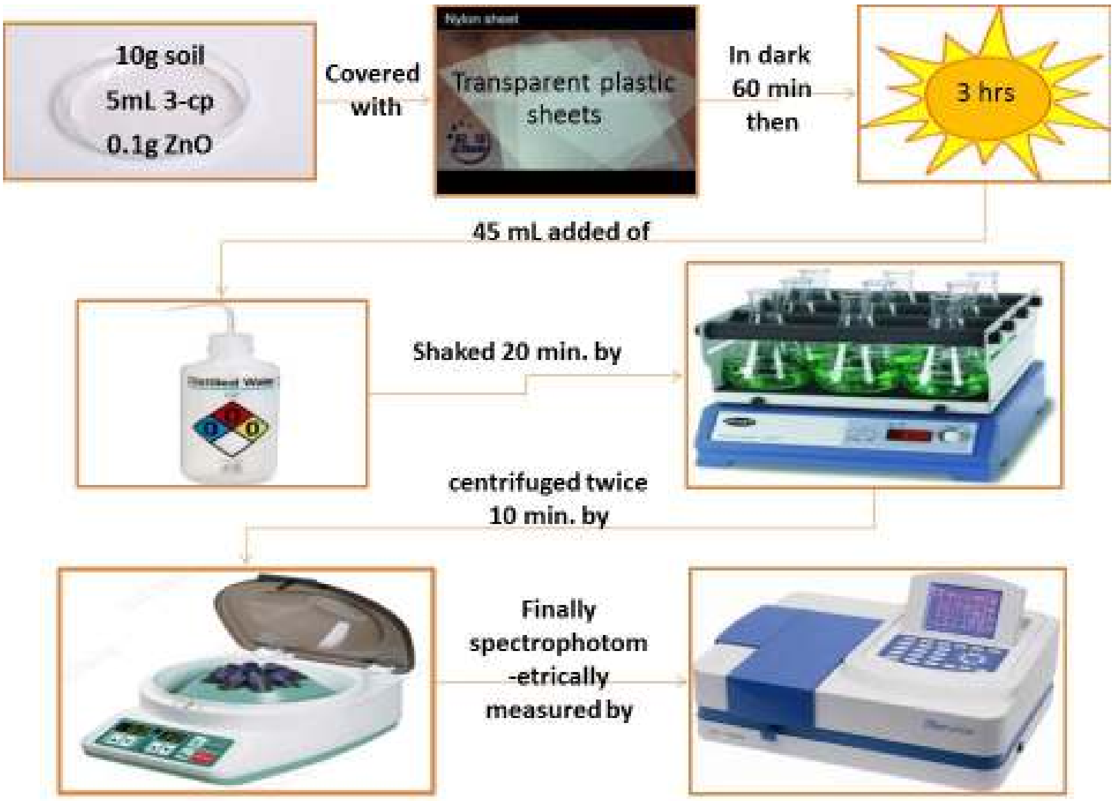


Figure (3.2): The photocatalytic experiment in the laboratory scale study.

3.3.4.2. Pilot-Plant Scale Study

In the pilot-plant scale study (field application) an experiment was carried out by applying the optimum conditions for contaminant degradation from the previous lab study by using five large basins of (50 x 38 cm^2) containing soil (6 kilogram) and pollutant solution (1.0 L). A specific amount of commercial ZnO catalyst (4.25 g) was spread out on the surface of the basins then covered with plastic transparent sheet. Four basins were kept under direct sun light for four days, while the last basin was kept in the dark as control experiment for the same period. Figure (3.3) summarizes the pilot-plant experiment.

Figure (3.3): Pilot-plant basins during experiment under sunlight.

3.3.4.3. Control Experiments

In the laboratory-scale study two control experiments were conducted, the first experiment was carried out by following the previous procedure and kept in the dark; the other was conducted under direct sun light with no catalyst spread out on the surface. In the pilot-plant scale study one control experiment was conducted in the dark as the other control experiment resulted from the lab-scale was of no use.

3.3.5. Calculation Method

Percent of degradation was calculated by comparing the absorbance of the degraded contaminant under sun light, in relation to the absorbance of the degraded contaminant in the dark. Experiment showed no degradation happened in the dark as the resulting absorbance did not change all over the whole experiment, it can be summarized as follows:

$$\% \text{ Photo-catalytic degradation} = (A_0 - A_t / A_0) * 100$$

Where,

A_0 : Absorbance in the dark

A_t : Absorbance after catalytic experiment under sun light.

No degradation occurred in the dark and no adsorption was happened on the surface of the soil in both dark and light, which was verified by the following two experiments:

3-cp contaminant (5mL, 200 ppm conc.) was added into a petri dish containing 10.00 g soil, and lab-prepared ZnO catalyst (0.1 g) was spread out on the surface and kept in the dark. After 2 hours 45.0 mL distilled water was added, stirred and filtered. The supernatant was centrifuged and spectrophotometrically analyzed. High absorbance of 3-cp, about 100% of contaminant amount was determined, which indicates no degradation happened in the dark. The soil was soaked in 25.0 mL ethanol, stirred and filtered. The supernatant layer of ethanol was also centrifuged and spectrophotometrically analyzed. It was found that the ethanol did not recover any of contaminant molecules in a sign of no adsorption happened on the soil surface.

The other experiment was carried out by the same previous procedure but it was kept under sun light for 2 hours. The supernatant layer of water solution resulted in 30% of contaminant remained; whereas the supernatant layer of ethanol resulted in no absorbance detected of 3-cp which confirms no adsorption happened on soil surface. Consequently, %degradation of 3-cp is 70 % at 200 ppm concentration.

HPLC analysis

3-chlorophenol contaminant (100 ppm) was detected at 274 nm wavelength, before, during and after photo-catalytic experiment using HPLC, C-18 column and mobile phase of 20:80 ratio of pure acetonitrile to phosphoric acid (0.01 M) at a rate of 1.0 mL min^{-1} at room temperature [53].

Chapter Four

Results and Analysis

Chapter Four

Results and Analysis

Preface

This Chapter presents the results of this work. The Chapter addresses first the characterization results of ZnO catalyst in its two forms, synthesized lab-prepared and commercially purchased, and the characterization result of 3-cp. Second, it presents the results of the lab-scale study, including all parameters studied and HPLC results. Finally, the Chapter shows the results of the pilot-plant scale study.

4.1. Characterization Results

4.1.1. Nanoparticle ZnO Characterization, Lab-prepared & Commercial

Lab-prepared and commercial ZnO powders were characterized by using UV-visible absorption spectrophotometry, X-Ray Diffraction and photoluminescence spectrometry.

4.1.1.1. UV-visible Spectral Characterization

UV- visible spectra was measured for the lab-prepared and commercial ZnO for the purpose of characterization. The absorption band for the lab-prepared ZnO was observed at λ_{max}= 373 nm, whereas it was observed at λ_{max}= 382 nm for the commercial ZnO, Figure (4.1).Therefore, the lab-prepared ZnO seems to have slightly shorter wavelength than the commercial ZnO.

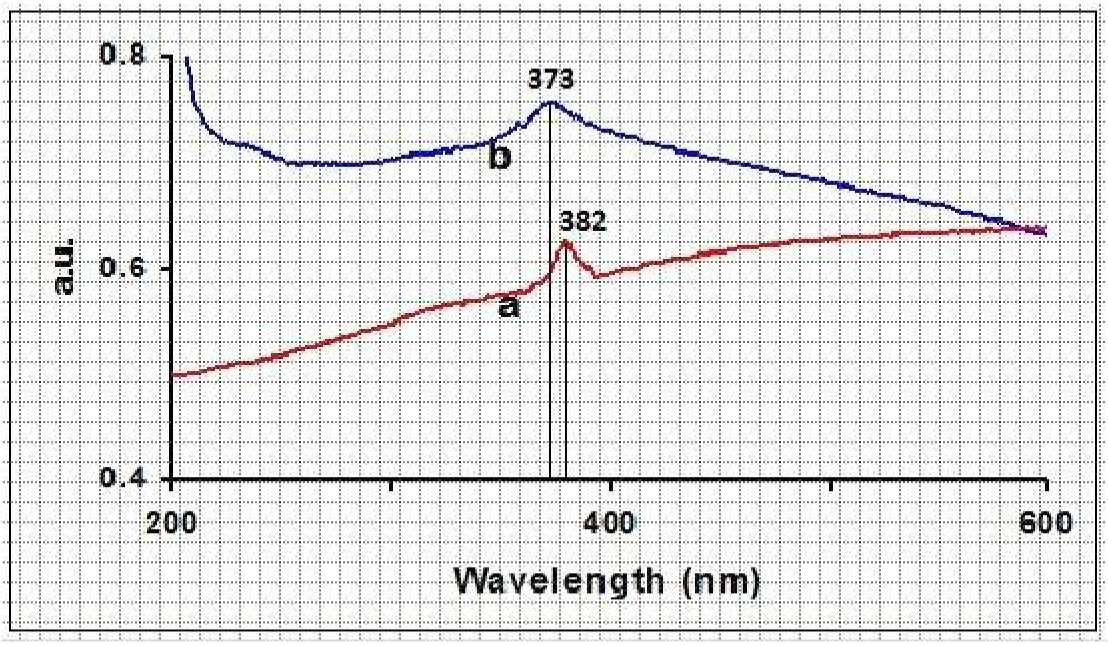


Figure (4.1) : Absorption spectra of a- commercial ZnO , b-lab-prepared ZnO suspended in water. Adapted from [82].

4.1.1.2. X-Ray Diffraction Characterization

Lab-prepared and commercial ZnO were characterized by using XRD technique. The X- Ray diffraction peaks at 31.8◦, 34.5◦,36.3◦, 47.6◦, 56.7◦, 62.9◦, 68.1◦ and 69.2◦ of the two forms indicate a hexagonal wurtzite crystal type. This result agreed with XRD pattern of ZnO in earlier studies, Figure (4.2) [83]. Average particle size of both forms of ZnO was calculated depending on the two different peaks at 100 and 101indices, Figure (4.3&4.4), and by applying the Scherrer equation. It was found that the lab-prepared ZnO has average particle diameter of 16 nm, while the commercial ZnO has an average diameter of 19 nm. Therefore, the lab-prepared ZnO seems to have smaller particle size compared to the commercial ZnO.

