

**An-Najah National University**

**Faculty of Graduate Studies**

**Continuous flow photodegradation of olive *zebar*  
contaminants with simulated solar light using  
supported ZnO nanoparticles**

**By**

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Requirements for the Degree of Master of Science in Chemistry,  
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## **Dedication**

To my dear family, who supported and encouraged me all the time. To them, I send all my appreciation and respect.

## **Acknowledgments**

Praise to Allah who guided my steps in all my work till the very end. I would like to express my gratitude and thanks for my supervisors, Prof. Hikmat Hilal, and Dr. Ahed Zyoud, who always supported me with their knowledge and experiences. I would also like to thank Mr. Nafith Dweikat, for facilitating my work in the labs and helping me during research. Thanks are due to Professor Tae Woo Kim of Korea Institute of Energy Research, in Korea, for kindly conducting the XRD and SEM measurements. The Palestinian-Holland PADUCO program funding for this work is acknowledged. Furthermore, I would like to thank my dad, mother, sisters, brothers, and friends especially, who have been on my side all the way during this research, and I wish that I made them proud of my hard work.

## الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

### **Continuous flow photodegradation of olive zebbar contaminants with simulated solar light using supported ZnO nanoparticles**

**التحطيم الضوئي بالتدفق المستمر لملوثات الزيبار باستخدام ضوء مضاء  
لأشعة الشمس وحبيبات أكسيد الزنك النانوية كحفاز**

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The work provided in this thesis, unless otherwise referenced, is the  
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## List of Abbreviations

CB	Conduction band
CO <sub>2</sub>	Carbon dioxide
E <sub>g</sub>	Energy band gap
eV	Electron volt
FT-IR	Fourier transform infrared
h <sup>+</sup>	Holes
HOMO	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
TLV	Threshold Limit Values
LUMO	Lowest Unoccupied Molecular Orbital
M	Molarity
OH•	Hydroxyl radical
ppm	Part per million
OMWW	Olive mill wastewater
rpm	Round per minute
SEM	Scanning Electron Microscopy
TiO <sub>2</sub>	Titanium dioxide
t <sub>R</sub>	Retention time
UV-Vis	Ultraviolet-Visible
VB	Valence band
XRD	X-Ray Diffraction
ZnO	Zinc oxide
λ <sub>EX</sub>	Excitation wavelength
TWA	Time weighted average
STEL	Short-term exposure limit
PEL	Permissible exposure limit
WEEL	Workplace environmental exposure limit
IDLH	Immediately dangerous to life or health
AOPs	Advanced oxidation processes

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**Abstract**

Photocatalysis and adsorption are of the modern methods for water purification from biological and chemical pollutants. Photocatalysis is based on the presence of a catalyst (Zinc oxide) that absorbs ultraviolet radiation to destroy the contaminant substances (phenolic compounds). Researchers have developed several systems that increase the effectiveness of this catalyst in destroying organic pollutants and thus enable the use of direct sunlight in photo-driven water purification.

The continuous flow system is designed to allow Zebar water (contaminated with phenols) to run continuously over the catalytic surface while exposed to radiation. There is an entrance connected to the glass container, on which the catalyst is installed. On the other hand, there is an outlet for the treated water to be collected in another container for the necessary tests.

The properties of the glass-based catalyst were examined using electronic microscopy (SEM) and X-ray diffraction (XRD). The treated waters were analyzed using UV-Visible spectrophotometer, TOC and high-performance liquid chromatography (HPLC).

In this study, photodegradation of organic compounds in Zebar water, that result from olive mills, was investigated using the zinc oxide nanoparticle films installed on the bottom of a glass container. Zinc oxide, supported onto natural clay particles, was also installed on the glass. Zebar water was passed over the catalyst film under direct sunlight for photodegradation purposes. Effects of different parameters on photocatalytic process were studied including Zebar dilution, time duration, and pH. In the case of ZnO/glass catalyst, 40.8% of organic contaminants disappeared in 30 h, while in the case of ZnO/clay/glass 42.5% of organic contaminants disappeared.

The supported catalyst was reused for several times. It showed no significant efficiency lowering after multiple uses.

The results show the feasibility of using ZnO catalyzed photodegradation process in reclaiming water from Zebar. The resulting water could be considered for agricultural use as it contains useful minerals.

# **Chapter One**

## **Introduction**

# Chapter One

## Introduction

### 1.1 Overview

Scarcity and limited access to water resources in Palestine have been a major issue, which requires preservation of existed resources from possible contamination with different pollutants. Different types of direct and nondirect pollution sources contribute to this problem, including industrial and agricultural activities. One of the major pollution sources is Olive Mill Wastewater (OMWW), generated seasonally from olive oil extraction processes. OMWW is discharged to wadies without pre-treatment and may contaminate groundwater resources, mainly due to its high phenolic content. Pollution from OMWW is a major problem in developing countries, where sophisticated treatment technologies are too expensive [1]. The current and future wastewater treatment plants in West Bank are designed on a basis that does not take into account sudden overloading, and shocks related to OMWW discharges, which may jeopardize their functionality. Therefore, effective and feasible pre-treatment of OMWW must be considered before discharge [2].

There are many types of pollution. Water pollution is a very big challenge to humans, as water is the most important thing for the survival of life.

As the drinkable water Earth surface is equal to only 0.02%, this is becoming too low to sustain human demands. Increasing industrial, agricultural and domestic activities have led to the presence of liquid wastes containing various hazardous pollutants that pollute the remaining drinkable water [3-6].

There are many types of water contaminants, including chemical, biological and radioactive contaminants. The chemical contaminants are divided into organic and inorganic materials. Organic chemical contaminants enter the environment, altering water properties so that few concentrations of organic matter make water unsuitable for drinking [7].

Various methodologies have been developed to treat polluted waters. Examples are coagulation, filtration, ion exchange, sedimentation, electrolysis, ozonation, chlorination, and chemical deposition. However, these methods have their own limitations, this is limitations have the problem of high cost and low efficiency and generation of toxic products especially for high phenol concentration in wastewater [8].

Biological treatment suffers from severe substrate inhibition for wastewater with high phenolic content.

The presence of other contaminants significantly decreases the catalyst activity or permanently denatures the catalyst and thus there is a need to add continuously fresh catalyst at regular intervals.

The chemical oxidation, as well as extraction, requires the addition of large quantities of chemicals, which is infeasible from an economical and

environmental point of view. Steam distillation and electrochemical techniques require high energy consumption and in most cases, they result in incomplete treatment. On the other hand, adsorption, and Advanced oxidation processes are the most widely used technique for the removal and degradation of organic compounds [9].

Recently, advanced oxidation and reduction processes have been applied using solar energy to purify water from many pollutants, especially organic compounds [10].

These processes use special photocatalyst systems in their mechanism.

## **1.2 Problem description**

OMWW is the most critical waste generated from olive oil extraction processes. The annual OMWW production of the Mediterranean olive growing countries is estimated to amounts ranging from 7 to over 30 million m<sup>3</sup> [11]. Olive mills in the West Bank generate about 200 thousand m<sup>3</sup>/year of OMWW [12], and thousands of tons of solid olive residue (olive husk) that can not be applied directly to fields without pre-treatment as shown as table (1.1). The olive mills contribute largely to the core problem of surface and groundwater pollution [13]. Large volumes of OMWW are produced within a few months (October to December). OMWW discharge into fresh water would destroy the self-purifying

capabilities of these environments and seriously alter their biological balance. The poor biodegradability of OMWW inhibits possible spreading onto fields. Non-biodegradable organic compounds (such as phenols and organic contaminants) would reach waterbed and pollute it. In addition, dramatic overloading would take place in wastewater treatment plants due to OMWW spill into sewer system, as pollution of 1 m<sup>3</sup> of OMWW is equivalent to 100-200 m<sup>3</sup> of domestic sewage [11, 14]. Different treatment and pretreatment options are proposed to reduce the environmental impact of OMWW. Still, the feasibility and sustainability of these processes are of big concern with reference to the scattered distribution and location of olive mills near residential areas, taking into consideration the seasonal generation of OMWW. The large amount of phenolic compounds in OMWW deaccelerates and hinders COD removal in biological processes, detracting their economic viability. Worldwide, the going trend is towards photodegradation of organic contaminants from OMWW. Advanced oxidation processes (AOPs) was proved to an efficient method for degradation of phenol and organic contaminants [14, 15]. After organic contaminants degradation process, traditional wastewater treatment processes will be able to reduce OMWW pollution load to legally accepted levels for disposal. Water in Palestine is the most

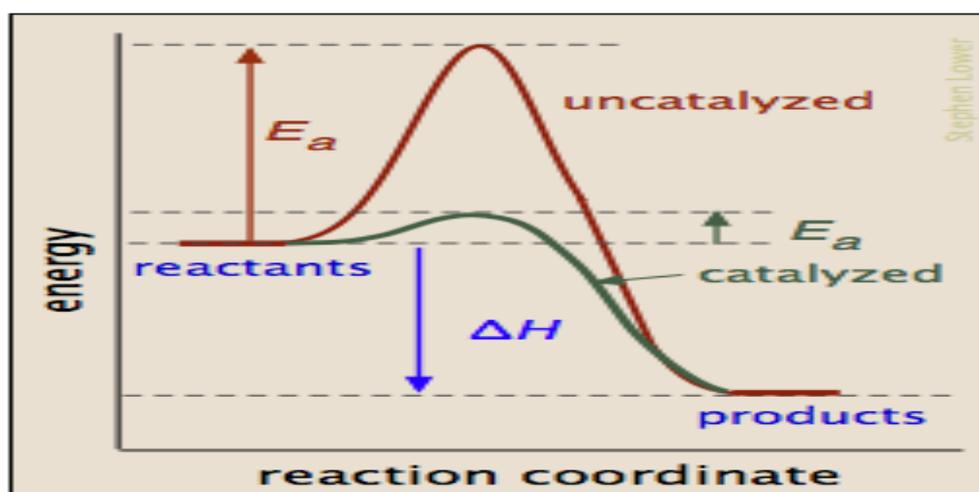
precious resource, where groundwater is the main water resource. Therefore, it is required to protect water resources and apply pre-treatment to OMWW before disposal. The table shows the percentage of organic pollutants and other characteristics found in olive zebar and solid olive residue resulting from olive mills according to the method of production. Table (1.1) shows Chemical compositions of olive fruit (%) [13].

**Table 1.1** Chemical composition of olive fruit (%) [13].

<b>Components</b>	<b>Olive-pulp</b>	<b>Stone</b>	<b>Seed</b>
Water	50-60	9.1	30
Oil	15-30	0.7	27.3
N	2-3	3.4	10.2
Sugar	3-7.5	41	26.6
Cellulose	3-6	38	1.9
Minerals	1-2	4.1	1.5
Poly phenols	2.25-3	0.1	0.5-1
Other compounds	-	3.4	2.4

### 1.3 Catalysts

The catalyst is defined as "a substance that increases the speed of the chemical reaction, without being consumed in the reaction, by lowering the activation energy of the reaction without affecting its equilibrium" [16]. Figure (1.1) describes how catalysis work.

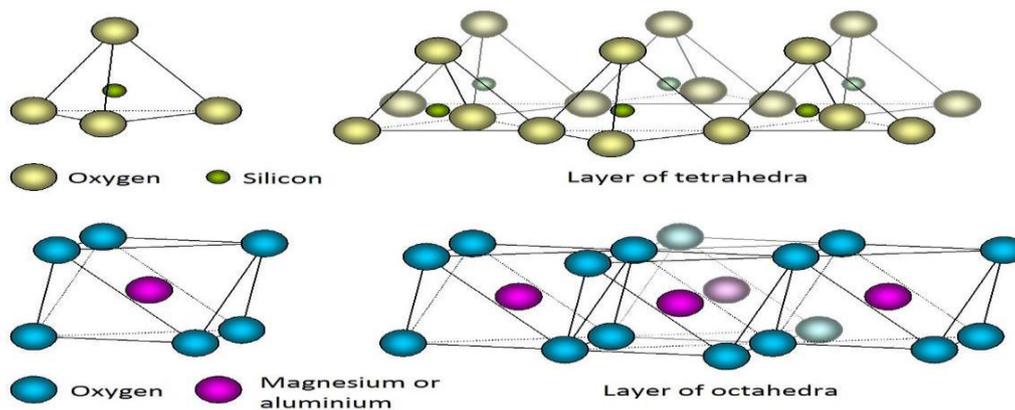


**Figure (1.1):** Activation energy for catalyzed and un-catalyzed reactions [16].

We can prepare catalysts in several processes such as degradation, reduction, impregnation and precipitation [17]. The catalysts are used in most industrial chemical processes [18], and are classified as homogeneous (e.g. most organometallic compounds) or heterogeneous (such as pellets with high surface areas, nanoparticles of  $\text{TiO}_2$ ,  $\text{ZnO}$  [19, 20] and layered structures. add Mud, and others) [21-23].

## 1.4 Clay

The clay is one class of aluminosilicate materials [24]. Clays are composed of multiple layers of octahedral and tetrahedral unit sheets [25, 26]. As shown in figure (1.2), the silica tetrahedral unit layer involves silicon atoms that are located in the centers of tetrahedrons at equivalent distances from four oxygen atoms. As a result of arrangement of tetrahedrons, a hexagonal network appears infinitely in two directions to form silica tetrahedral sheet [25, 27, 28]. Octahedral unit sheets involve closely packed oxygens and hydroxyls. Different types of cations in octahedral sheets produce many types of sheets. For example, gibbsite sheets contain aluminum cations while in brucite sheets the cations are magnesium ions.

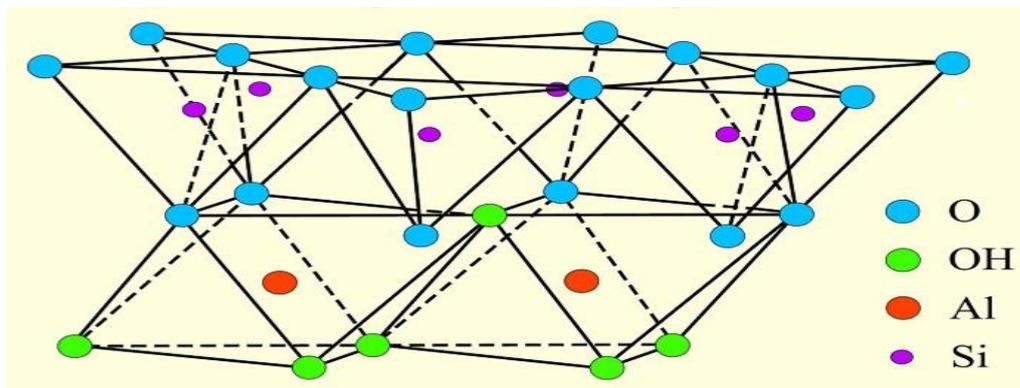


**Figure (1.2):** The structure of clay mineral [27-29].

Clays are stacked in polymeric tetrahedral and octahedral layers. The layer types depend on number and arrangement of these sheets and on type of cations between them such as ( $\text{Mg}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$ ) [29].