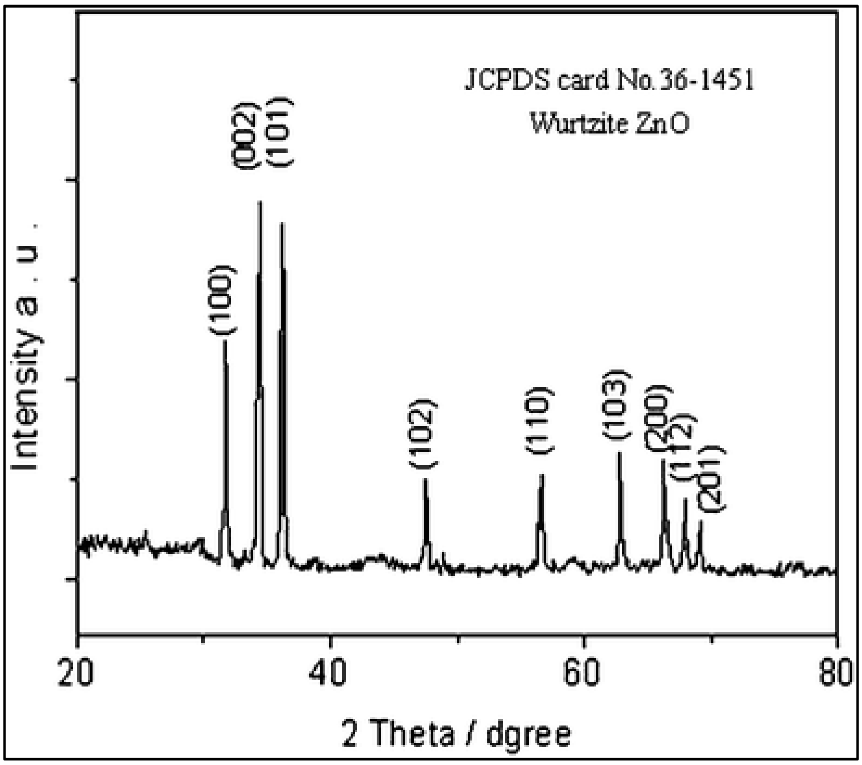


Figure (4.2) : XRD pattern of hexagonal wurtziteZnO[83].

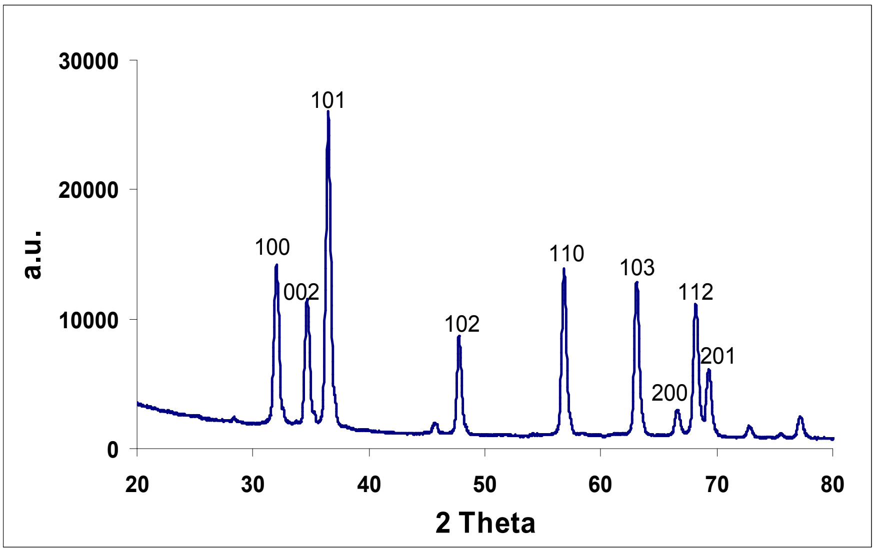


Figure (4.3) : XRD pattern for the lab-prepared ZnO [82].

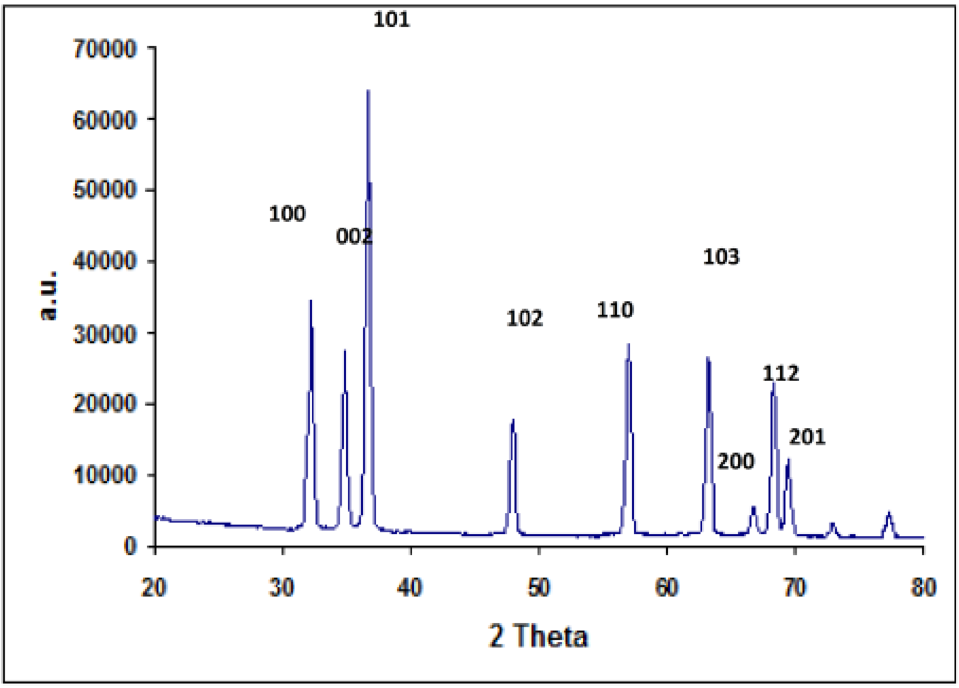


Figure (4.4) : XRD pattern for the commercial ZnO. Adapted from [82].

4.1.1.3. Photoluminescence Characterization

Lab-prepared and commercial ZnO were characterized using Photoluminescence (PL) emission spectra at excitation λ= 325 nm. The emission peak of lab-prepared ZnO was at λ = 382 nm, whereas, it was at λ = 386 nm for the commercial ZnO, Figure (4.5). The shorter emission peak of the lab-prepared ZnO may due to its smaller particle size compared to the commercial ZnO.

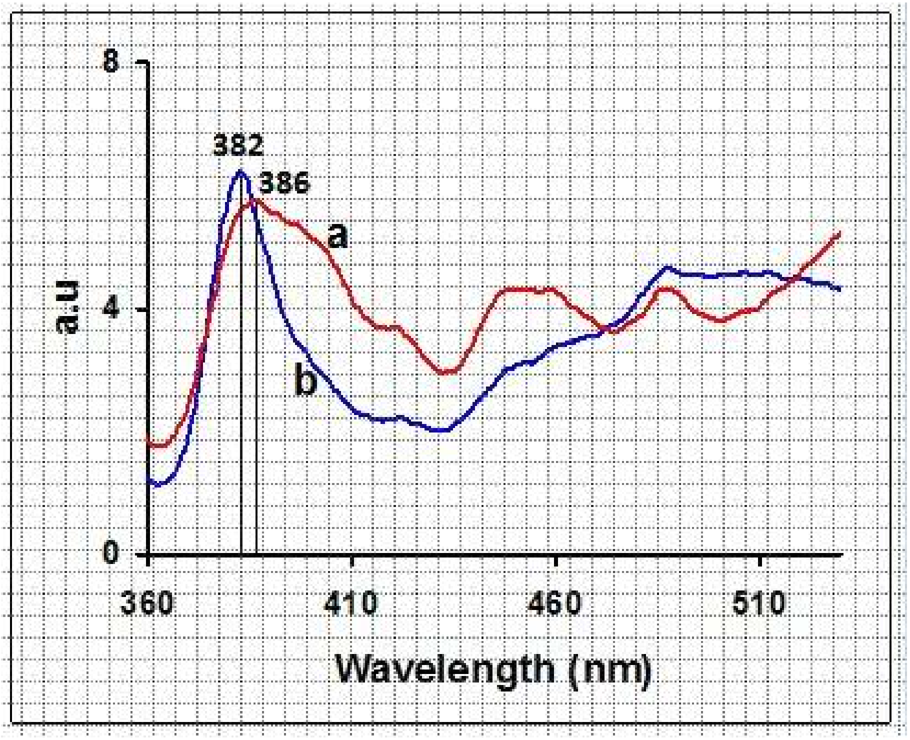


Figure (4.5) : Photoluminescence spectra for a. commercial ZnO, b. lab-prepared ZnO at excitation λ= 325 nm. Adapted from [82].

All the characterization results of the electronic absorption, XRD and PL of ZnO catalyst indicates that the lab-prepared catalyst has smaller particle size compared to the commercial catalyst.

4.1.2. Characterization of 3-Chlorophenol

The contaminant 3-cp was characterized by using UV-visible spectrophotometer. A solution of 100 ppm concentration of 3-cp was prepared. The absorption band was observed at λ_{max}= 274 nm, which will be detected in all experiments, as shown in Figure (4.6).

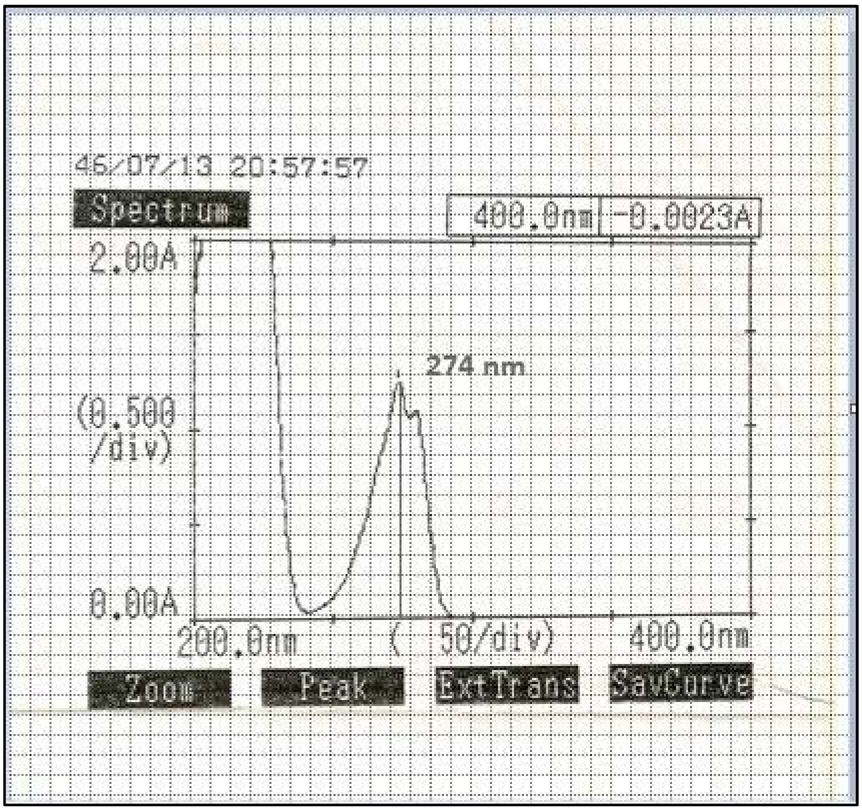


Figure (4.6) : UV-visible absorption spectra of 3-cp.

4.2. Laboratory Scale Photo-degradation Results of 3-Chlorophenol using ZnO Catalysts

4.2.1. Control Experiment Results

4.2.1.1. Result of the Dark Control Experiment

The first control experiment was conducted in the dark, by adding 5 mL of 100, 200, 300 and 400 ppm concentration of 3-cp contaminant to 10.00 g of soil and 0.1 g of ZnO catalyst of the two forms (lab-prepared and commercial) was spread out to the surface. Petri dishes were kept in the dark for 2 hours as average time. Results of the control experiment presented in Figure (4.7) show that no degradation happened in the dark. These results agreed with some earlier reports [53].

4.2.1.2. Result of No Catalyst Control Experiment

The second control experiment was conducted by following the same procedure of the first control experiment, but petri dishes were kept under direct sunlight with no catalyst spread out on the surface of the soil. Results also show that no degradation happened under these conditions, Figure (4.7).

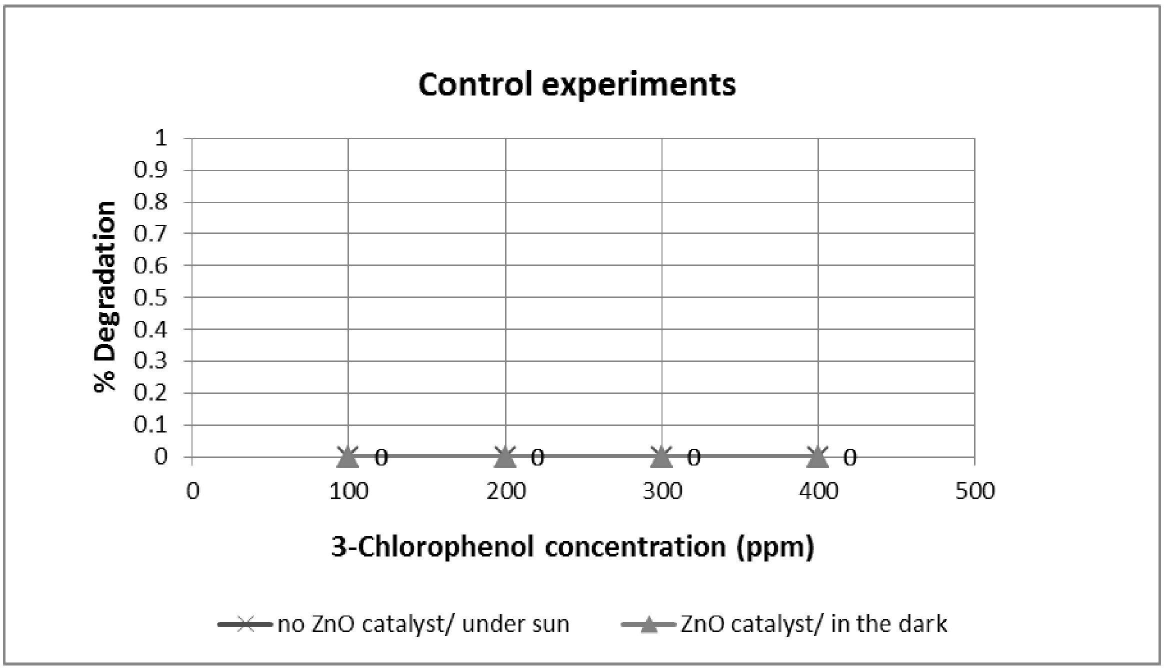


Figure (4.7) : Control experiments: The dark control experiment and no catalyst control experiment.

4.2.2. Effect of 3-cp Concentration

Initial contaminant concentration effect was studied on the degradation process by adding 5 mL of 100, 200, 300 and 400 ppm of initial concentration of the contaminant to 10.00 g of soil and 0.1 g of both lab-prepared and commercial ZnO. They were kept in the dark for 1 hour, then under direct sun light for one hour and 3 hours, respectively. Results of the conducted experiments after one hour and 3 hours are shown in Figures (4.8&4.9), respectively.

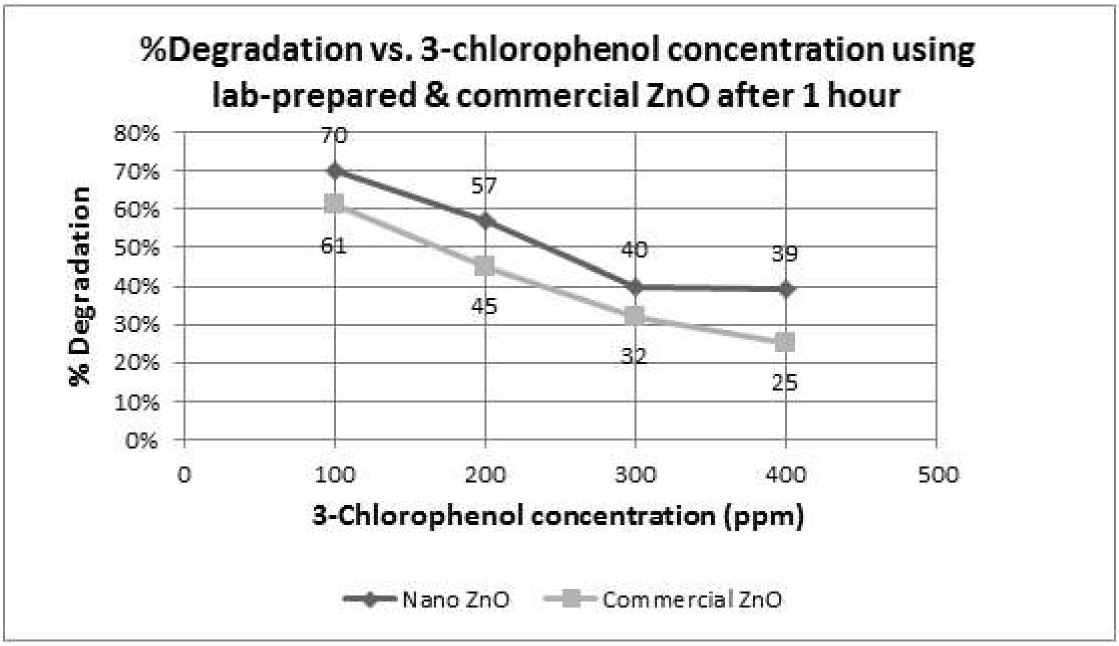


Figure (4.8): Effect of 3-cp initial concentration on the degradation process, using 5 mL contaminant, 0.1 g of lab-prepared & commercial catalysts and 10.0 g soil for 1 hr, (lux= 0.01314 W/cm^2).

Results presented in Figure (4.8) show a decrease in the percent degradation with the increase of contaminant concentration. They also show higher %degradation of the lab-prepared ZnO compared with the commercial ZnO catalyst.

Calculations of turnover number (TN), turnover frequency (TF) and quantum yield (QY) values were performed after one hour of reaction time. For calculation methods, see Appendix B. The results of the calculations regarding the contaminant concentration parameter using lab-prepared and commercial ZnO are summarized in Tables (3.1) and (3.2), respectively.

Table (4.1): Values of %degradation, TN, TF and QY after 1 hr of irradiation time for different 3-cp concentrations using lab-prepared ZnO

3-cp concentration/ppm	Degraded amount /ppm	% Degradation	TN	TF /min^{-1}	QY molecule/photon
100	70	70	2.20 E-3	3.67 E-5	3.26 E-4
200	114	57	3.60 E-3	6.00 E-5	5.40 E-4
300	120	40	3.80 E-3	6.33 E-5	5.60 E-4
400	156	39	4.95 E-3	8.25 E-5	7.60 E-4

Results in Table (4.1) display a decrease in %degradation, with the increase of contaminant concentration, while they show an increase in the degraded amount. Results of TN, TF and QY also show an increase with the increase of contaminant concentration using lab-prepared ZnO.

Table (4.2): Values of %degradation percentage, TN, TF and QY after 1 hr of irradiation time at different 3-cp concentrations using commercial ZnO

3-cp concentration /ppm	Degraded amount /ppm	% Degradation	TN	TF min^{-1}	QY molecule/ photon
100	61	61	1.9 E-3	3.17 E-5	2.80E-4
200	90	45	2.8 E-3	4.67 E-5	4.20 E-4
300	96	32	3.1 E-3	5.17 E-5	4.60 E-4
400	100	25	3.2 E-3	5.33 E-5	4.80 E-4

Results in Table (4.2) also display a decrease in %degradation with the increase of contaminant concentration, while they show an increase in the degraded contaminant amount. Results of TN, TF and QY also show an increase with increasing contaminant concentration using commercial ZnO.