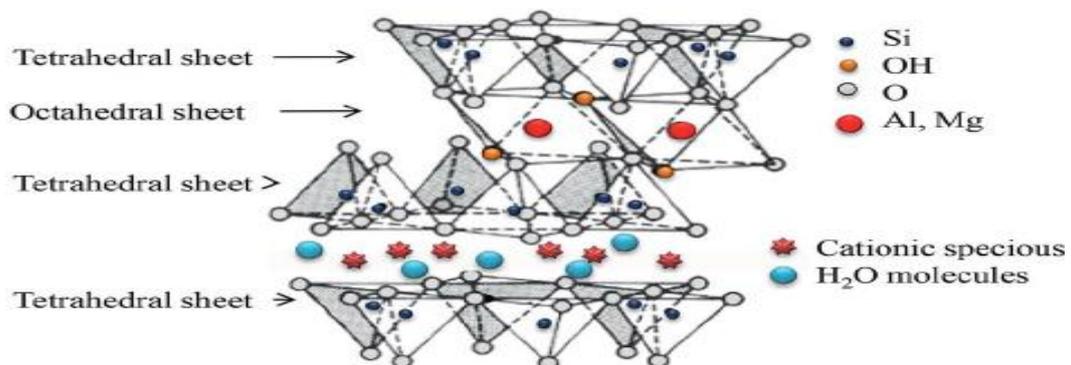
Clays may be expandable and non-expandable depending on bonding between layers. Examples of clays are:

- 1- Kaolinite 1:1 clay mineral, Figure (1.3). It is a non-expandable clay with one tetrahedral sheet and one octahedral sheet per layer.



**Figure (1.3):** Structure of 1:1 clay mineral (kaolinite) showing one tetrahedral sheet and one octahedral sheet [30].

- 2- Montmorillonite is a 2:1 clay mineral, Figure (1.4). An expandable clay that has two tetrahedral sheets and one octahedral sheet per layer.



**Figure (1.4):** Structure of a 2:1 clay mineral (montmorillonite) showing two tetrahedral sheets [29].

### **1.4.1 Catalytic Applications of clay**

In the clay frameworks, there are excessive negative charges, which are equaled by other free positive charges (cations). The charges may adsorb water and other polar solvents and trap them inside clay's cavities [31, 32]. They may initiate reactions by activating different trapped molecules, like in zeolites. Cavities and layers may also speed up reactions by bringing reactants in close distances inside cavities. Clays are thus used as heterogeneous catalysts or as supports for catalysts. Clays are commonly used in waste management, health-care products and therapeutic products [33].

### **1.5 Phenols**

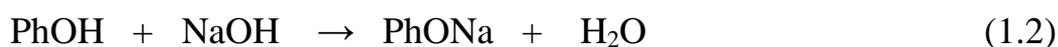
Phenols are a class of aromatic compounds having one or more hydroxyl (OH) groups anchored to an aromatic hydrocarbon group. Pure phenol is a colorless compound with the chemical formula  $C_6H_5OH$  that dissolves in water. Phenol is a flammable and corrosive substance [34]. Table (1.1) summarizes some physical properties of phenol.

**Table 1.2:** The main physical properties of phenol compound

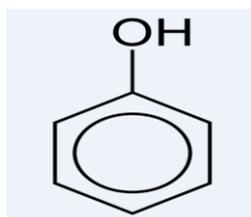
<b>Properties</b>	<b>Values</b>
Molecular formula	C <sub>6</sub> H <sub>5</sub> OH
Molar mass	94.11 g/mol
Odor	Sweet and tarry
Liquid density	1.07 g/cm <sup>3</sup>
Melting point	40.5 °C
Boiling point	182 °C
Solubility in water	8.3 g/100 ml (20 °C)
Maximum Wavelength	270.5 nm
Dipole moment	1.7 D
Acidity constant, pK <sub>a</sub>	10

Phenols are naturally present in many foods. They are naturally produced from benzene in the atmosphere in the presence of light. They are formed during forest fires. Phenol compounds may be produced during industrial and agricultural processes such as olive oil extraction, especially in Palestine. As they resist biodegradation, phenols can be hazardous to the living environment [35]. Phenol has a moderate solubility in water (8.5 g/100 ml) [5, 7] and remains in surface waters and groundwater for a long time without being biodegraded. Phenol and its derivatives are hazardous compounds being considered as carcinogenic substances, even at low concentrations, Phenol and its derivatives are dangerous compounds are considered carcinogens, even in low concentrations, where the threshold

limit value (TLV) of phenols equal to 5 ppm and immediately dangerous to life or health (IDLH) up to 250 ppm [35-37]. Phenol is weakly acidic, it is more acidic about one million times than aliphatic alcohols, despite being a weak acid. Phenol completely reacts with aqueous NaOH to lose H<sup>+</sup>, and gives sodium phenoxide, while most other alcohols react only partially. as shown in Equations (1.1) and (1.2) with unpleasant order [38, 39].



Phenol structural formula is shown in figure (1.5).



**Figure (1.5):** Structural formula of phenol.

Phenol leaks to environment and water when used in pesticides, dyes, plastics and pharmaceuticals. The olive mill residues obtained in olive oil extraction contain high concentrations of phenols together with other toxic organic compounds. Phenols may also be attached to soil particles and sediments at the bottom of rivers, lakes and water streams [40, 41].

They are highly hazardous to environment and health as it can affect kidneys, liver and immune system [42-44].

## **1.6 Adsorption**

Adsorption is a low cost, simple, efficient and important process. It is commonly used in technology, environment preservation, biological and industrial processes [45]. Adsorption is widely used in treatment of industrial effluents to remove toxic materials and keep them away from water, soil and air [46]. Adsorption immobilizes solutes from water onto surfaces of solid materials [47]. Adsorption is heavily involved in many catalytic reactions. Various adsorbents are widely used such as clays [48], montmorillonite [49, 50], kaolinite [49], sand [51], carbon nanotubes [52], aluminum oxide [53], and graphene oxide [54].

## **1.7 Photocatalytic degradation**

Photocatalysis is defined as the “*speeding up of the photoreaction by the presence of a catalyst*” [55]. It is advantageous for many solar light applications. Photocatalysts are classified based on the phase of the catalyst used, as:

- 1) Homogenous photocatalysts: where reactants and catalysts exist in same phase with no barriers. One example is ozone and photo-Fenton systems ( $\text{Fe}^+$  and  $\text{Fe}^+/\text{H}_2\text{O}_2$ ) [56].

2) Heterogeneous photocatalysts: where the catalyst and the reactants exist in different phases (with phase barriers). Examples are most semiconductor photocatalysts such as ( $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{Fe}_2\text{O}_3$ ).

Photocatalytic degradation attracting interest in wastewater treatment [57]. It involves degradation of toxic organic compounds inside water into mineral species such as  $\text{CO}_2$  and others [58-60].

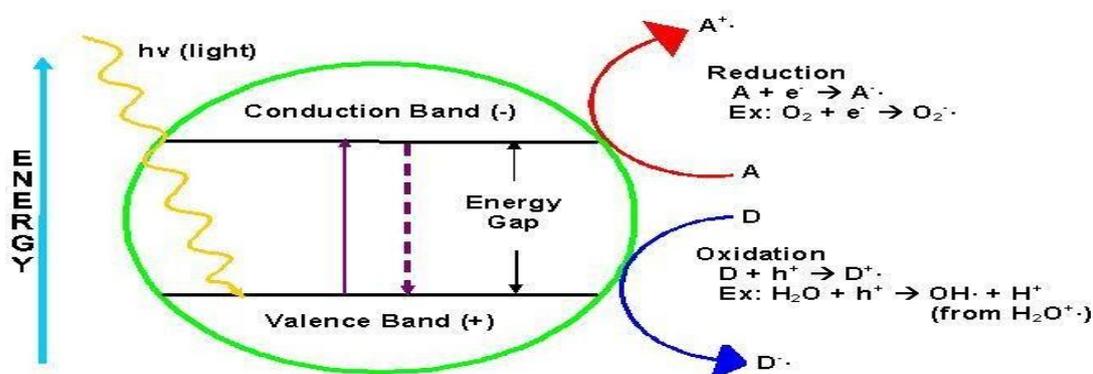
## **1.8 Semiconductor**

Semiconductors are mostly solids [61], with electrical conductivity values between conductors and the insulators [62]. A semiconductor contains two energy bands, one filled with electrons (Valence Band, VB), and one is empty (Conduction Band, CB). Semiconductors are widely used in many applications for example, solar energy, soil purification, water and air purification of micrograms, organic pollutants and others [63].

### **1.8.1 Semiconductor photocatalysts**

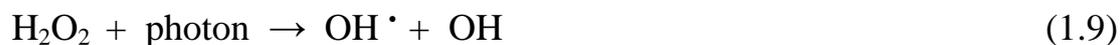
Semiconductor photocatalysis is an efficient and promising technology for complete removal of aqueous organic pollutants [64]. In a photocatalyst nanoparticle (e.g.  $\text{ZnO}$ ), the two bands VB and CB are separated by a band gap [65]. If a photon (with energy greater than the band gap energy) is absorbed by a semiconductor particle, excitation of electrons occurs from the (VB) to the (CB), leaving a hole ( $\text{h}^+$ ) in VB and an electron in CB. These separated holes and electrons move to the

semiconductor surface and react with other species. On one hand, the holes react with a reducible species to produce an oxidized product (Oxidation Process). On the other hand, the excited electrons react with oxidants (Reduction process). The two reactions are responsible to degrade organic pollutant molecules yielding  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and other minerals, as shown in figure (1.6) [67].



**Figure (1.6):** How semiconductor photo catalyst reaction occurs [68].

The basic reactions of degradation process, reported in literature [69], are shown below:



### 1.8.2 ZnO semiconductor photocatalyst

Zinc oxide is a white inorganic, nano-size insoluble powder with the formula ZnO [70, 71]. It is widely used in many applications such as semiconductor devices, additive material (in glass, paints, pigments, food, batteries) and others [72, 73].

ZnO is a semiconductor that is used as a powder photocatalyst. It has several advantages such as high photosensitivity, low cost, strong oxidizing power, stability and nontoxicity [74]. ZnO has a wide band gap value (3.2 eV) and therefore needs UV light, of ~380 nm wave length or shorter, for excitation. It is therefore being investigated as a semiconductor photocatalyst to degrade organic pollutants in water under UV or direct sunlight (which contains UV tail) [73].

The reactions of ZnO depend on the pH value of the medium. It is an amphoteric oxide that reacts with acids as a base, and reacts with bases as an acid [75], as shown in Equations (1.11) and (1.12).



## 1.9 Composite Catalysts ZnO/Clay

Composite materials are solid materials that are composed of two or more different substances. The composite material has properties that the separate materials cannot have individually. The composite materials also have advantageous properties over the separate constituent substances. In general, a composite material involves two phases: *reinforcement (filler)* and *binder (matrix)* [76]. The matrix embeds the reinforcement and holds it in place. Composites were known long time ago (~1500 B.C.). Nowadays, composite catalysts are developed to meet certain features of high activity, high selectivity and good stability. One main advantage of composite catalysts is the ease of recovering and reusing them from reaction mixtures. When the catalytic powder (such as ZnO powder) is added to aqueous solution, it becomes difficult to recover. To solve this technical difficulty, nanoparticle catalysts (such as TiO<sub>2</sub> and ZnO) were supported on various insoluble materials [77]. Large surface area materials such as silica, clay minerals, zeolite or activated carbon and aggregate oxides were used as support [24, 52].

The adsorption of the contaminant molecules is one major step in composite catalysis process during the equilibrium step. Then, the excited electrons and holes initiate the photocatalysis reaction. With higher adsorption capacity for organic molecules onto the supported material surface, the catalytic photodegradation efficiency is expected to increase.

### **1.10 Olive mill wastewater (OMWW)**

The wastewater generated from three-phase centrifugal olive mills contains wash water, decanter water in addition to vegetation water. The fraction of water in Palestinian olive fruit has an average value  $\sim 0.4$ [78]. This is in addition to total water used to represent the total amount of wastewater resulting from olive oil extraction.

The average value of  $1.25 \text{ m}^3/\text{ton}$  of OMWW is significant due to the limited resources of water in Palestine. This value is also high to compared with known OMWW generation rate ( $0.81\text{-}1.13 \text{ m}^3/\text{ton}$ ) [79]. OMWW generation rate from semi- automatic olive mills ( $< 0.55 \text{ m}^3/\text{ton}$ ) is needed in processing [79]. The average wastewater generation rate in Palestine to be  $1.7 \text{ m}^3/\text{ton}$ . The difference between the results is possibly be due to differences in quality of olives to various season [80]. The total amount of OMWW generated from the study area (West Bank) during the olive season 2010 is shown in Table (1.2).

**Table (1.3):** Total volume of OMWW generated in the study (\*West Bank) area during 2010 olive season[81].

<b>Item</b>	<b>Semi Automatic</b>	<b>Full-Automatic</b>	<b>Total</b>
Number of olive mills*	33	158	191
Quantity of pressed olives (ton)*	6880.7	69075.6	75956.3
OMWW generation rate (m <sup>3</sup> /t)	0.55	1.25	–
Volume of OMWW (m <sup>3</sup> )	3784.4	86344.5	90128.9

### 1.11 Objectives

The main purpose of this work is to reclaim water from olive mill *Zebar*. *Zebar* is heavily polluted with phenols and other organic materials. In this work, the organic contaminants will be removed from *Zebar* in two ways: adsorption and catalytic degradation under simulated sunlight (which resembles direct solar light) using a safe, low cost semiconductor material (ZnO). ZnO nanoparticles are supported on solid natural clay for easy reuse. The evaluation of the process will be verified in terms of efficiency, cost and environmental and economic values. The reuse of the compound catalyst will also be investigated.