Effect of initial concentration was also studied after 3 hours of irradiation time. The same procedure was followed but they were kept under direct solar light for 3 hours. The results confirmed those resulted after 1 hour. In addition, the results show complete degradation of 3-cp of 100 ppm using lab-prepared ZnO after this period, Figure (4.9).

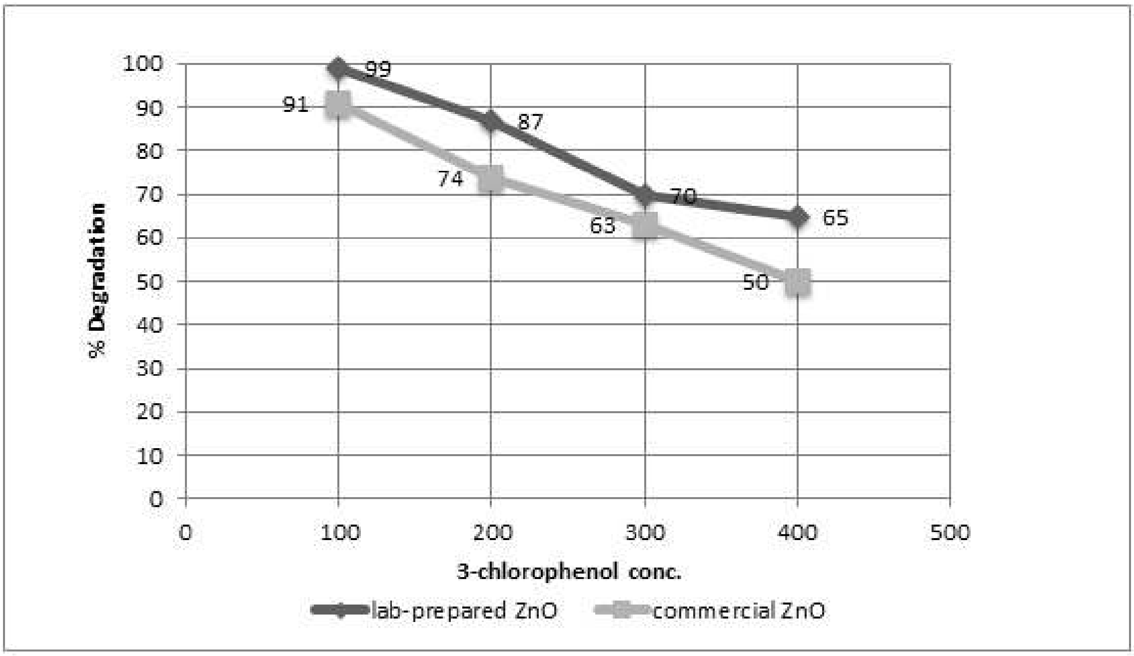


Figure (4.9): Effect of 3-cp initial concentration on the photo-degradation process, using 5 mL contaminant, 0.1 g of lab-prepared & commercial catalysts and 10.0 g soil for 3 hrs (lux= 0.01314 W/cm^2).

Calculations related to the contaminant concentration experiment after 3 hours of exposure to sun light using lab-prepared and commercial ZnO are presented in Tables (4.3 & 4.4), respectively.

Table (4.3): Values of %degradation, TN, TF and QY after 3 hrs of irradiation time for different 3-cp concentrations using lab-prepared ZnO

3-cp concentration /ppm	Degraded amount /ppm	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
100	99	99	3.15 E-3	1.75 E-5	1.55 E-4
200	174	87	5.53 E-3	3.07 E-5	2.73 E-4
300	210	70	6.67 E-3	3.70 E-5	3.30 E-4
400	260	65	8.29 E-3	4.60 E-5	4.09 E-4

Results displayed in Table (4.3) confirm the results of the concentration effect by using lab-prepared ZnO after 1 hour, as they show a decrease in the %degradation with the increase of 3-cp concentration, and an increase in degraded amount, TN, TF and QY values.

Table (4.4) : Values of %degradation, TN, TF and QY after 3 hrs of irradiation time for different 3-cp concentrations using commercial ZnO.

3-cp concentration /ppm	Degraded amount / ppm	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
100	91	91	2.89 E-3	1.60 E-5	1.43 E-4
200	148	74	4.70 E-3	2.60 E-5	2.32 E-4
300	189	63	6.00 E-3	3.33 E-5	2.96 E-4
400	200	50	6.34 E-3	3.52 E-5	3.13 E-4

Similar results are presented in Table (4.4) by using commercial ZnO after 3 hours of irradiation time. They show a decrease in %degradation and an increase in the degraded amount, TN, TF and QY values.

4.2.3. Effect of Solar Irradiation Time

The effect of solar irradiation time was studied on the photo-degradation process using both forms of the catalyst, lab-prepared and commercial ZnO. Five samples with constant catalyst amount of 0.10 g and constant initial 3-cpconcentration of 100 ppm &200 ppm, respectively, were placed first in the dark for one hour, then under direct sun light for different periods of time (30, 60, 120 and 180 minutes). Results of irradiation time effect are shown in Figure (4.10).

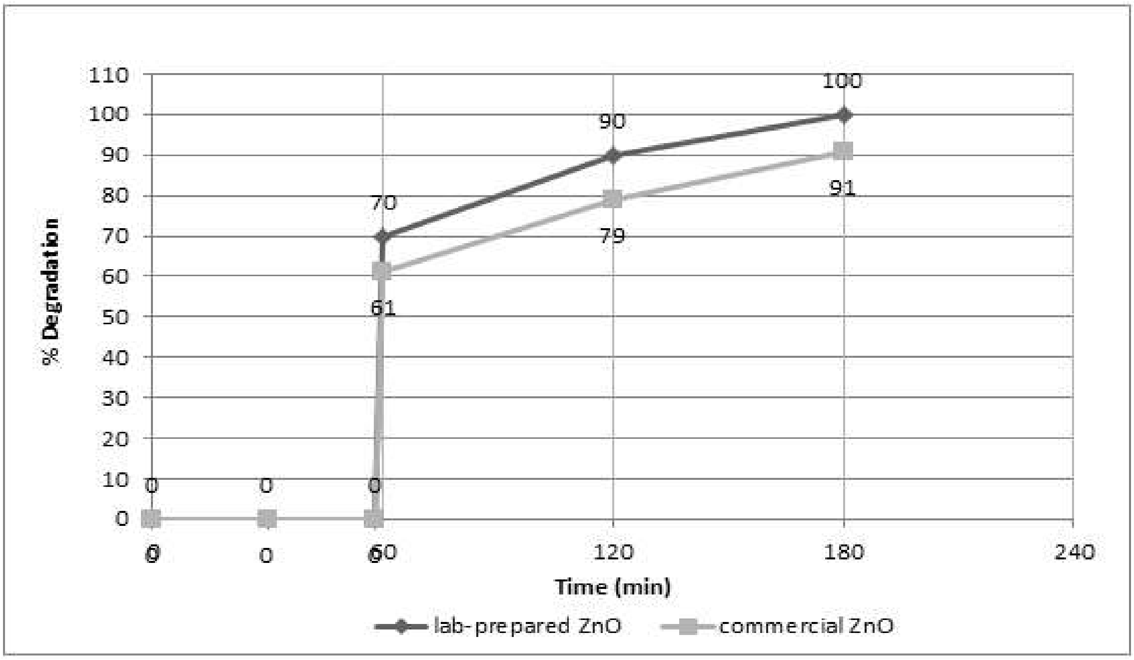


Figure (4.10): Effect of solar irradiation time on photo-degradation process, using 5 mL, 100 ppm concentration 3-cp and 10.0 g soil for both catalyst forms (lux= 0.01314W/cm^2).

It is clear from Figure (4.10) that the relationship between the %degradation and the irradiation time is proportional relationship, as the increase in time resulted in an increase in %degradation. The contaminant 3-cp of 100 ppm concentration degraded completely after 3 hours of exposure time. No photo-degradation was observed during the first hour. The influence of irradiation time on degradation using lab-prepared and commercial ZnO catalysts are presented in Tables (4.5) and (4.6) respectively.

Table (4.5): Values of % degradation, TN, TF and QY of 100 ppm 3-cp after different periods of irradiation time using lab-prepared ZnO.

Irradiation time/min	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
30	0	0	0	0
60	70	2.20 E-3	3.67 E-5	3.29 E-4
120	90	2.85 E-3	2.38 E-5	2.10 E-4
180	100	3.17 E-3	1.76 E-5	1.57 E-4

Results of Table (4.5) show an increase in %degradation and TN value, and a decrease in TF and QY values. Similar results obtained by using commercial ZnO, as the Table (4.6) shows a decrease in %degradation and TN by the increase of irradiation time, and a decrease in TF and QY values.

Table (4.6): Values of %degradation, TN, TF and QY of 100 ppm 3-cp after different periods of irradiation time using commercial ZnO.

Irradiation time /min	% Degradation	TN	TF min^{-1}	QY molecule/ photon
30	0	0	0	0
60	61	1.93 E-3	3.22 E-5	2.87 E-4
120	79	2.51 E-3	2.10 E-5	1.86 E-4
180	91	2.89 E-3	1.60 E-5	1.43 E-4

To verify the influence of the irradiation time, an experiment using 200 ppm of 3-cp was carried out by following the same previous procedure. Results are shown in Figure (4.11).