**Technical objectives include:**

- 1- Preparation of nano-sized powder ZnO from  $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ .
- 2- Compare between characteristics of prepared nano-ZnO (with commercial ZnO) using XRD, and other techniques.
- 3- Preparation of new nano-sized composite material (ZnO/Clay) and characterize it using XRD.
- 4- Using the prepared ZnO powder in photodegradation of organic compounds in *Zebar* with simulated solar light.
- 5- Using ZnO/Clay composite material in photodegradation of organic compounds with simulated solar light.
- 6- Studying effects of pH, contaminant concentration, and time of contact on photocatalyst activity and photodegradation process efficiency.
- 7- Studying the possibility of multiple use of the ZnO/Clay catalyst (reusing the photocatalyst for multiple times in photodegradation process).

This work is expected to reduce the concentration of pollutants in water, especially phenols, using a simple and inexpensive method without using any expensive or dangerous chemicals.

### **1.12 Novelty of this work**

During recent years the photocatalysis process has been widely investigated for the purification of water from many toxic organic pollutants. It is a new promising environmental protection technology. Naked  $\text{TiO}_2$  and ZnO have been used as photocatalysts for degradation of widespread pharmaceutical wastes [63]. Other studies used pristine and kaolinite supported ZnO catalyst in the degradation of 2-chlorophenol in water under direct sun light [9]. Another study used ZnO/montmorillonite nanoparticles as catalyst for the adsorption and photodegradation of tetracycline in water [62]. Earlier studies did not use embedded ZnO in clay as photocatalysts. In this work, nano ZnO particles embedded in natural clay are used for the degradation of phenols under direct sun light. To our knowledge, ZnO particles were not supported on natural clay for photocatalysis purposes. The newly prepared composite ZnO/Clay is used for photocatalytic degradation of Phenols, by solar simulated light, for the first time.

On one hand, Nano-ZnO embedded inside natural clay would provide high efficiency due to clay distinctive physical properties, such as large specific area, layered structure and high adsorption. On the other hand, supporting the catalyst will allow catalyst recovery and reuse for additional degradation process [24, 82, 83].

The mechanism of continuous flow of contaminated water has benefits and advantages, the most important of which:

1. Give a clear picture of the reactor in which the treatment is done, which provides a clear idea for engineers to build a large reactor that absorbs the water of olive mills at each mill.
1. Do not contaminate the treated water with the catalyst, as the catalyst is supported on the surface on which the flow of water will be.
2. Design of the reactor in a manner that allows the consumption of water after treatment in irrigation.

**Chapter Two**  
**Materials and methods**

## Chapter Two

### Materials and methods

#### 2.1 Materials

Commercial Zinc oxide with serial number of 14439 was purchased from sigma Aldrich. Zinc acetate dihydrate  $[\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}]$  was purchased from Sigma Aldrich and NaOH from Frutarom Co. Natural clay was purchased in its paste state from local pottery workshop at Jaba, Jenin, Palestine. All these materials were used for the preparation and synthetic the composite ZnO/Clay nanoparticles. A sample of wastewater of olive mill (*Zebar*) was taken from an olive mill from *Seilat Al-Harthyia*, Jenin, North Palestine.

#### 2.2 Equipment

Special glass dishes (165 cm<sup>2</sup> area) were prepared with help from the Chemistry Department glass blowing facility to immobilize layers of ZnO nanoparticle catalyst and ZnO/Clay catalyst. The dish was equipped with tow tubes, one as inlet and one as outlet to pass *Zebar* flow over the catalyst layer. A Lux-meter (Lux-102 light meter) was used to measure the incident light intensity that reaches the water sample under study.

A Büchner funnel was used as a vial to separate the solid components from the *Zebar* solution. Water 1525 High performance liquid chromatography, equipped with water 2998 photodiode array detector and detection wavelength of 280 nm, was used to study the remaining phenol and organic contaminants concentrations in the *Zebar* during and after photodegradation experiments. The eluent solution was [50% water, 50% methanol] with flow rate 0.8 ml/min. The injection volume was 20  $\mu$ l move to proper place HPLC. HLX64657 EVC 24V250W halogen lamp which provides super bright light was used as simulated solar light.

A Shimadzu UV-1601 spectrophotometer, equipped with a thermal printer Model DPU-411-040, type 20 BE, was used for a quantitative determination of phenol in the *Zebar* solution.

A Perkin-Elmer LS50 Luminescence Spectrophotometer was used for photoluminescence measurements of each catalyst. Crystal structure of ZnO and ZnO/Caly catalysts were measured on X-Ray diffractometer (XRD) with  $\text{CuK}\alpha$  ( $\lambda_{1.5418}$  Å) as source, in South Korea. A Jenway 3510 pH meter was used to adjust the reaction mixture pH as desired. A mercury thermometer was used to measure temperature. The accurate masses were measured by using a four digit balance (AR-3130 from OHAUS Crap).

## 2.3 Preparation of solutions

### **Olive mill wastewater (OMWW) *Zebar* stock solution preparation:**

1- One liter of olive mills wastewater OMWW was filtered through a Büchner flask to filter off the insoluble solid particles. The process was repeated again, and then the stock solution was kept in the dark for further uses.

2- Dilute solution of NaOH was prepared to control the pH in the catalytic experiments. Sodium hydroxide NaOH (0.9 M) solution was prepared by dissolving 9 g in 250 ml aqueous solution.

3- Zinc acetate (0.68 M) was prepared by dissolving 37.5 g of zinc acetate dihydrate in 250 ml aqueous solution.

## 2.4 Catalyst preparation

### **2.4.1 Supporting ZnO catalyst onto glass dishes:**

Commercial ZnO particles were supported onto the surface of the bottoms of glass dishes, based on the following procedure [66]:

1- The dish was washed with detergent and dried in on oven at 120 °C.

2- ZnO powder (10 g) was suspended in distilled water (100 ml)

3- The ZnO was placed in a sonicator for 1 h to disperse agglomerates

- 4- The ZnO suspension was stirred for 10 minutes
- 5- An aliquot of ZnO suspension (20 ml) was placed in the glass dish and left over night to evaporate excess water.
- 6- After 24 hours, the dish with the ZnO catalyst layer was placed in an oven and heated. The temperature was raised gradually to 450 °C, and left at that temperature for 1 hour.
- 7- A ZnO layer adhered to the dish surface. The dish with ZnO catalyst layer was cooled down (throughout 3 hours) and carefully stored for further use.

#### **2.4.2 Supporting ZnO powder onto clay particles:**

ZnO/clay composite paste was prepared as follows:

- 1- Clay paste (10 g) was placed in 250 ml of 0.9 M sodium hydroxide solution.
- 2- The mixture was heated to 55 °C with magnetic stirring, and Zinc acetate solution (250 ml, 0.68 M) was added drop wise.
- 3- The solution was removed from the precipitate and washed with distilled water until was neutral.

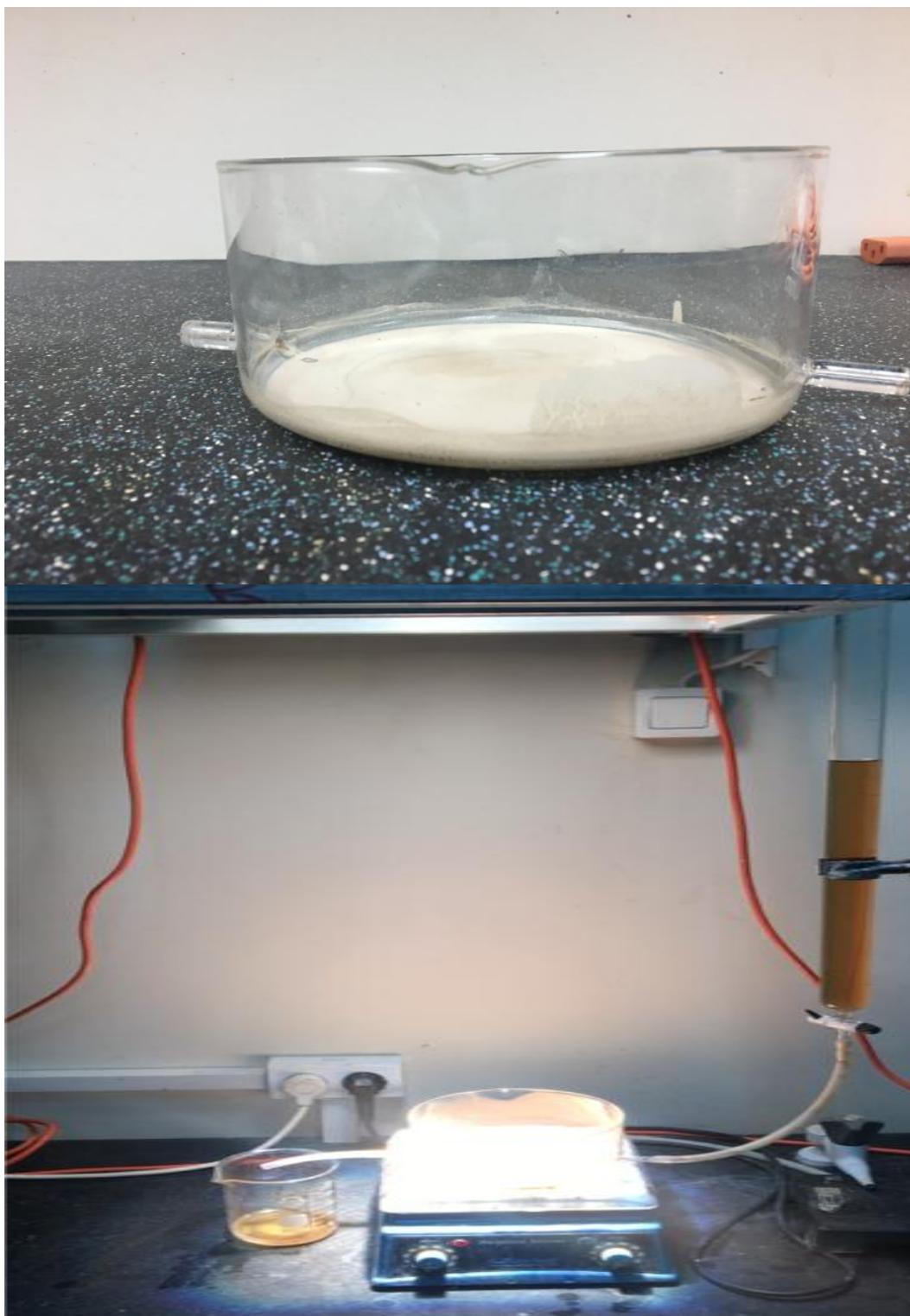
### **2.4.3 Supporting ZnO/Clay catalyst onto glass dishes:**

The ZnO/Clay component on the glass dish is installed as follows:

- 1- The reaction dish was washed with detergent, rinsed with distilled water and dried in an oven at 120 °C.
- 2- An amount of ZnO/Clay suspension (20 ml) was placed in the glass dish and left overnight to evaporate excess water.
- 3- After 24 hours the dish with the ZnO/Clay catalyst layer was placed in an oven and heated. The temperature was raised gradually to 450 °C, and kept for 1 hour at that temperature.
- 4- A ZnO/clay layer adhered to the dish surface. The dish with ZnO catalyst layer was cooled down gradually (through 3 hours) and carefully stored for further use.

### **2.4.4 Photocatalysis:**

The glass dishes with ZnO layer and ZnO/Clay layer inside were used as reactor vessels. The reaction dish was placed under a solar simulator lamp. A 250 ml burette was connected to the entrance of the dish with a tube to let the *Zebar* solution flow above the catalyst film. The dish outlet was connected with a 250 ml beaker to collect and analyze the oncoming solution. Figure (2.1) describes the reaction dish and the reaction setup used in photodegradation experiments.



**Figure (2.1):** The continuous flow reactor used in photodegradation experiments.

## **2.5 Photocatalytic experiments:**

### **2.5.1 Phenol photodegradation:**

Continuous flow rate photodegradation experiments were typically conducted as follows:

A solution (200 ml) of *Zebar* was flowing above the supported catalyst for time, the collected solution in the beaker back to the burette. To keep the solution flowing over the catalyst layer, and the reaction duration was continued for 30 hours.

The photocatalytic reaction was conducted under solar simulated light. The measured light intensity was 200,000 Lux (0.0292 w/cm<sup>2</sup>).

UV-Visible spectrophotometry, TOC, and HPLC analysis was used to measure the change in phenol and organic contaminants concentrations with time during the photocatalytic degradation reaction.

The photocatalytic reaction was studied under different conditions. Effect of type of Catalyst, pH value and *Zebar* solution concentration were all studied.

### 2.5.2 Effect of *Zebar* dilution on the phenol degradation by photocatalyst:

Different solutions of *Zebar* dilutions (2.5%, 5%, and 7.5%) by V/V were prepared. Solutions (200 ml) of *Zebar* were diluted as required from the original stock solution of *Zebar* that contains organic contaminants including phenols. **Table (2.1)** shows *Zebar* solutions prepared. The table shows corresponding amounts of stock solutions used to prepare 200 ml of each concentration.

**Table 2.1:** Preparation of different concentration of *Zebar*.

Dilution percent of <i>Zebar</i> V/V%	Volume needed from stock solution (ml)	Volume of distilled water added (ml)
<b>2.5</b>	<b>5.0</b>	<b>195.0</b>
<b>5.0</b>	<b>10.0</b>	<b>190.0</b>
<b>7.5</b>	<b>15.0</b>	<b>185.0</b>

The different *Zebar* concentrations were used in the continuous flow reaction experiments. The *Zebar* solutions were passed over the catalyst film under solar simulated light for periods to 30 hours using a fixed pH value at room temperature ( $25 \pm 2$  °C). The same ZnO plate was reused in different experiments conducted under different conditions. Similarly, the same ZnO/Clay plate was used in different photocatalytic experiments as well.

### **2.5.3 Effect of pH:**

Initially, the pH of the diluted *Zebar* solution was measured to be 4.5. The pH value was controlled by adding drops of diluted sodium hydroxide (NaOH) solution. To study the effect of the change in the value of pH, different pH values were examined: (Naturally acidic 4.5, neutral 7 and basic 9.5). The reaction was carried out using 200 ml of *Zebar* solution at a concentration of 5%, passed as a continuous flow system over the stationary catalyst film, under solar simulated light for 30 hours.

### **2.5.4 Effect of clay support:**

To study the effect of clay support on the ZnO catalyst efficiency, both ZnO and ZnO/Clay catalysts were studied phenol degradation. ZnO and ZnO/Clay catalyst plates were used as films anchored on the dishes. The continuous flow reaction was carried out using 200 ml of *Zebar* solutions using 5% dilution (Acidic, neutral and basic media) under the solar simulated light for up to 30 hours.

### **2.5.5 Effect of exposure time:**

To study the effect of exposure time on the degradation process, a *Zebar* solution 200 ml (2.5%, 5.0% 7.5%) was passed through the continuous flow reactor under the solar simulation light intensity of 200000 lux (0.0292 W/ cm<sup>2</sup>) for different exposure times (10, 20, and 30 hours). The remaining phenol concentrations were measured at end of each time by UV-Visible spectrophotometry and TOC.

### **2.5.6 Catalyst reuse:**

Catalyst reuse was studied by recovering the glass/catalyst films and reusing them for fresh *Zebar* solutions in new degradation experiments. The recovered catalyst plate was used many times. In each time a *Zebar* solution (200 ml) was used under fixed conditions of light intensity 200000 lux (0.0292 W/ cm<sup>2</sup>) and acidity for 30 hours.

## **Chapter Three**

### **Results and Discussions**

## Chapter Three

### Results and Discussions

#### 3.1 Catalysts characterization

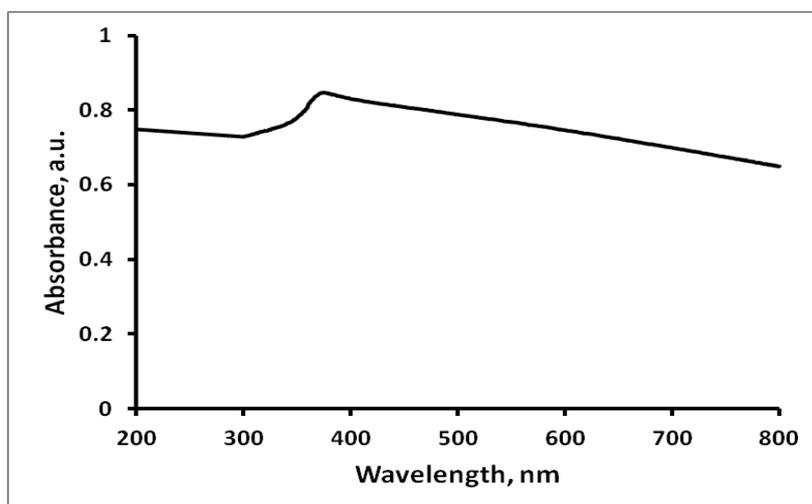
Characterizations of catalysts were carried out by solid state UV-Visible absorption spectrophotometry, XRD, and SEM techniques.

##### 3.1.1 UV-Visible absorption spectrophotometry characterization

Solid state UV-Visible electron absorption spectra were measured in quartz cell, as suspension in water. Water was used as baseline correction.

###### 3.1.1.1 ZnO catalyst:

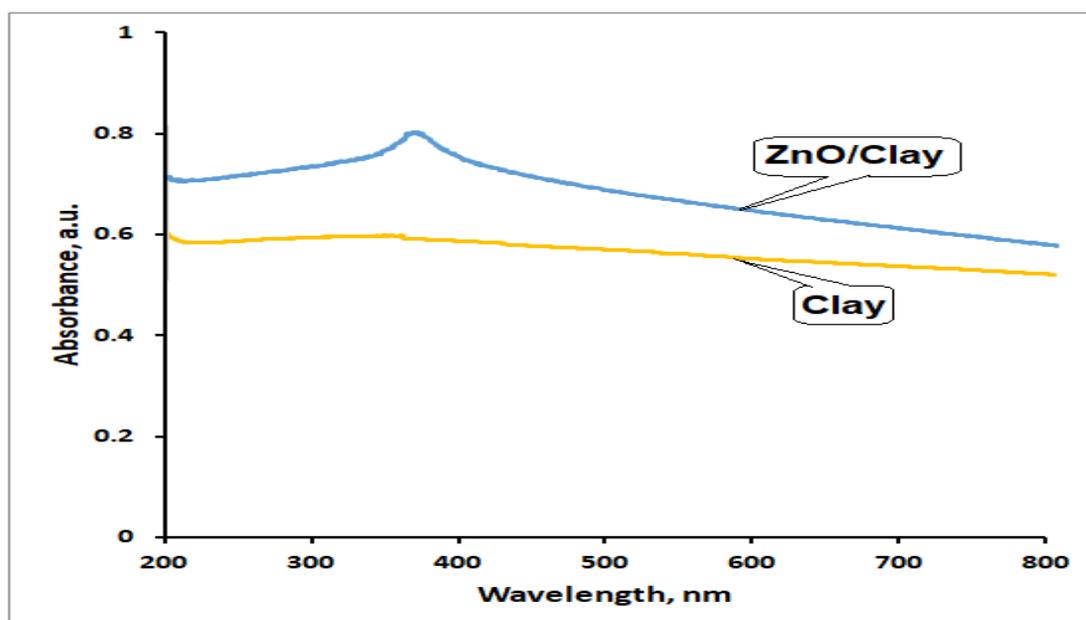
Figure (3.1) represent the absorption spectrum of ZnO powder, the absorption spectrum shows absorption maximum ( $\lambda_{\max} \approx 380$  nm) similar to that of literature [67].



**Figure (3.1):** The Electronic absorption spectra of ZnO powder.

### 3.1.1.2 ZnO/Clay composite catalyst

Figure (3.2) shows the electronic absorption spectrum for **ZnO/Clay** catalyst and clay. Naked clay shows no absorption maxima in the range 200-800 nm, while the other system of **ZnO/Clay** show absorption maxima at  $\lambda_{\text{max}} \approx 375$  nm with shorter wavelength than the naked ZnO powder. The slightly blue shift compared with the prepared ZnO is attributed to smaller particle size of ZnO supported onto clay [84].



**Figure (3.2):** Electronic absorption spectra of a) ZnO/Clay catalyst, and b) Naked Clay.

### 3.1.2 X-Ray diffraction results

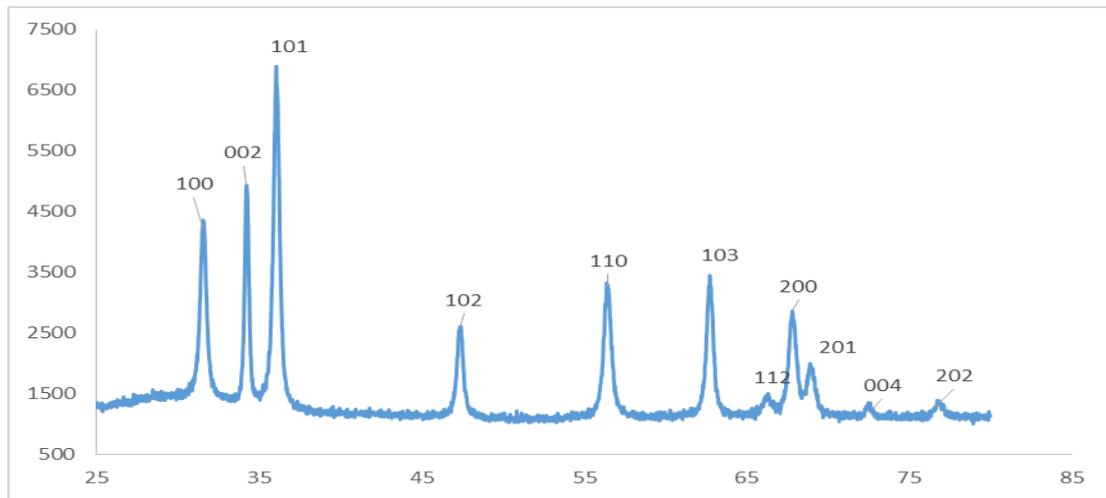
X-ray diffraction (XRD) patterns were measured with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) as a source. The Scherrer equation (3.1) was used to calculate average particle size, using all reflections.

$$d = \frac{K\lambda}{B \cos\theta} \quad (3.1)$$

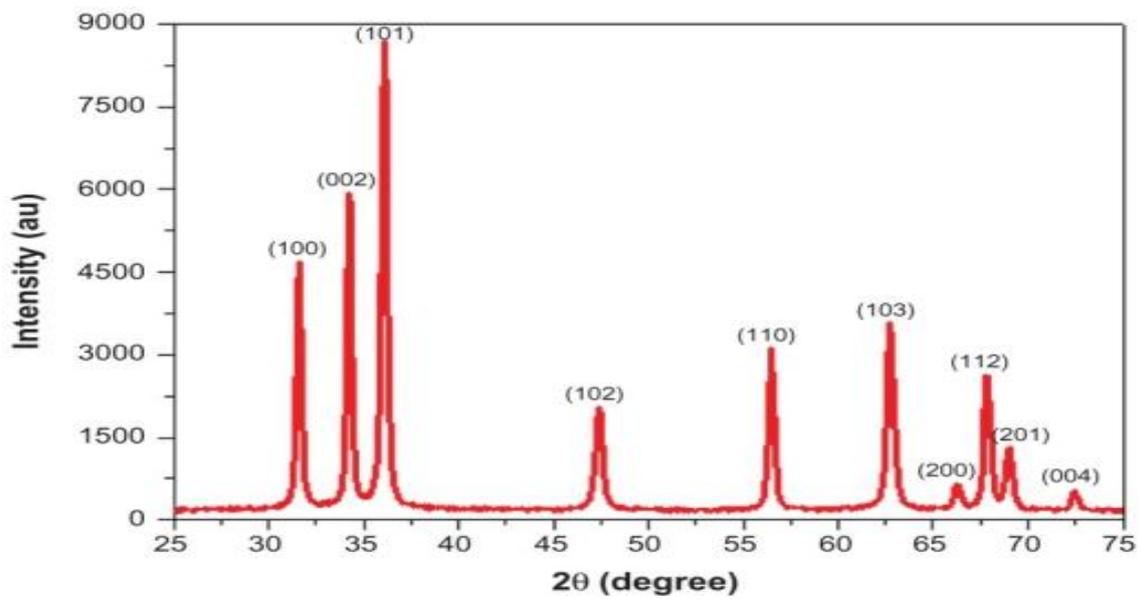
Where  $d$  is the mean particle size, which may vary for different particles,  $K$  (about 0.9) is the shape factor,  $\lambda$  (0.154 nm) is the x-ray wavelength,  $B$  is broadening at half the maximum intensity in radians, and  $\theta$  is the Bragg angle.

#### 3.1.2.1 X-Ray analysis of commercial ZnO nano-powder:

X-ray pattern for commercial ZnO nano-powder is shown in Figure (3.3). The figure shows characteristic peaks for ZnO at  $2\theta = (31.6^\circ), (34.2^\circ), (36^\circ), (47.4^\circ), (56.4^\circ), (62.7^\circ), (67.8^\circ)$  and  $(68.6)$ . These peaks resemble those reported as figure (3.4) for (100), (002), (101), (102), (110), (103), (112), and (201) crystal planes, respectively, with wurtzite-like structure [85, 86].



**Figure (3.3):** Measured XRD-pattern measured for commercial ZnO nano-particles.



**Figure (3.4):** Literature XRD-pattern of Wurtzite Crystal ZnO nano-material [87].

The XRD pattern thus confirms that the commercial solid is ZnO. The powder involves nano-size particles. The average particle size was calculated using Scherrer equation using reflections (100, 002, 101, 102, 110, 103, 200, 112, 201, 004) and was found to be ~43 nm.

### 3.1.2.2 X-Ray analysis of ZnO/Clay:

X-Ray pattern was measured for prepared **ZnO/Clay** composite, Figure (3.5). The XRD pattern in Figure (3.5) shows distinguished peaks for hexagonal wurtzite type of ZnO powder. The calculation based on Scherrer equation using reflections values (100, 002, 101) shows a decrease in the particle size of ZnO on clay surface, the calculated ZnO particle size is ~15.2 nm. The difference in nanoparticles size between ZnO and ZnO/clay is the presence of clay substrate in the second type so that ZnO particles deposited on clay before the particles growth thus the size is smaller.

The inter layer distance of the clay was 0.3 nm, as calculated by Bragg's law[72],  $d = n\lambda/2\sin\theta$  (Where d is the inter planer distance in the crystal,  $\theta$  is the Bragg angle, and n is an integer = 1, and  $\lambda = 1.5418 \text{ \AA}$ ). Comparison of XRD pattern for prepared **ZnO/Clay** catalyst with the clay is prepared. Figure (3.6) shows the pattern for the used clay [88, 89]. The results confirm the following:

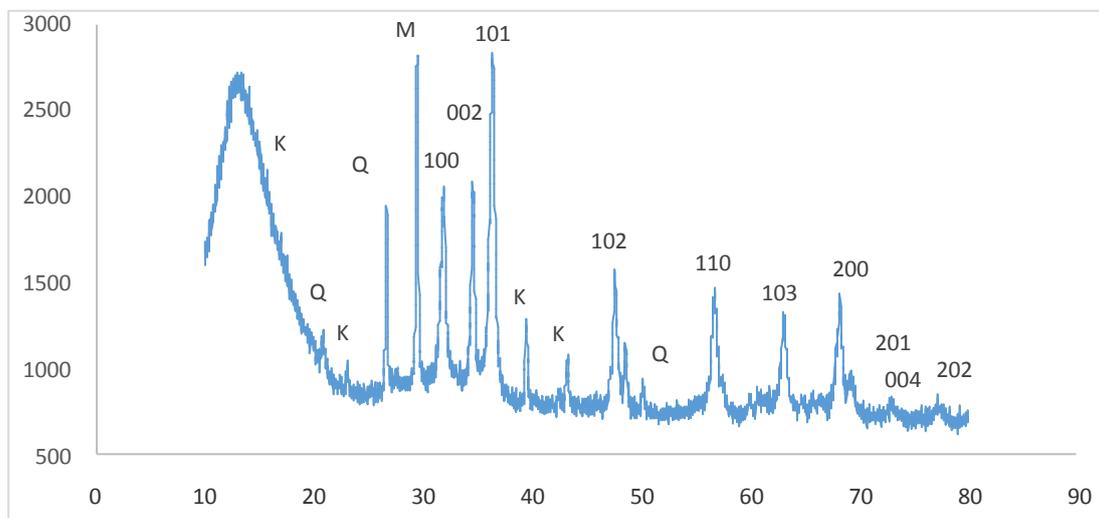
- 1- Kaolinite: the kaolinite peaks are at  $2\theta = (13.3^\circ), (23^\circ), (39.5^\circ)$  and  $(43^\circ)$ . The interlayered distance of kaolinite clay exists in prepared clay was 0.3 nm. The value resembles that of literature sample interlayer distance 0.29 nm [90, 91]. Kaolinite is a non-expandable clay with small

interlayer distance. Therefore, ZnO nanoparticles can't penetrate between Kaolinite layers.