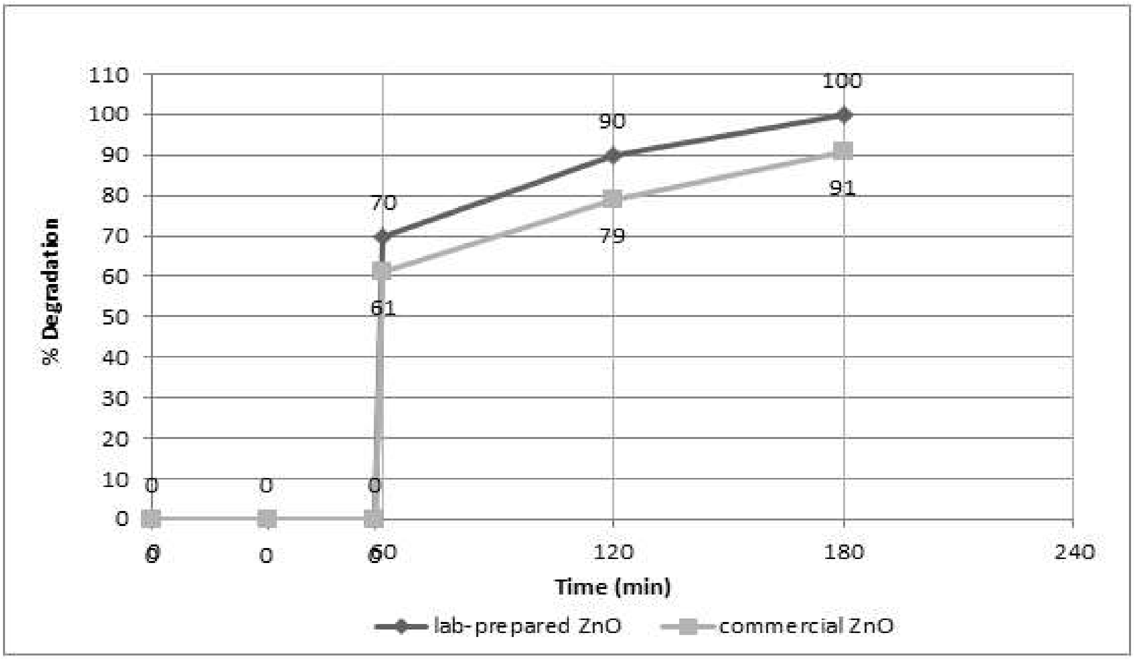


Figure (4.11) : Effect of irradiation time on photo-degradation process, using 5 mL, 200 ppm concentration 3-cp and 10.0 g soil for both catalyst forms (lux= 0.01314W/cm^2).

Results of the Figure (4.11) confirm the effect of irradiation time as they show an increase in %degradation with the increase of time for up to 3 hours for both forms of catalyst, and no degradation was observed at the first hour. The results of the calculations regarding the irradiation time parameter for lab-prepared and commercial ZnO are summarized in Tables (4.7) and (4.8), respectively.

Table (4.7): Values of %degradation, TN, TF and QY of 200 ppm 3-cp after different periods of irradiation time using lab-prepared ZnO.

Irradiation time /min	% Degradation	TN	TF min^{-1}	QY molecule/ photon
60	57.2	3.63 E-3	6.1 E-5	5.38E-4
120	86.7	5.50 E-3	4.6 E-5	4.08 E^{-4}
180	86.7	5.50E-3	3.1 E-5	2.72E-4

It is clear from Table (4.7), that %degradation and TN values increase with the increase of time for up to 3 hours and they become stable after that time. Whereas, TF and QY values decrease by using lab-prepared ZnO.

Table (4.8): Values of %degradation, TN, TF and QY of 200 ppm 3-cp after different periods of irradiation time using commercial ZnO.

Irradiation time /min	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
60	55	5.37 E-3	8.95 E-5	5.18 E-4
120	85	3.49 E-3	2.90 E-5	2.59 E-4
180	85	3.49 E-3	1.94 E-5	1.72 E-4

Results of the Table (4.8) also show an increase in %degradation and TN with the increase of time for up to 3 hours, and a decrease in TF and QY using commercial ZnO.

4.2.4. Effect of pH Medium

Degradation process of 3-cp was studied at different pH values. A concentration of 300 ppm of the contaminant was used in the study and 0.1 g of the two forms of ZnO catalyst was added to 10 g soil for 1 hour of irradiation time.

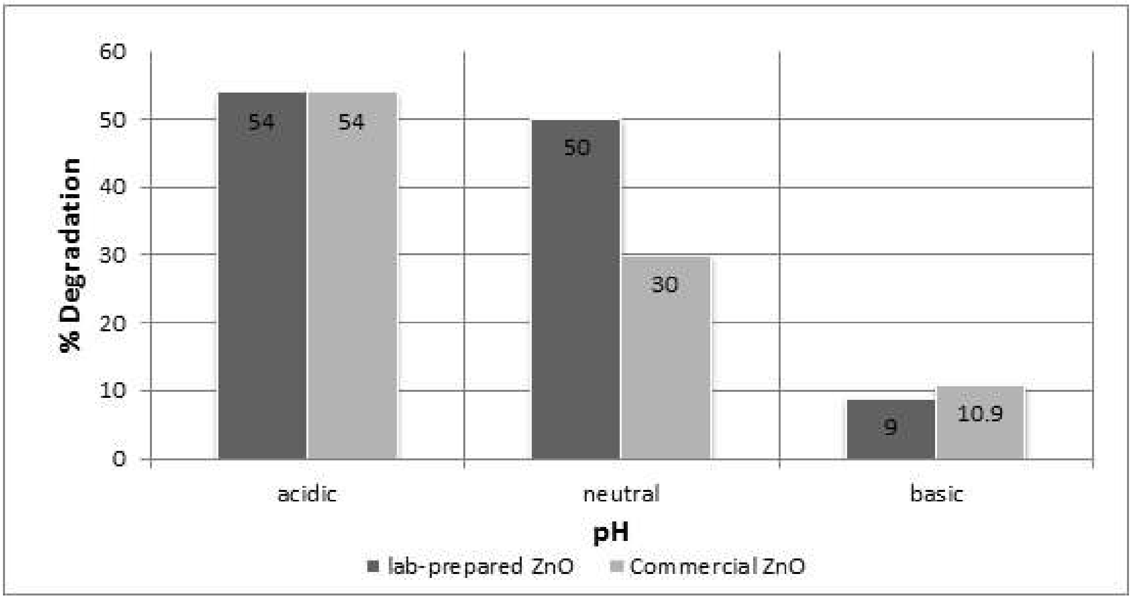


Figure (4.12) : Effect of pH medium on 3-cp degradation, 5 mL of 300 ppm using 0.1 g of both forms of catalyst for 1 hr, (lux= 0.01314W/cm^2).

Effect of pH, as shown in Figure (4.12), can be summarized as follows:

%photo-degradation: in acidic medium ~ neutral >> basic, using lab-prepared ZnO. For the commercial ZnO the tendency was:

%photo-degradation: in acidic > neutral >> basic.

The calculations regarding the pH parameter using lab-prepared & commercial ZnO are summarized in Tables (4.9) and (4.10) respectively.

Table (4.9) : Values of %degradation TN, TF and QY with different pH medium using 0.1 g of lab-prepared ZnO and 5 mL, 300 ppm of 3-cp after 1 hr.

pH medium	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
Acidic	54	5.27 E-3	10.6 E-5	7.60 E-4
Neutral	50	4.76 E-3	7.93 E-5	7.00 E-4
Basic	9	0.88 E-3	1.47 E-5	1.27 E-4

Results presented in Table (4.9) can also be summarized as follows: %degradation, TN, TF and QY: in acidic medium~neutral>>basic, using lab-prepared ZnO. For commercial powder, the results of Table (4.10) can be summarized as follows: %degradation, TN, TF and QY: in acidic medium~neutral>>basic.

Table (4.10) :Values of %degradation TN, TF and QY with different pH medium using 0.1 g of commercial ZnO and 5mL, 300 ppm of 3-cp after 1 hr.

pH medium	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
Acidic	54	5.15 E-3	8.58 E-5	7.6 E-4
Neutral	30	2.93 E-3	4.88 E-5	4.2 E-4
Basic	10.9	1.06 E-3	1.77 E-5	1.5 E-4

4.2.5. Effect of Catalyst Loading

The effect of catalyst amount on %degradation was also studied. Overall results show that, different values of %degradation were observed when different amounts of ZnO catalyst were used. Lab-prepared and commercial catalysts were added to 5 mL of 300 ppm contaminant under direct sunlight for 1 hour. An increase in %degradation was associated with an increase in the amount of both catalysts up to certain limit after which %degradation decreased. It was noticed that 0.2 and 0.3 g weight of lab-prepared and commercial catalysts achieved the highest %degradation, respectively, Figure (4.13).

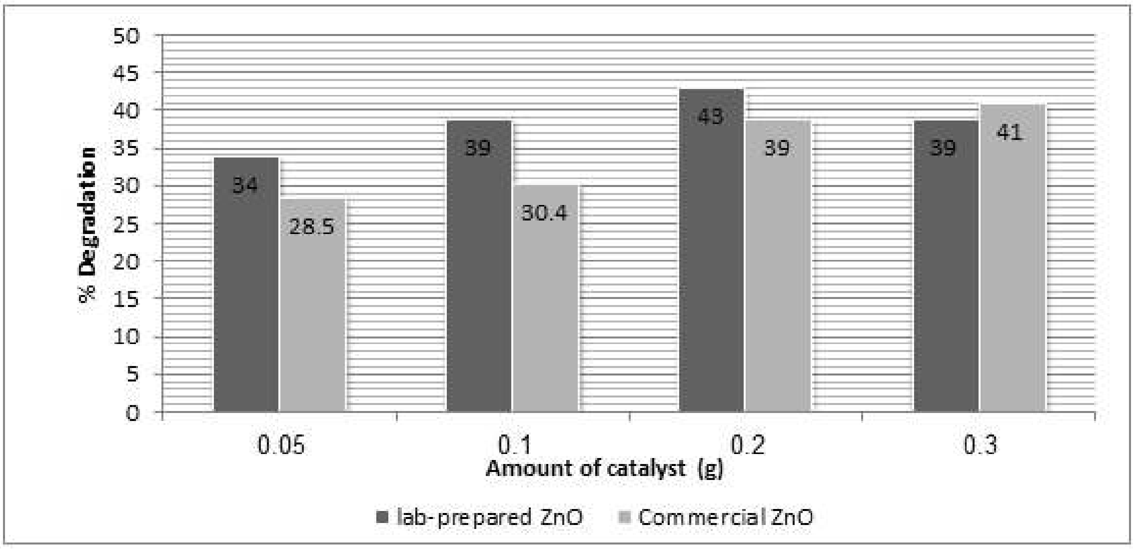


Figure (4.13) :Effect of catalyst amount (g) on %degradation using neutral solution of 5mL, 300 ppm of 3-cp, for 1 hr, (lux= 0.01314W/cm^2).