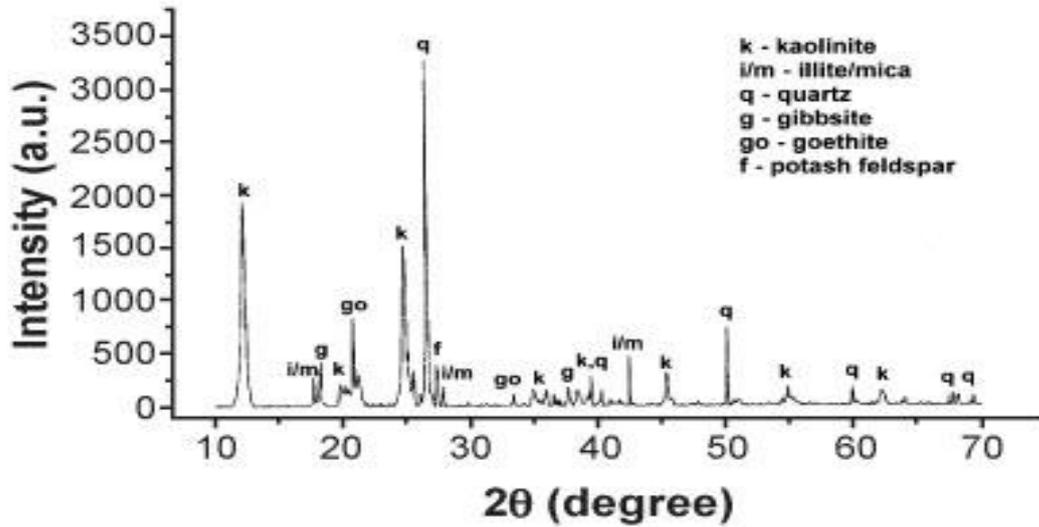
2- Quartz: the quartz peaks are at  $2\Theta = (20.8^\circ), (26.6^\circ)$  and  $(50.2^\circ)$ . Quartz is non-layered structure, and the ZnO particles also can't penetrate inside [92].

3- Montmorillonite: the montmorillonite is at  $2\Theta = (29.5^\circ)$  with interlayer distance  $\sim 0.31$  nm.

The results thus confirm that ZnO particles are present only on the clay surface (not intercalated inside clay layers).



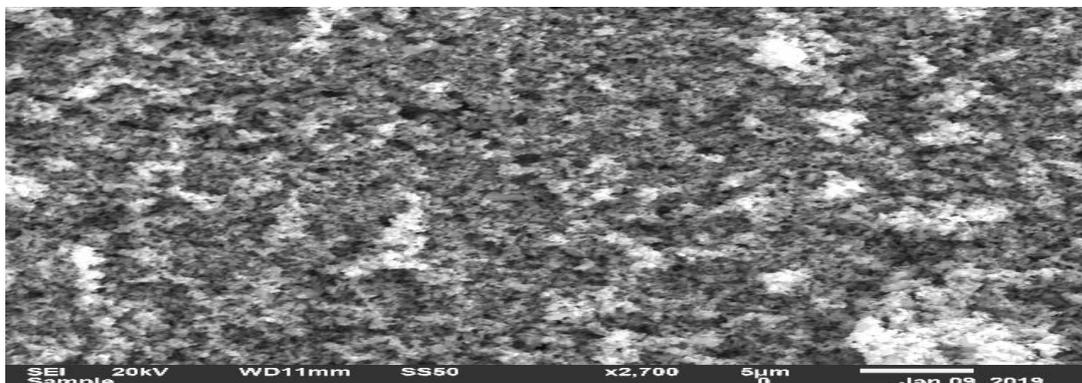
**Figure (3.5):** Measured XRD-pattern of ZnO/Clay composite catalyst.



**Figure (3.6):** Literature XRD-pattern of clay sample [93, 94].

### 3.1.3 SEM results for ZnO supported glass:

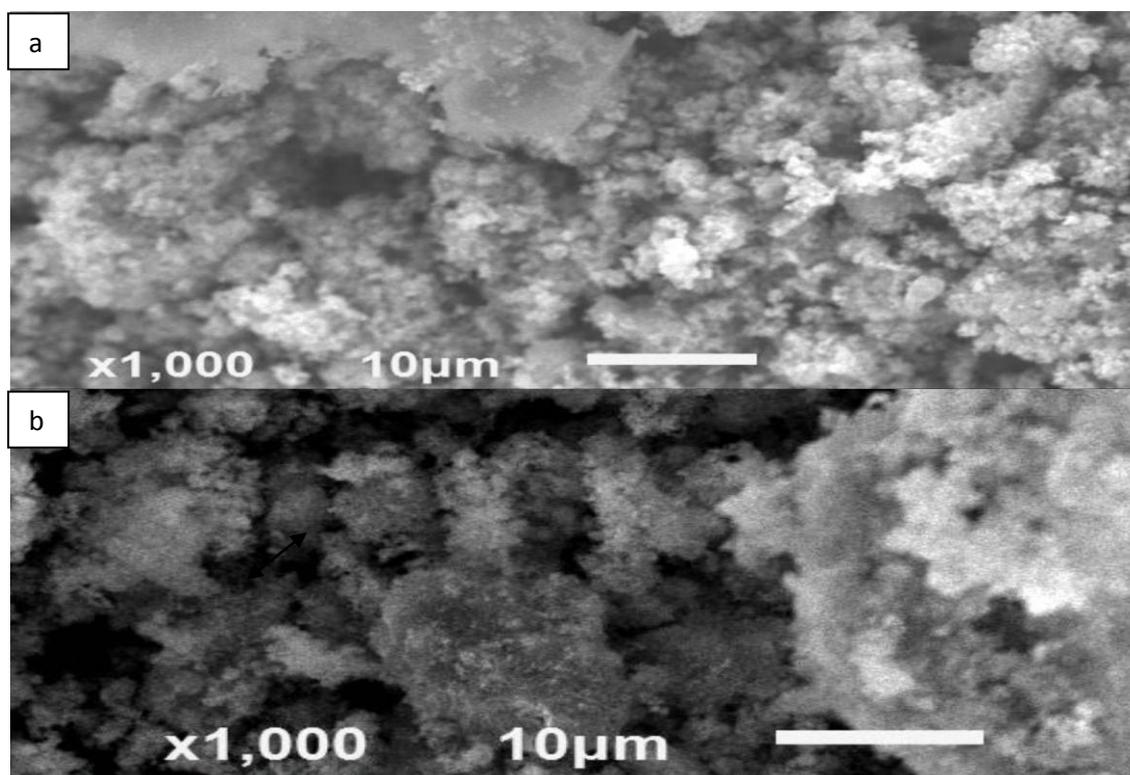
Field emission scanning electron microscopy using the energy dispersive spectroscopic FE-SEM/EDS technique was used to find Surface morphology for glass-supported ZnO catalyst film. The SEM micrograph shows that the catalyst film has soundly uniform distribution of agglomerated nano particles on the glass substrate, As shown in Figure (3.7).



**Figure (3. 7):** SEM micrographs measured for Supported ZnO catalyst.

### 3.1.4 SEM results for ZnO and ZnO/Clay

Surface morphology and estimated size were measured for **ZnO/Clay** composite catalyst with field emission scanning electron microscopy using the energy dispersive spectroscopic FE-SEM/EDS technique. Figure (3.8a) shows the SEM micrograph for prepared unsupported **ZnO** catalyst. Figure (3.8b) shows the SEM micrograph of prepared **ZnO/Clay** catalyst, and shows ZnO particles living in agglomerates on the clay surface. The unsupported ZnO powder involves larger agglomerates (~ 400 nm) than the supported ZnO (~ 200 nm).



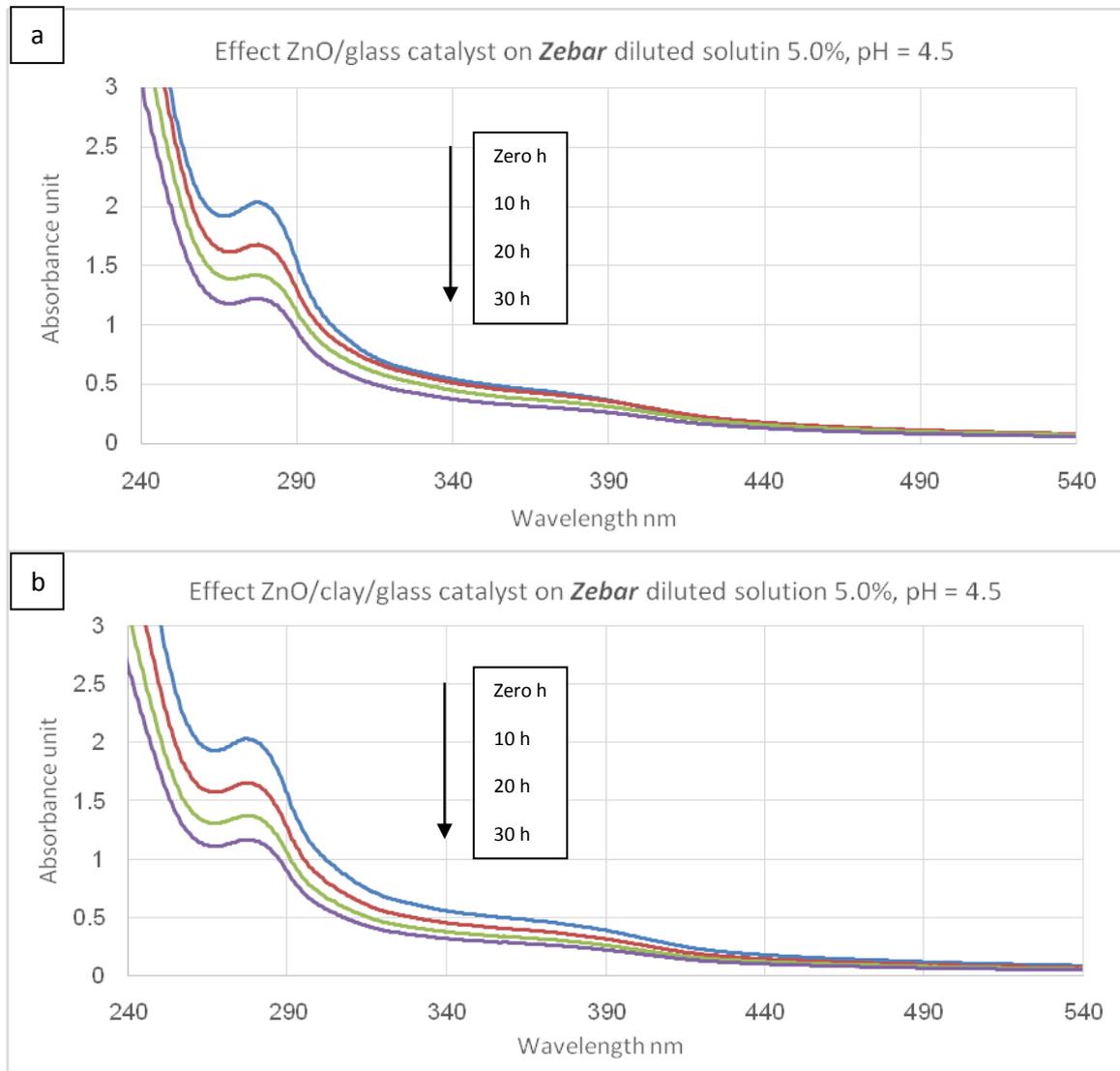
**Figure (3.8):** SEM micrographs measured for a) prepared naked ZnO particles, and b) supported ZnO/Clay catalyst.

### **3.2 Photodegradation reaction results:**

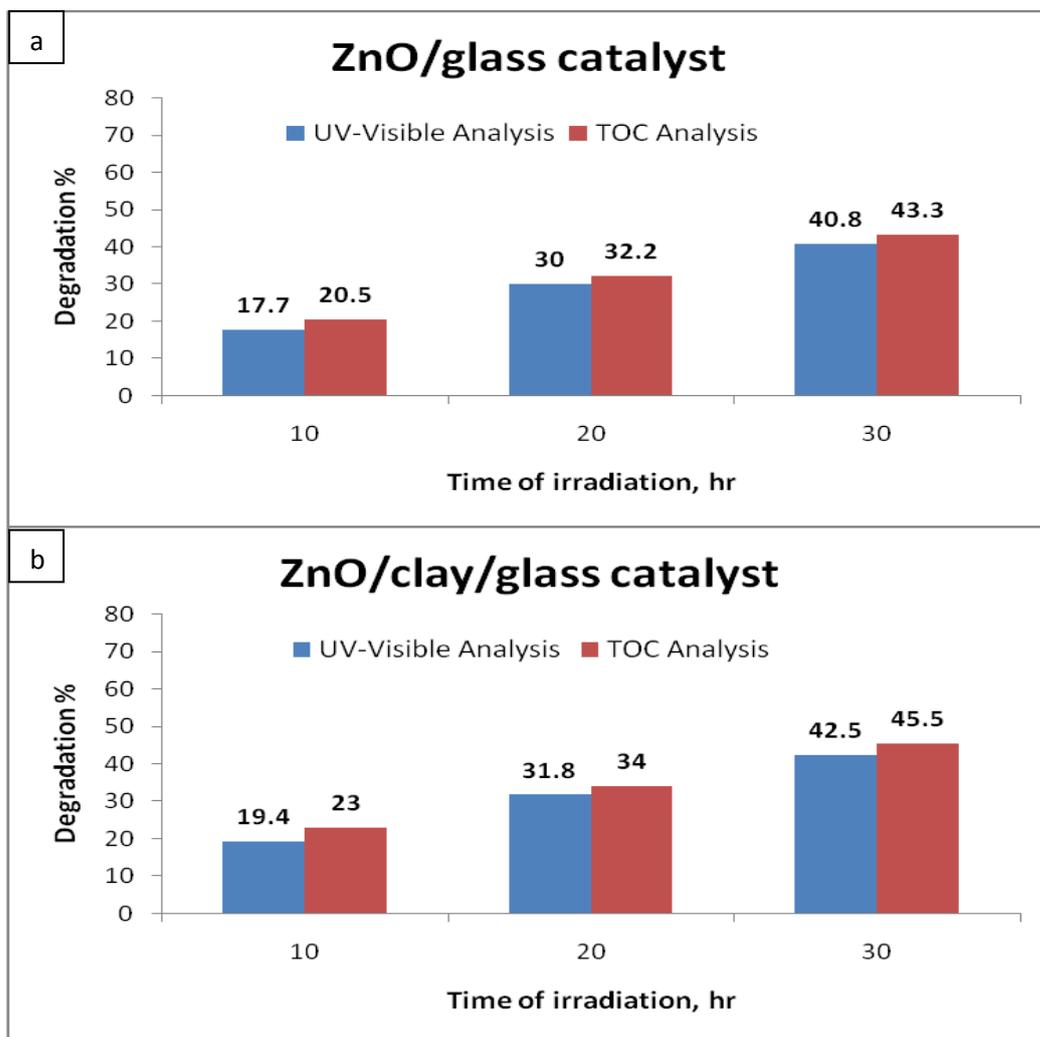
As stated above, effects of different reaction parameters on photodegradation reaction progress were studied light intensity uses. The results are described below. Amount of degraded organic matter was measured in two ways: the lowering in spectral absorption band at 280 nm (due to phenyl group) and lowering in total organic carbon (TOC) in the treated *Zebar* solution. Both ways *Zebar* are shown in this work and the two ways are consistent with each other.

#### **3.2.1 Effect of type of Catalyst:**

Figures (3.9a) and (3.10a) show that using ZnO/glass catalyst, in diluted *Zebar* at (5%) with original pH = 4.5, phenol and other organic compounds degraded on to exposure to solar light. After 30 h of exposure to solar light, phenol degradation of 40.8% occurred by solar light. Figure (3.9b) and (3.10b) shows that using ZnO/clay/glass, the rate of phenol degradation slightly increased, reaching 42.5% in 30 h. The reason for the increased adsorption ratio is the presence of clay with zinc oxide.



**Figure (3.9):** Effect of type of catalyst. UV-Visible absorbance spectra measured for Phenol at various times using diluted *Zebar* 5.0% at room temperature under direct solar light use in different catalysts a) ZnO/glass and b) ZnO/clay/glass.



**Figure (3.10):** Effect of catalyst type, Value of % degradation for *Zebar* organic matter measured after different reaction times using *Zebar* 5.0% at room temperature, catalyst a) ZnO/glass and b) ZnO/clay/glass.

The photodegradation result for the two catalyst systems are summarized in Table (3.1). The table shows continued increase in % degradation with time for two catalyst systems. TOC content also decreased with reaction time.

**Table (3.1):** Values of % loss of organic compound in *Zebar* solution (5.0%) after treatment. UV- Visible spectra and TOC results are shown. Different catalysts are used.

Dillution by 5%, using ZnO/glass , pH ~ 4.5 (Acidic)				
Sample	1	2	3	4
Time in hours	Zero hour	10 hours	20 hours	30 hours
Absorbance in wavelength at 276.5 nm	2.062A	1.698A	1.441A	1.220A
Percentage of degradation of phenol	0 %	17.7 %	30.0 %	40.8 %
TOC mg/L	1509	1200	1024	856
% Loss	0 %	20.5 %	32.2 %	43.3 %
Dillution by 5%, using ZnO/Clay/glass , pH ~ 4.5 (Acidic)				
Sample	1	2	3	4
Time in hours	Zero hour	10 hours	20 hours	30 hours
Absorbance in wavelength at 276.5 nm	2.035A	1.640A	1.387A	1.170A
Percentage of degradation of phenol	0 %	19.4 %	31.8 %	42.5 %
TOC mg/L	1489	1147	983	812
% Loss	0 %	23.0 %	34.0 %	45.5%

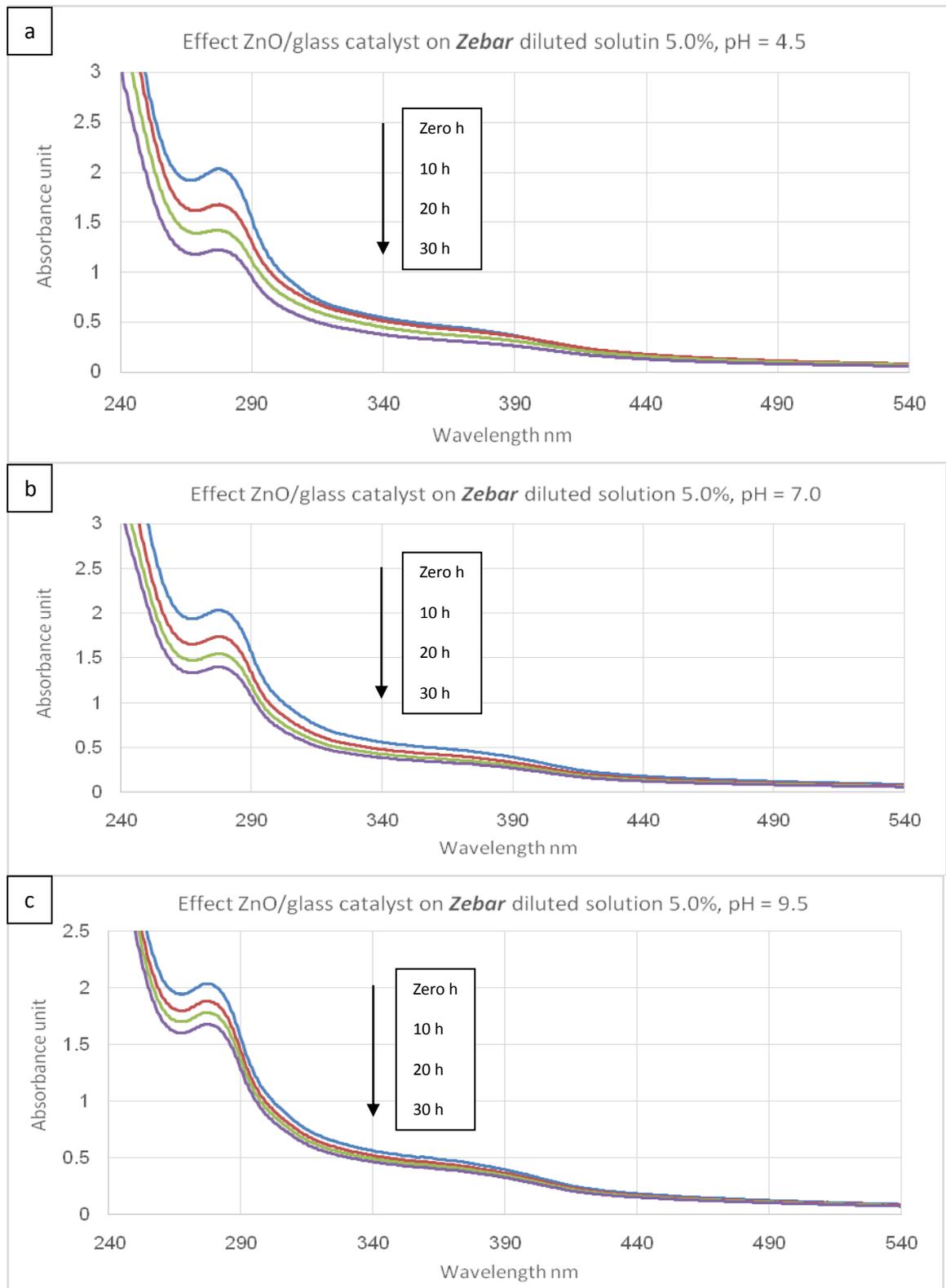
The results show that the ZnO/clay/glass is more efficient catalyst than the ZnO/glass. This is due to ability of the clay to adsorb organic molecules and bring them closer to ZnO catalyst surface. When closer to surface the organic molecules are closer to the OH• radical created near ZnO particles, and are more possible to be photodegraded.

### **3.2.2 Effect of of pH on photocatalytic degradation of phenols by ZnO/glass catalyst :**

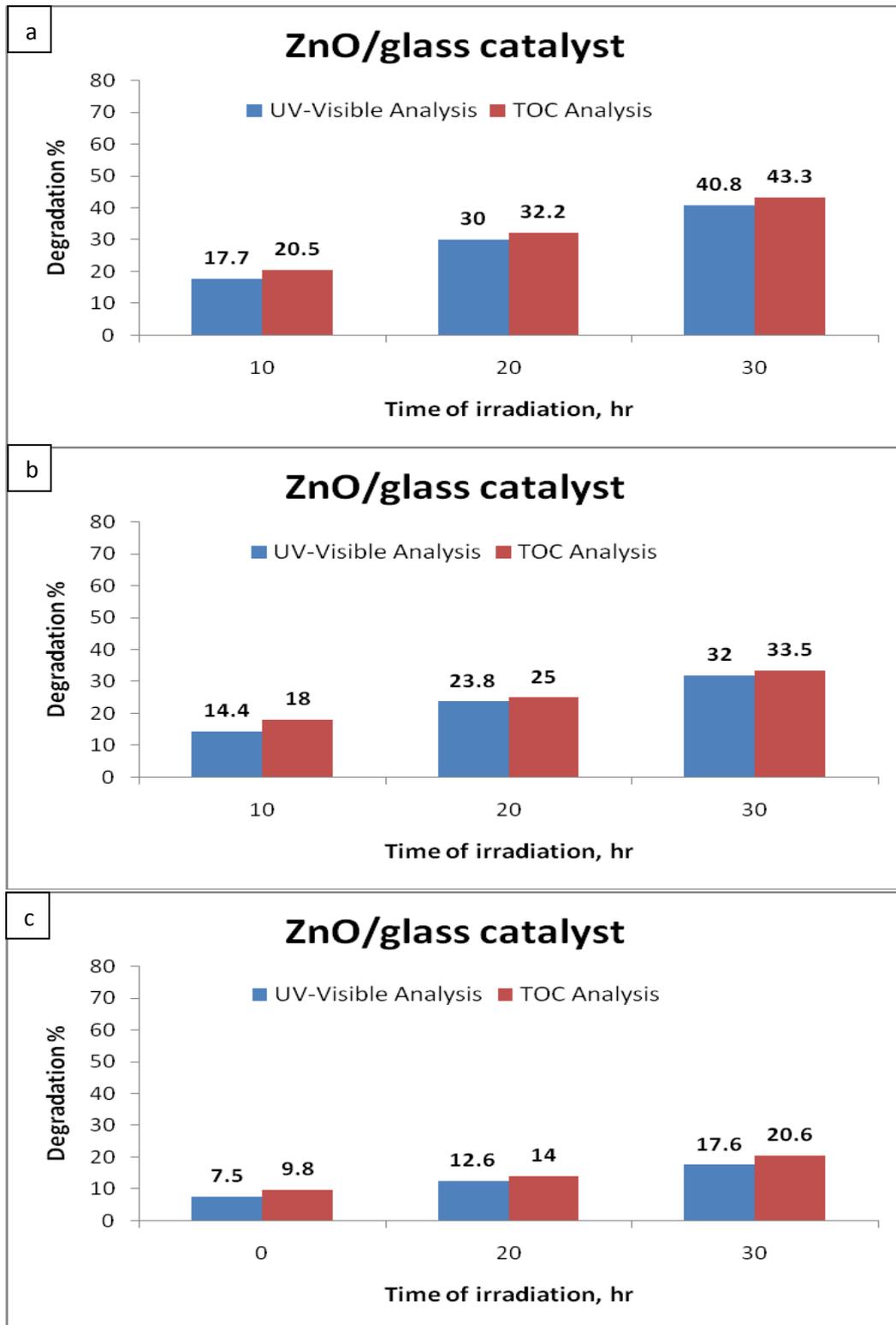
The effect of pH on the diluted *Zebar* solution (5.0%) was studied using different values of pH (4.5, 7.0, and 9.5). Under the solar simulation light with light intensity = 200000 Lux for 30 hours. Figures (3.11) and (3.12) describe the results. The results are summarized in Table (3.2). The Table shows that pH affects the degradation process. The degradation process changed with pH as follows: 4.5 > 7.0 > 9.5. At pH 4.5 and higher, pH affected the % degradation until it reached 9.5 where the % degradation sharply decreased. This is due to the repulsion between negatively charged phenoxide ion (which results from phenol by high NaOH concentration) [59], and the negatively charged ZnO surface. The value of pH at Zero point charge for ZnO is 9. Therefore, if pH value < 9 the ZnO surface is in the H<sup>+</sup> form while if pH value > 9 the catalyst surface is negatively charged [60].

Collectively, the results show that the lower pH (4.5) is the optimal condition for higher photodegradation process. This is important in our work, as the *Zebar* solution (5.0%) has pH = 4.5.

Therefore, purification can be performed at the natural *Zebar* condition (pH = 4.5) with no need to extra costs of changing the pH value.



**Figure (3.11):** Effect of pH on degradation reaction. UV-Visible spectra measured for remaining organic matter in *Zebar* solution (5.0%) under photodegradation reaction conditions a) pH = 4.5 b) pH = 7.0 c) pH = 9.5.



**Figure (3.12):** Effect of pH on % degradation of phenol measured by UV-Visible and TOC after different times. All reactions were performed using a solution of diluted *Zebar* 5.0% at room temperature under direct solar light.