Data concerning degradation percentage, turnover number, turnover frequency and quantum yield values after 1 hour, using different amounts of lab-prepared and commercial ZnO catalysts are presented in Tables (4.11) and (4.12), respectively.

Table (4.11): Values of %degradation, TN, TF and QY after 1 hour using different amounts of lab-prepared ZnO catalyst.

Catalyst amount /g	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
0.05	34	7.40 E-3	12.3 E-5	5.50 E-4
0.1	39	3.24 E-3	5.40 E-5	4.79 E-4
0.2	43	2.05 E-3	3.40 E-5	6.07 E-4
0.3	39	1.24 E-3	2.07 E-5	5.50 E-4

Table (4.11) shows some increase in %degradation associated with the increase in catalyst amount up to certain limit. On the other hand, values of TN and TF decreased with higher catalyst concentrations, as shown in the Table. This means that relative efficiency of the catalyst decreases with its amount. This will be discussed in Chapter 4. The value of QY remained constant win increasing catalyst amount, which means that the catalyst efficiency is smaller.

Table (4.12): Values of %degradation, TN, TF and QY after 1 hour using different amounts of commercial ZnO catalyst.

Catalyst amount / g	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
0.05	28.5	5.43 E-3	9.00 E-5	4.02 E-4
0.1	30.4	2.89 E-3	4.82 E-5	4.29 E-4
0.2	39	1.86 E-3	3.10 E-5	5.50 E-4
0.3	41	1.30 E-3	2.17 E-5	5.78 E-4

Table (4.12) also illustrates some increase in %degradation associated with the increase in catalyst amount up to certain limit, using the commercial form. The values of TN and TF decreased with increasing catalyst amount, as shown above for the lab-prepared catalyst system. The QY value was not much affected by increasing catalyst amount, which again show that catalyst efficiency is lowered.

4.2.6. Effect of Catalyst Application Method

The relationship between type of catalyst application method (spray or powder) and photo-degradation of the contaminant was studied by adding 5 mL of 300 ppm concentration of contaminant and 0.1 g of both forms of the catalyst into10.00 g of soil for 1 hour under direct sunlight.

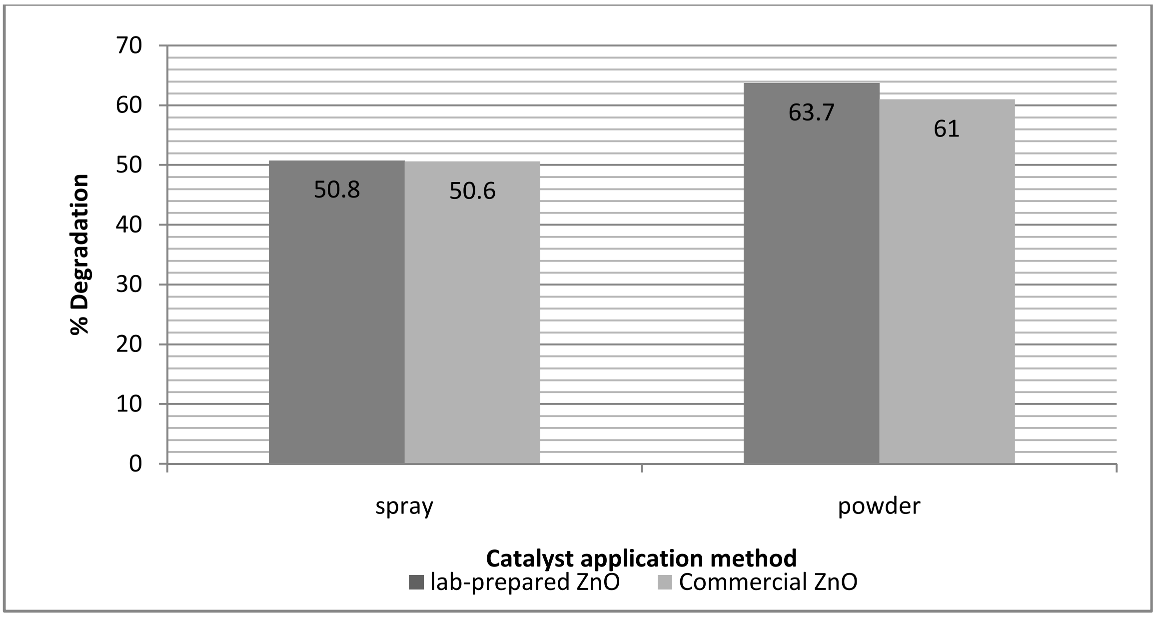


Figure (4.14) : Effect of catalyst application method (spray or powder) on photo-degradation of 5 mL of 300 ppm of 3-cp using lab-prepared& commercial ZnO for 1 hr, (lux= 0.01314W/cm^2).

Results obtained in Figure (4.14) indicate that there is no significant difference between using the two application methods of the catalysts, (spray form or dry powder). Table (4.13) summarizes the effects of type of applying the catalyst (both types) on %degradation, TN, TF and QY.

Table (4.13): Values of %degradation, TN, TF and QY with the change of application method of both forms of catalyst

Catalyst application method	% Degradation	TN	TF /min^{-1}	QY molecule/ photon
Spray/ lab-prepared	50.8	4.84 E-3	8.10 E-5	7.17 E-4
Powder/ lab-prepared	63.7	6.07 E-3	10.1 E-5	8.98 E-4
Spray/ commercial	50.6	4.82 E-3	8.03 E-5	7.14 E-4
Powder/Commercial	61	5.80 E-3	9.70 E-5	8.61 E-4

It can be observed from Table (4.13) that values of %degradation, TN, TF and QY related to powder form are slightly higher than the values related to spray form for both types of catalyst.

4.2.7. HPLC Results

HPLC equipped with C18 column was used to find if lost 3-chlorophenol has been converted into other organic products or it was totally mineralized into CO_2 gas. Three solutions of 5 mL, 100 ppm of contaminant concentration were exposed to irradiation for different times (0 h, 2 h and 3 h). The first solution time showed a primary single peak of height of 6.7 at retention time of 7.02+0.5 minutes, referring to 3-chlorophenol before degradation. After 2 h irradiation, only a small peak (with height 0.413 at the same retention time) due to 3-chlorophenol was observed. No other organic products were observed. After 3 h irradiation, the 3-chlorophenol completely disappeared with no other new organic products appearing. This indicates complete mineralization of 3-chlorophenol into water and CO_2. Figure (4.15) shows HPLC chromatograms for each experiment.

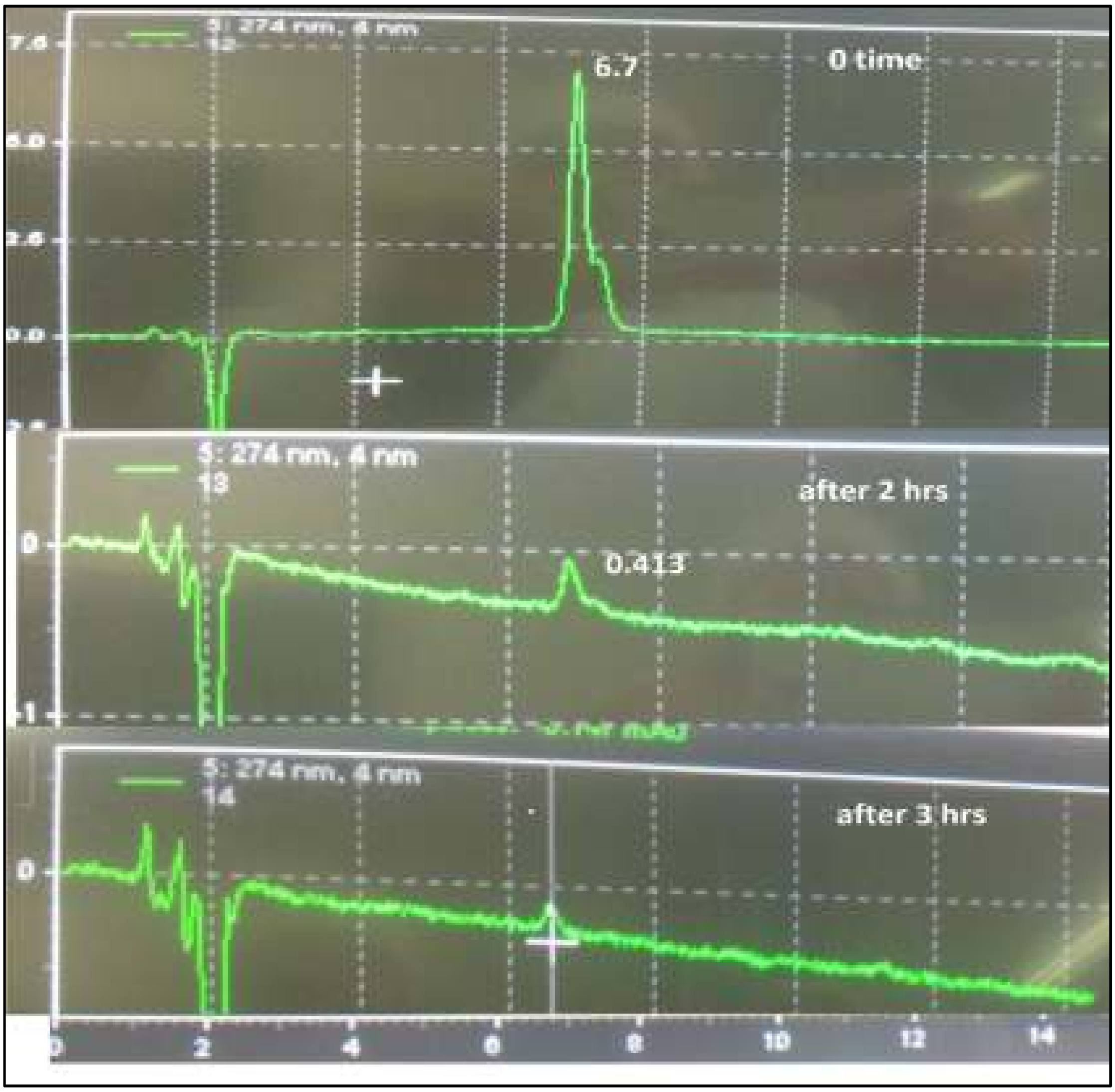


Figure (4.15): HPLC results for 5mL, 100 ppm 3-cp after (0), (2) and (3) hours of irradiation time.

4.3. Pilot Plant Scale Photo-degradation Results of 3-cp Using Commercial ZnO Catalyst [Field Application]

Results from pilot plant scale study, including the control experiment, were consistent with those obtained from lab-scale study. Figure (4.16) shows the effect of irradiation time on %degradation in the pilot-plant scale study. It is clear that %degradation increases with the increase of irradiation time.

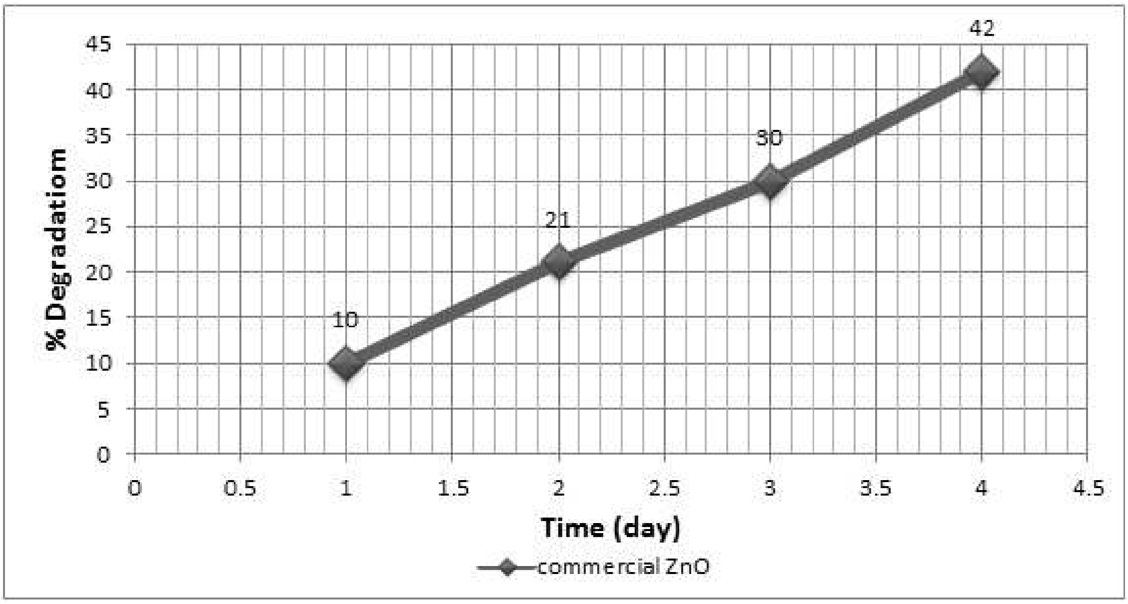


Figure (4.16): Relationship between %degradation and time of solar irradiation (day) using commercial ZnO in spray form, in the pilot plant study.

Calculations regarding the pilot-plant study are summarized in Table (4.14).

Table (4.14): Effects of irradiation time on the %degradation, TN, TF and QY values during the photo-degradation process of 3-cp, using commercial ZnO in spray form, in pilot plant study.

Irradiation time /day	% Degradation	TN	TF /min^{-1}	QY (molecule/ photon)
1 day	10	4.36 E-3	3.02 E-6	3.52 E-5
2 days	21	9.18 E-3	3.19 E-6	3.70 E-5
3 days	30	13.1 E-3	3.03 E-6	3.53 E-5
4 days	42	18.3 E-3	3.17 E-6	3.71 E-5

Results obtained in Table (4.14) indicate that the %degradation and TN increase with time, whereas, TF and QY do not significantly change. These results are normal and expected, and are consistent with the laboratory scale results. Details of calculations in pilot-plant scale study are shown in Appendix (C).

Chapter Five

Discussion

Chapter Five
Discussion

Preface

This Chapter discusses the results that have been presented in Chapter 4, comparing them with previous studies on the same subject. It also offers the interpretations of the hypotheses mentioned earlier. It starts with the characterization results of the electronic absorption, XRD and PL. Then, it discusses control experiments conducted, and all parameters studied on the laboratory scale work, the results of the HPLC analysis. The discussion ends with the interpretation of field work results.

5.1. Discussion of Characterization Results:

Results regarding electronic absorption spectra for the two forms of catalyst showed that the lab-prepared ZnO has shorter wavelength than the commercial catalyst, which indicates that the lab-prepared catalyst has smaller particle size than the commercial catalyst. This difference could be attributed to the wider band gap of the nanoparticles prepared in the laboratory. This result agrees with the other characterization results in this study and it also agrees with earlier reports [84]. The XRD patterns for both catalyst forms indicate hexagonal wurtzite crystal structure depending on the diffraction peaks. This result agreed with the hexagonal wurtzite patterns (JPCDS card number: 36-1451) in literature [83]. The result of smaller particle size of the lab-prepared ZnO compared to commercial ZnO is in agreement with the electronic absorption and the PL spectra results which involved in this study. It is also consistent with other reports[84, 85]. The PL result was also consistent with the electronic absorption and XRD results. As it indicated that commercial ZnO has larger particle size compared to lab-prepared ZnO. It also was consistent with other studies [85].

5.2. Discussion of Laboratory Scale Study Results:

5.2.1. Control Experiments

Results of the first control experiment showed that no photo-degradation of 3-cp contaminant has taken place in the dark, even in the presence of ZnO catalyst. Under direct sun light and in the presence of ZnO catalyst, a complete photo-degradation of 100 ppm of 3-cp contaminant was observed within 3 hours of irradiation time. This result is in agreement with the first hypothesis. The second control experiment also showed that there was no photo degradation of 3-cp under direct sun light in absence of ZnO photo catalyst. This is also consistent with the second and the third hypotheses. It should be noted that only 0.1 g amount of ZnO was used to degrade all the contaminant showing 100 %degradation. This also supports the third hypothesis and shows the importance of this work.

The higher efficiency of the lab-prepared ZnO, compared to the commercial powder, in this work is attributed to its smaller particle size. This behavior appeared in many places of this work. With smaller particle size the particles are expected to have higher relative surface area which increases the relative number of active sites. Moreover, the lab-prepared powder showed wider band gap, as appeared in Figure (4.1). This increases the oxidizing power of the lab-prepared powder. The catalytic results are thus consistent with the characterization results of electronic absorption, XRD and PL.

5.2.2. Discussion of Parameters Studied:

5.2.2.1 Effect of Contaminant Concentration

Results regarding contaminant concentration effect showed a decrease in %degradation with increasing concentration. This is due to the increase in contaminant molecules reacting on the active sites of the catalyst surface. This result is consistent with earlier studies which reported the dependence of photo-degradation reaction on the initial concentration of organic contaminants like phenol and other dyes [53, 86, 87]. Pardeshi and Patil, for example, observed a decrease in the photo-degradation percentage by increasing the initial concentration of phenol from 25 to 300 ppm using ZnO. They attributed the decrease to the additional phenol molecules and intermediates that adsorb on ZnO catalyst surface and deactivate the active site [88].

Despite the difference in %degradation, the degraded amount of 3-cp increased as a result of the increase in its concentration. The increase in TN, QY and TF is reasonable due to the increase in (number of moles of reacted contaminant/number of moles of ZnO catalyst). When the number of reacted contaminant molecules increased while keeping other conditions the same, an-increase in TN occurred. TF is related to TN, as TF= TN/time, where time was kept constant. Similar explanation could be extrapolated to quantum yield, as QY = (number of contaminant molecules reacted/ total number of photons used). The results suggest that the reaction goes faster with increased contaminant amount.

5.2.2.2. Solar Irradiation Time

Results related to irradiation time effect showed an increase in %degradation with longer exposure time to solar light for up to 3 hours, which represents the time of reaction completion. This applied to both lab-prepared and commercial forms of ZnO for all concentrations higher than 100 ppm. The same interpretation could be applied to TN values. Values of TF & QY decrease because both of them are affected by the increase of time. This is understandable, because in most processes the reaction rate decreases with time due to consumption of reactant molecules.

The observed zero percent of degradation during the first 60 min is also understandable. The 60 min induction time was needed in order to enable contaminant molecules diffuse from the soil to the ZnO catalyst sites. After such diffusion occurred, and the reaction started, degradation continued as explained above.

5.2.2.3. Effect of pH medium

The pH medium affected the photo-degradation of 3-cp. The acidic medium showed higher activity compared to the basic medium for both forms of the catalyst. For ZnO, the value for pH_{zpc} is 9.0, and therefore the catalyst surface is negatively charged when pH is higher than 9.0 and positively charged if it is below. However, chlorophenols seem to be negatively charged (become anions) if pH ▪ pKa, and in the molecular form when pH ▪ pKa. The value of pKa for 3-cp is 8.4, which means 3-cp is in its molecular form when pH < 8.4. Therefore, the photo-degradation reaction goes faster due to the increasing chance of adsorption of contaminant molecules on the surface of ZnO catalyst. The opposite happens when pH ▪ pH_{zpc} as both of 3-cp and ZnO surfaces are negatively charged, and so photo-degradation reaction tends to be slower because of the repulsive effect of same charge. The same tendency occurred with the values of TN, TF and QY at different pH medium values. The results agreed with earlier reported works conducted under field conditions [51, 53]. Parida et. al, studied the photo-degradation of 4-nitrophenol using ZnO catalyst under solar light. They reported that the optimum value of pH, with 92% degradation, was 6, and the %degradation decreased at higher pH value [89]. It should be noted that some organic compounds could be preferably degraded in acidic media, while others are more degraded in alkaline media, according to their nature. Khodja et al, for instance, reported that the optimum pH value needed to achieve best %photo-degradation of 2-phenylphenol was 12, using ZnO and UV light [90].