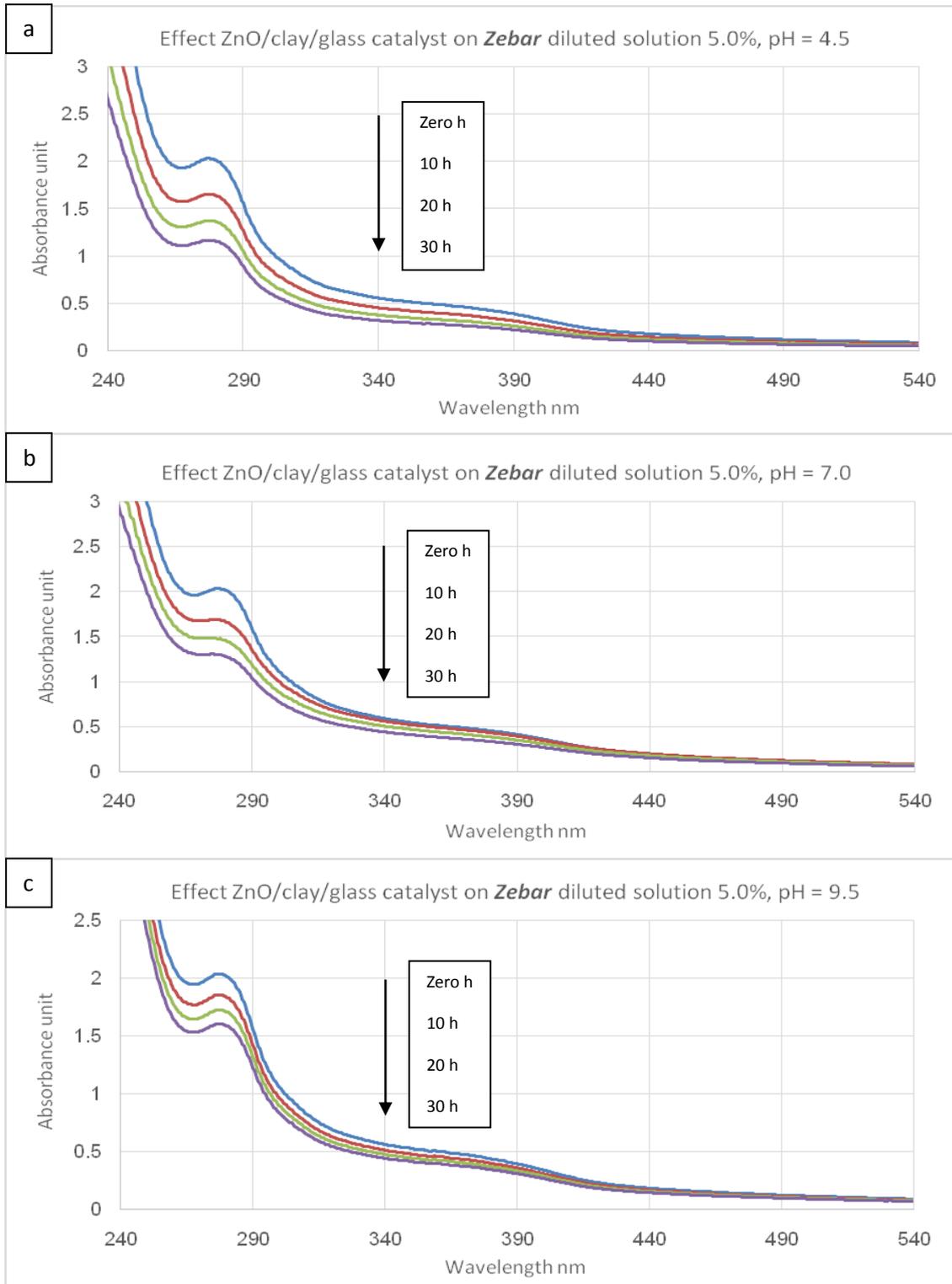
The photodegradation result for ZnO/glass catalyst at different pH are summarized in Table (3.2). The table shows continued increase in % degradation with time for ZnO/glass catalyst. TOC content also decreased with reaction time.

**Table (3.2):** Values of % loss of organic compounds, measured by spectra and TOC, using different pH values and different catalysts.

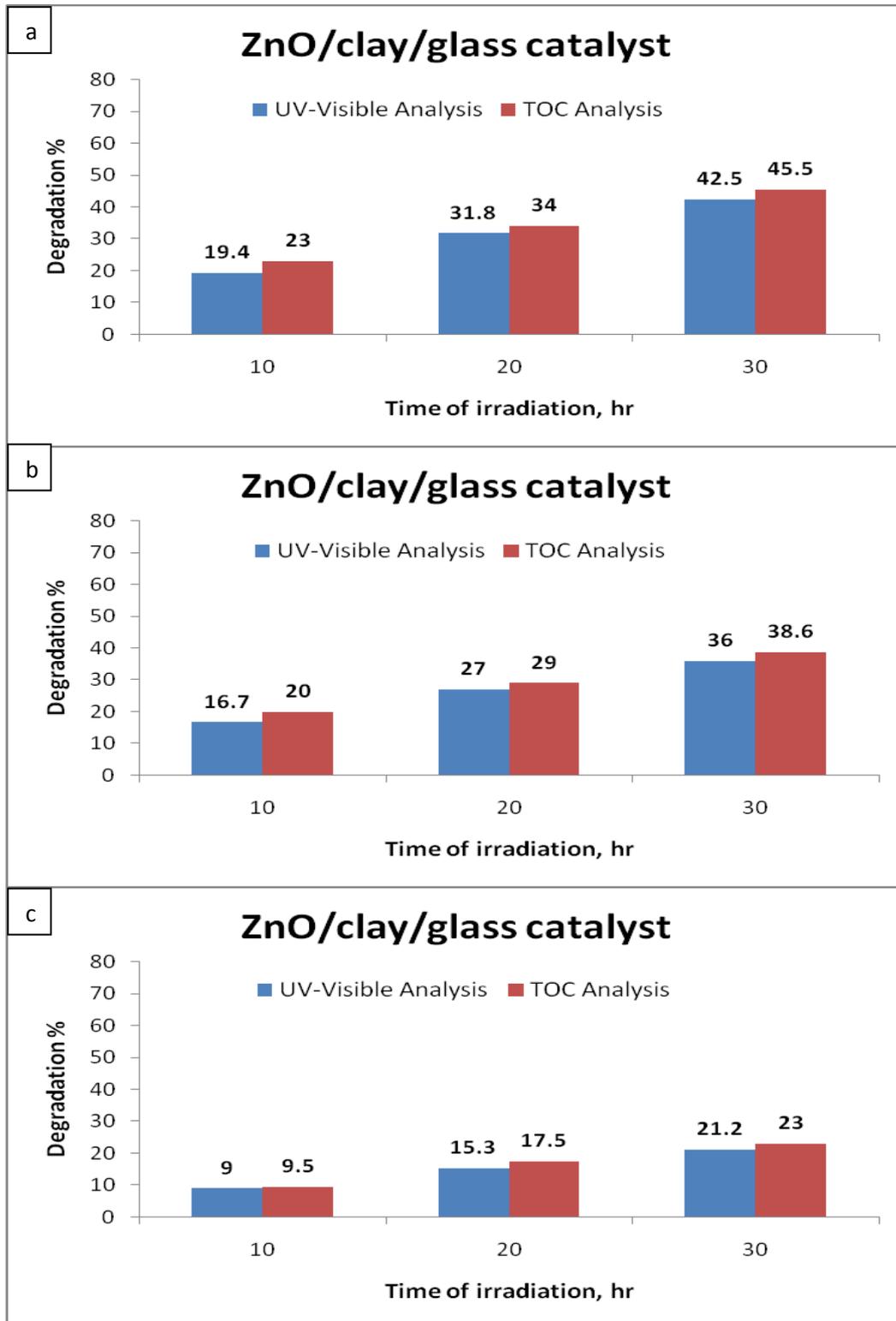
Dilution by 5%, using ZnO/glass , pH ~ 4.5 (Acidic)				
Sample	1	2	3	4
Time in hours	Zero hour	10 hours	20 hours	30 hours
Absorbance in wavelength at 276.5 nm	2.062A	1.698A	1.441A	1.220A
Percentage of degradation of phenol	0 %	17.7 %	30.0 %	40.8 %
TOC mg/L	1509	1200	1024	856
% Loss	0 %	20.5 %	32.2 %	43.33 %
Dilution by 5%, using ZnO , pH ~ 7.0 (Neutral)				
Sample	1	2	3	4
Time in hours	Zero hour	10 hours	20 hours	30 hours
Absorbance in wavelength at 278 nm	2.035A	1.740A	1.550A	1.382A
%degradation of phenol	0 %	14.4 %	23.8 %	32.0 %
TOC mg/L	1485	1218	1114	988
% Loss	0	18.0%	25.0%	33.5%
Dilution by 5%, using ZnO , pH ~ 9.5 (Basic)				
Sample	1	2	3	4
Time in hours	Zero hour	10 hours	20 hours	30 hours
Absorbance in wavelength at 276 nm	2.036A	1.883A	1.780A	1.677A
%Degradation of phenol	0 %	7.5 %	12.6 %	17.6 %
TOC mg/L	1497	1350	1287	1189
% Loss	0	9.8%	14%	20.6%

### **3.2.3 Effect of of pH on photocatalytic degradation of phenol by ZnO/Clay/glass catalyst :**

The effect of ZnO/Clay/glass catalyst on the diluted *Zebar* solution (5.0%) was studied with different values of pH (4.5, 7.0, and 9.5). Under the solar simulation light with light intensity = 200000 Lux For 30 hours. Figure (3.13) describes the results. The degradation has changed with pH as follows: 4.5 > 7.0 > 9.5. At pH 4.5 and higher, acidity change has affected the % degradation until it reached 9.5 where the % degradation sharply decreased. This is due to the repulsion between negatively charged phenoxide ion (which results from phenol at high NaOH concentration) [59], and the negatively charged ZnO surface. The value of pH at Zero point charge for ZnO is 9. Therefore, at pH value < 9 the ZnO surface is in the H<sup>+</sup> form while at pH value > 9 the catalyst surface is negatively charged [60]. Figures (3.13) and (3.14) show that at all pH values, the ZnO/clay/glass catalyst was more efficient than ZnO/glass.



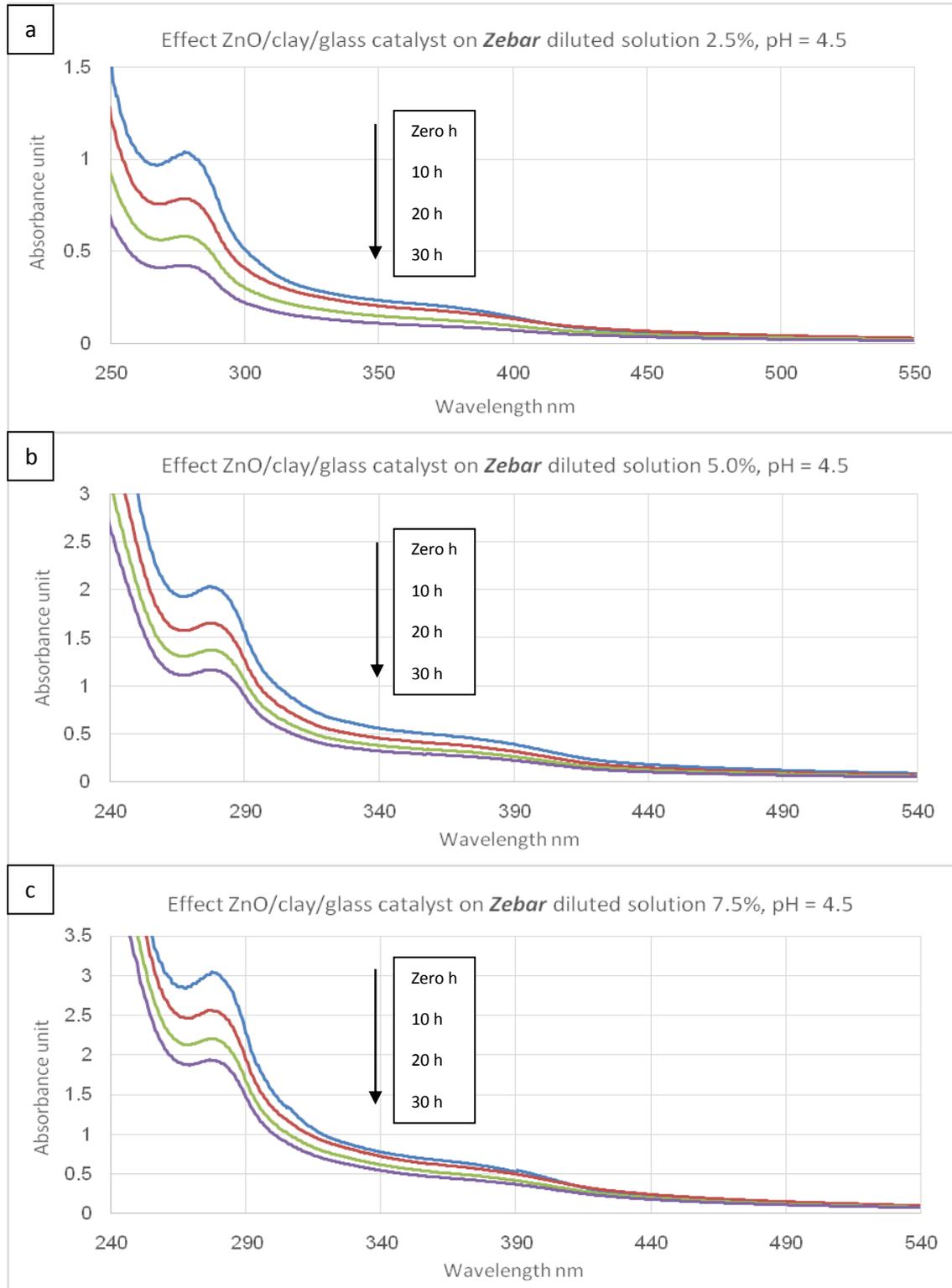
**Figure (3.13):** UV-Visible absorbance spectra measured effect of pH on Phenol degradation by ZnO/clay/glass catalyst with different time: a) acidic at pH= 4.5 b) neutral at pH= 7.0 c) basic at pH= 9.5.