5.2.2.4. Effect of Catalyst Amount

Increasing catalyst concentration, up to a certain limit, increased the value of %degradation. Optimum points which exhibited highest

%degradation were 0.2 g and 0.3 g of lab-prepared and commercial forms of the catalyst, respectively. This confirms the higher efficiency of lab-prepared form of the catalyst compared to the commercial form. By increasing catalyst amount, the total number of active sites on catalyst surface is increased and thus %degradation is expected to increase. However, the relative efficiency of the catalyst varied in different manner. Values of TN and TF decreased with higher ZnO loading, while QY did not change. The lowering in catalyst efficiency is understandable, due to high turbidity of suspension and low light penetration as a result of additional catalyst amounts. These results are consistent with previous studies [53]. Parida et al, reported that the optimum loading of ZnO was 0.6 g/L through varying the range of catalyst loading from 0.2 to 2.0 g/L [89]. Lathasree et al, reported that the optimum loading of ZnO needed to degrade the phenol was 2.0 g/L through varying the range from 1.0 to 3.0 g/L using UV light [91]. Our system is therefore more practical than earlier reports, as much smaller ZnO amounts are needed here to increase relative efficiency of the catalyst.

5.2.2.5. Effect of Catalyst Application Method

In studying the effect of catalyst application method on %degradation, it was noticed that the dry powder form of the catalyst was slightly more efficient than the spray form for both lab-prepared and commercial ZnO. The difference in efficiencies was not significant. However, we recommend using the spray method due to its ease. It may also yield more uniform catalyst layer on the soil surface.

5.2.2.6. HPLC Results

Results of the HPLC results have successfully confirmed the applicability of the proposed method. The first primary peak in the HPLC chromatogram observed at retention time 7.0 min, for the reaction solution after zero reaction time, is referred to 3-cp before degradation. The second peak observed at same retention time for reaction solution measured after 2 h reaction time is smaller and indicates about 94% of degradation in 2 hours. The last figure showed complete mineralization of 3-cp contaminant as no peak appeared referred to 3-cp. No peak was observed for other organic compounds, which indicates that the 3-cp was totally mineralized yielding no organic side products. Several studies [53, 88, 92] were conducted in the area of chlorophenols degradation. These studies utilized HPLC for the investigation of the degradation process and resulted in complete conversion of such contaminants into harmless materials such as water and CO_2, and possibly Cl_2 or HCl. It should be noted that this method is applicable at low contaminant concentrations, as the HPLC results showed complete destruction of 100 ppm of 3-cp contaminant.

5.3. Pilot-Plant Scale Study [Field Application]

The pilot-plant scale study showed complete agreement with the laboratory scale study. Control experiment conducted in the dark showed no photo-degradation. The %degradation of 3-cp increased with time, which is consistent with the lab results. The values of TN and QY measured for the pilot-plant scale experiments agreed with those measured for the lab-scale experiments. The results achieved in the field work suggest the applicability of the method described here for purifying soils from 3-chlorophenol.

Chapter Six

Conclusions and Recommendations for Future Work

Chapter Six

Conclusions and Recommendations for Future Work

6.1. Conclusions

The following conclusions could be deduced from the present work:

1- Photo-catalytic degradation of 3-cp was successfully achieved under solar light using nanoparticle of the catalyst ZnO (lab-prepared and commercial forms).

2- Lab-prepared ZnO showed higher photo-degrading efficiency than the commercial ZnO.

3- Percentage of photo-catalytic degradation decreased with the increase of the contaminant concentration for both forms of the catalyst.

4- Percentage of photo-catalytic degradation increased with the increase of time till the completion of reaction for both forms of the catalyst.

5- Percentage of photo-catalytic degradation increased with the increase of the catalyst quantity until it reached the highest rate, which then became decreasing.

6- Slightly acidic medium was more preferable for photo-degradation than basic medium.

7- The dry powder form of catalyst showed little higher %degradation than the spray catalyst form.

8- The HPLC proved the photo-catalytic degradation of 3-cp.

9- The results of the pilot-plant scale study were consistent with those of the lab-scale study.

10- Objectives of the pilot-plant scale study have been achieved, shows the applicability of the technique in future strategies.

6.2. Recommendations for Future work:

1- It will be a meaningful benefit to study the photo-degradation of pesticides which are currently used in the Palestinian agriculture, with some photo-catalyst systems.

2- Using combined semiconductors to increase the efficiency of photo-degradation, such as ZnO and SnO_2 together.

3- Using semiconductors doped with other elements such as Al, Co and Mn to enhance the photo-catalytic activity.

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Appendices

Appendix A:

BIRZEIT UNIVERSITY

المؤتمر الفلسطيني لأبحاث طلبة الدراسات العليا

في العلوم الطبيعية والتطبيقية

جامعة بيرزيت 22 آذار 2014

تشهد اللجنة التحضيرية للمؤتمر الفلسطيني لأبحاث طلبة الدراسات العليا في العلوم الطبيعية و التطبيقية

بان رزان خريم من جامعة النجاح الوطنية

قد شارك/ت بعرض شفهي في فعاليات المؤتمر، تحت عنوان

Purification of Agricultural Soil from Organic Contaminants by Solar_Driven Photodegradation with ZnO Nanoparticles: Laboratory andPilot_Plant Scale Study

عميد كلية العلوم

د. وائل قراعين

عميد كلية الدراسة العليا

د. طلال شهوان

Appendix B:

- TN = number of moles of reacted contaminant/number of moles of ZnO catalyst.
- Number of contaminant moles reacted = (Initial concentration in ppm × percentage of degradation × 5 /1000000)/Mwt. 3- chlorophenol (128).
- Turnover frequency = TN/ time (120 minutes)
- QY = number of contaminant molecules reacted/ total number of photons used.

Whereas,

- E (J) = Incident power per unit area X Total area or incident powerX Exposure time in second.

= [(0.01314 W/cm^2)× 56.7 cm^2] × [120×60 second] = 5364.27 J

❖ Assuming average wavelength of incident light is 370 nm for UV light, then,

- $\upsilon = c/\lambda$

$= 3\times10^{8}\ ms^{-1} / 370\times 10^{-9}\ m$

$= 8.1\times10^{14}\ s^{-1}$

❖ using Planks equation, E (J) = nhυ

- n = J/h υ

= 5364.27/ (8.1×1014 ×6.62×10-34)

$= 1.00\times10^{22}$ photons

Example:

Calculations of 5 mL of 100 ppm, after 1 hr, 70%degradation :

degraded amount ppm = 70%×100= 70 ppm

No. of 3-cp moles = (100×70%×5) E^{-6}/ (128)

= 2.73 E^{-6} moles

No. of ZnO moles = 0.1/ 81.29

= 1.23 E^{-3} moles

Therefore, TN= 2.7 E^{-6}/ 1.23 E^{-3}

= 2.20 E^{-3}

TF= 2.2 E^{-3} / 60 min

= 3.67 E^{-5}

QY= number of contaminant molecules reacted (calculated before)/ total number of photons used.

No, of 3-cp molecules= 2.7 E^{-6} × 6.022 E^{23}

= 16.3 E^{17} molecules

Therefore,

QY= 16.3 E^{17} / 5 E^{21}

= 3.26 E^{-4}

Appendix C

Calculations of pilot-plant scale study

- TN = number of moles of reacted contaminant/number of moles of ZnO catalyst.

- (Initial concentration in ppm × percentage of degradation ×1000 (contaminant sample of pilot-plant) /1000000)/Mwt. 3- chlorophenol (128).
- QY = no. of 3-cp molecules reacted/ total no of photons used.

Whereas,

- E (J) = Incident power per unit area X Total area or incident power X Exposure time in second.
- = [(0.01314 W/cm^2)× (50×38 cm^2)] × [24×60×60 second]

And so, no of photons after the first day = E (J)/ h υ

= 4 E24 photons.

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إعداد

رزان احمد علي خريم

إشراف

أ. د. حكمت هلال

أ. د. يعقوب بطة

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2015م

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الملخص

لقد تم في البحث الحالي دراسة تنقية التربة الزراعية من الملوثات العضوية السامة باستخدام التحطيم بالطاقة الشمسية. استندهذا النوع من التحطيم على توافر أشعة الشمس كمصدر رئيسي للطاقة ، وانخفاض تكلفة المحفز وإمكانية التحطيم الكيميائي الضوئي.

الهدف من هذه البحث هو إيجاد طريقة فعالة ومنخفضة التكلفة لتحطيم الهيدروكربونات المكلورة التي تلوث التربة الزراعية إلى مركبات أولية، تم اختيار ثالث- كلويد الفينول كمركب ضار الذي ينجم عن استخدام المبيدات ، ومخلفات بعض المصانع ويلوث الماء و التربة.

شملت الدراسة الحالية نوعين من التجارب: دراسة على نطاق المختبر ودراسة على نطاق ميداني. تم إعداد نوعين من الحفاز: أكسيد الزنك المحضر مخبريا ، وأكسيد الزنك التجاري.

تم دراسة تأثير عدة عوامل، مثل تركيز الملوث، مدة الإشعاع، ودرجة الحموضة، كمية الحفاز وطريقة التطبيق على سير التفاعل. أظهرت النتائج زيادة في نسبة التحلل الضوئي مع كمية الحفاز المتزايدة ومدة الإشعاع إلى حد معين، وانخفاضا في نسبة التحلل الضوئي مع زيادة تركيز الملوث. وقد وجد أن الوسط الحمضي أكثر ملاءمة من الوسط القاعدي. لم يكن هناك فرق كبير في طريقة تطبيق المحفز سواء بشكل البودرة او بشكل الرذاذ. كانت نتائج العمل الميداني متفقة مع نتائج العمل المخبري، حيث أن نسبة التحطيم زادت مع زيادة الوقت على مدى أربعة أيام من الإشعاع.

وأخيراً، لقد أثبتت هذه الطريقة فعاليتها في تحطيم مركب ثالث كلوروفينول، على مستوى العمل المخبري والعمل الميداني، وباستخدام شكلين من الحفاز، أكسيد الزنك المحضر مخبريا والتجاري.