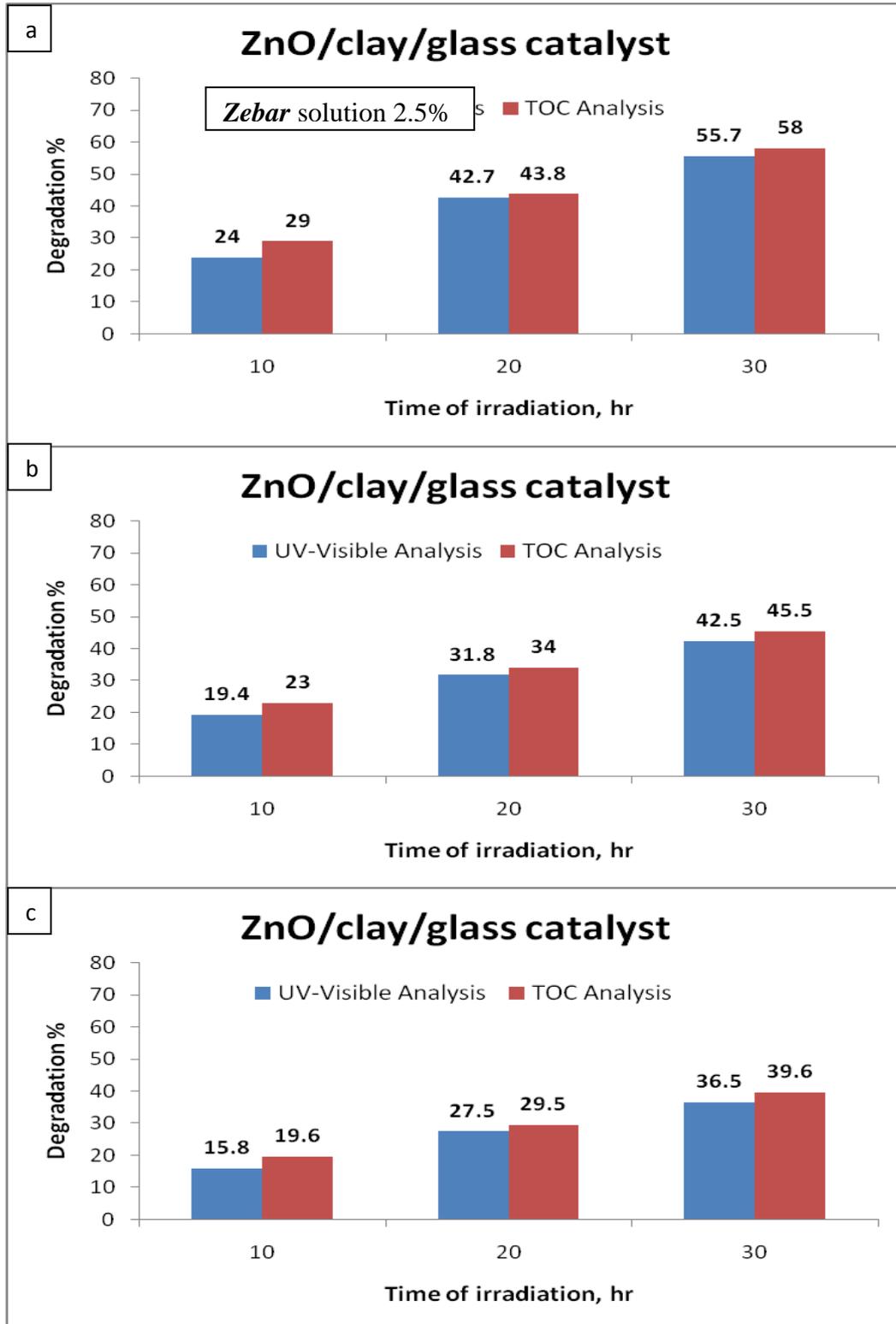
**Figure (3.14):** Effect of different pH on degradation of reaction measured in UV-Visible and TOC after different times. All reactions were performed using *Zebar* solution (5.0%) at room temperature under direct solar light.

### **3.2.4 Effect of *Zebar* dilution:**

As the ZnO/clay/glass is more efficient than ZnO/glass, it was recommended to use the ZnO/clay/glass in future particles. In this section, ZnO/clay/glass was studied. Figure (3.15) shows spectra measured for treated *Zebar* solutions under photodegradation conditions. Different *Zebar* dilutions were used, only 2.5%, 5.0%, and 7.5% concentrations for degradation study. The pH in each case was 4.5. Figure (3.15) shows that % loss of organic matter is higher in case of lower *Zebar* concentration. However, the amount of degraded organic matter is higher in case of higher *Zebar* concentration. Therefore the actual catalyst efficiency is higher with higher *Zebar* concentration. Figure (3.16) shows spectra and TOC results together. The TOC results confirm the spectral results measured for remaining organic materials.



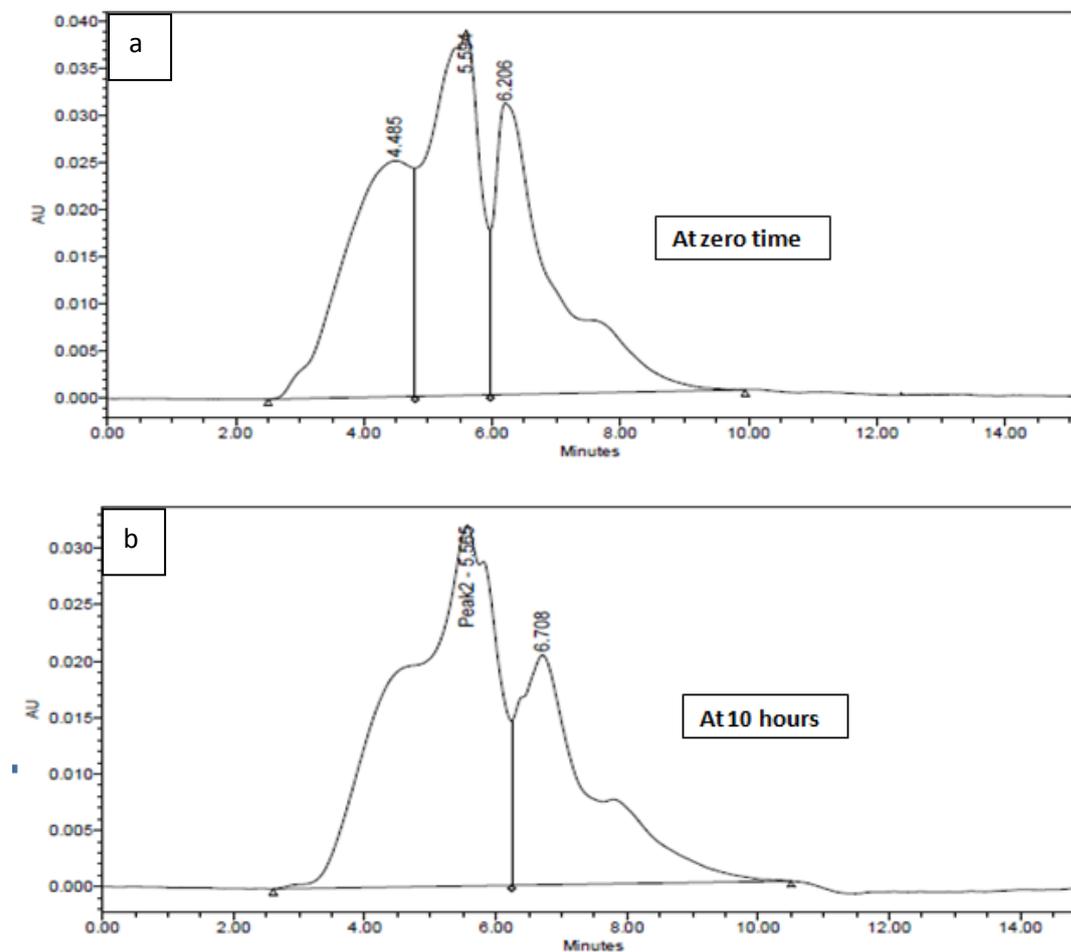
**Figure (3.15):** UV-Visible spectra measured for *Zebar* solutions under photodegradation experiments. Different *Zebar* concentrations were studied using ZnO/Clay/glass at natural acidity (4.5) and room temperature.



**Figure (3.16):** Values of spectra and TOC measurements for *Zebar* organic compounds remaining under photodegradation experiments. Different *Zebar* solution concentrations were studied. Measurements were made at different times with ZnO/clay/glass catalyst.

### 3.3 Photodegradation reaction results of HPLC

As stated above, the effects of different parameters on the progress of photodegradation reaction under simulated sunlight were studied using UV-Visible spectrophotometer and TOC techniques. Here, the following results are described by HPLC analysis, where results confirm what has been measured previously. The amount of degraded organic matter in the diluted *Zebar* solution was measured at 5% at pH 4.5 using a ZnO/clay/glass catalyst under solar simulator light for 10 hour. The *Zibar* solution was compared before exposure to light and after exposure. Figure (3.17a) shows the HPLC measurement of the *Zebar* solution before exposure to light. Figure (3.17b) shows the result of the analysis of the *Zebar* solution for exposure to light for 10 hours. The result was that the degradation of organic pollutants reached 19% after 10 hours of treatment. AS the table (3.3) shows Value of percent loss of organic compounds in *Zebar* solution (5.0%) after treatment with ZnO/clay/glass catalyst for 10 hours.



**Figure (3.17):** Values of HPLC measurements for *Zebar* organic compounds remaining under photodegradation experiments. Measurements were made at different times with ZnO/clay/glass catalyst.

**Table (3.3):** Values of % loss of organic compound in *Zebar* solution (5.0%) after treatment with ZnO/clay/glass catalyst for 10 hours, HPLC results are shown.

Sample	1	2
Time in hours	Zero hour	10 hours
Aria of peaks	5904823 ( $\mu\text{V}\cdot\text{sec}$ )	4793039 ( $\mu\text{V}\cdot\text{sec}$ )
Concentration of residual chemical pollutants	100%	81 %
% degradation of organic contaminants	0%	19%

## **Chapter Four**

# **Conclusions and Recommendations**

## Chapter Four

### Conclusions and Recommendations

#### 4.1 Conclusions

1. XRD-characterization results of prepared **ZnO/Clay** catalyst showed no intercalation of ZnO nano-particles inside clay layer, The particles are adsorbed onto clay particle surfaces.
2. Adsorption and photodegradation process of Phenol and organic contaminants with both catalyst systems was affected by the pH.
3. Photodegradation of phenol and organic contaminants was successfully studied under solar simulation light using prepared **ZnO/Clay** composite catalyst.

#### 4.2 Recommendations for future work

1. Study the effect of **ZnO/Clay** composite catalyst in there sensitized and non-sensitized forms on other contaminants (phenols, chlorophenols, drugs).
2. Using anthocyanin dye from different sources with different colors, as sensitizers for **ZnO/Clay** catalyst.
3. Do more mechanistic study on photo degradation of contaminants by **ZnO/Clay** systems (trapping intermediates for example)

4. Study the photodegradation of different contaminants under different conditions (temperature, flow rate, radiation intensity).
5. Determine the occurrence levels of different pollutants in Palestine waste and drinking water.

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كلية الدراسات العليا

**Continuous flow photodegradation of olive *zebar*  
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التحطيم الضوئي بالتدفق المستمر لملوثات الزيبار باستخدام ضوء مضاهٍ  
لأشعة الشمس وحببيبات أكسيد الزنك النانوية كحفاز

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إشراف

أ. د. حكمت هلال

د. عاهد زيود

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

2019م

## التحطيم الضوئي بالتدفق المستمر لملوثات الزيبار باستخدام ضوء مضاء لأشعة الشمس وحبيبات أكسيد الزنك النانوية كحفاز

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### الملخص

تعتبر عملية التحطيم الضوئي والامتزاز من أكثر الطرق الحديثة فعالية في تنقية المياه من الملوثات الحيوية والكيميائية. تعتمد عملية التحطيم الضوئي على وجود حفاز (أكسيد الزنك النانوي) الذي يعمل على امتصاص الأشعة فوق البنفسجية القادمة من الشمس لتحطيم المادة الملوثة (الفينول والمركبات العضوية). طور الباحثون العديد من الأنظمة التي تساعد وتزيد من فعالية هذا الحفاز في تحطيم الملوثات العضوية وبالتالي تمكنوا من استخدام أشعة الشمس المباشرة في عملة التحطيم الضوئي.

تم تصميم نظام التدفق المستمر بحيث يسمح للمياه بالجريان بشكل مستمر فوق سطح الحفاز، حيث يوجد مدخل مرتبط بالوعاء الزجاجي المثبت عليه الحفاز، ومن جهة أخرى يوجد مخرج للمياه المعالجة تسمح لها بالتجمع في وعاء آخر لإجراء الفحوصات اللازمة لها.

ولقد تمت دراسة خواص الحفاز المثبت على الزجاج باستخدام المسح المجهر الإلكتروني (SEM) وتمثيل الأشعة السينية (XRD)، وقد تم دراسة النتائج بتقنية UV-Visible spectrophotometer وتقنية TOC في تحليل التراكيز العضوية علاوة على تقنية الكروماتوغرافيا السائلة عالية الكفاءة (HPLC).

في هذا البحث تم دراسة التحطيم الضوئي لمركب الفينول والملوثات العضوية الموجود في المياه الناتجة من معاصر الزيتون باستخدام حبيبات أكسيد الزنك النانوي المثبتة على الزجاج، كما تم استخدام حبيبات أكسيد الزنك النانوي المدعمة بالفخار الطبيعي والمثبتة على الزجاج تحت أشعة الشمس المباشرة بطريقة التدفق المستمر. تم تحقيق التحطيم الضوئي بواسطة كلا الحفازين في ظروف مختلفة (تأثير تركيز الملوثات، المدة الزمنية، ودرجة الحموضة). كما وأظهرت نتائج دراسة التحطيم الضوئي لمادة الفينول أن نسبة التحطيم الأعلى كانت عند استخدام الحفاز المدعم بالصلصال وتساوي 42.5% على درجة حموضة ~ 4,5 و درجة حرارة 25 °C، بينما كانت تساوي 40.8% عند استخدام الحفاز غير المدعم بالصلصال عند نفس درجة الحموضة و الحرارة والتركيز.

وقد تم أيضا دراسة كفاءة الحفاز المثبت بعد استخدامه في عملية التحطيم وقد لوحظ أن الحفاز لم يظهر أي نقصان ملحوظ في كفاءته حتى بعد استخدامه عدة مرات في المعالجة.