**An-Najah National University**

**Faculty of Graduate studies**

# Photocatalytic Degradation of Organic Pollutants from Secondary Reclaimed Water with Simulated Solar Light

**By**

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# Dedication

To the reason for my existence in life, the owner of the fighting forearms, my father.

To the source of love, and who taught me resilience, my mother.

To my loving husband, who has always been my biggest supporter and source of happiness.

To my daughter, who put up with me during my university years(Raghad).

To whom do you share with me my success and my companions, my teachers and my friends.

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Thanks to Nafez Dwekat, the laboratory supervisor, for his continued support to finish my thesis.

Thank you very much. Deanship of Graduate Studies, College of Science, Department of Chemistry, An-Najah National University, represented by its doctors, professors, and laboratory supervisors.

# الاقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

# Photocatalytic Degradation of Organic Pollutants from Secondary Reclaimed Water with Simulated Solar Light

أقر بأن ما اشتملت عليه هذه الرسالة انما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة اليه حيثما ورد، وأن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل أي درجة علمية أو بحث علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

## 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 degree or qualification.

**Student Name:** **اسم الطالبة: بتول هاشم محمود نور**

**Signature:** **التوقيع:**

**Date:16/06/2021** **التاريخ: 16/6/2021**

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# List of Abbreviations

| | |
|---|---|
| °C | Celsius |
| CB | Conduction Band |
| D% | Degradation Percentage |
| EDS | Dispersive X- ray |
| EDTA | Ethylene Diamine Tetra Acetate |
| $E_g$ | Energy Band Gap |
| eV | Electron Volt |
| h | Hour |
| $h^+$ | Holes |
| KHP | Potassium Hydrogen Phthalate |
| mg | Mass Unit |
| nm | Wavelength Unit(nm) |
| SEM | Scanning Electron Microscopy |
| TC | Total Carbon |
| TIC | Total Inorganic Carbon |
| TOC | Total Organic Carbon |
| UV-Vis | Ultraviolet-Visible |
| VB | Valence Band |
| ZnO | Zinc Oxide |
| WHO | World Health organization |

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## Abstract

Waste waters are being purified in Palestine at a large scale in treatment plants in different areas. The plants use secondary treatments for water, and the resulting water may still include different types of soluble organic pollutants. The treated water follows by various methods such as chlorination, peroxidation, ozonation and UV radiation is commonly used globally, however, all these are costly. In the present work we used direct solar light to photo-degrade organic pollutants from secondary treated water. Using the charcoal-supported ZnO (charcoal/ZnO) is as photo-degradation catalyst. This method is safe as the organic contaminant materials are expected to be converted into safe mineral compounds. We have seen promising results as using 0.6g ZnO per 100ml of wastewater, at pH 10 for 1 h. We found that the organic compounds as TOC exist in the claimed water in concentrations with up to 45 ppm as TOC before purification. Out of these organics, 80% have been totally degraded leaving no organic traces, as confirmed by Total Organic Carbon (TOC) analysis, the removal of organic contents was improved when we used ZnO/charcoal, and the TOC reach were 5 ppm, which is a safe limit according to world health organization (WHO).

We have studied the properties of the catalyst (commercial zinc oxide) and charcoal supported ZnO (ZnO/charcoal) using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Energy Dispersive X-ray Spectroscopy (EDS). We have studied different parameters (such as catalyst loading, pH and time) to identify optimum condition for the studied parameters. The results show that using 0.6g ZnO per 100ml of wastewater, at pH 10 for 1 h gives best results.

# Chapter One

# Chapter One

# Introduction

## 1.1Water situation in Palestine:

Since ancient times, water has been considered one of the most essential elements for the continuation of life on the surface of the earth. God has made this grace the basis of creation for all living things. Water plays an important factor in the emergence and progress of civilizations. Water abundance influences all areas of life such as transport, agriculture, industry, animal husbandry and others [1].

The water sector in Palestine faces an acute and accumulating problem in the shortage of water quantities to meet our domestic, industrial, drinking and agricultural water needs [2]. The problem is increasing year by year, as a result of the increase in the population, the decline in rainwater levels, and more importantly the continued abuse and plunder of our water by the Israelis [3]. The average amount of water produced from the annual rain that falls within the borders of the West Bank exceeds 650-800 million cubic meters per year, in addition to our share in the Jordan River basin, which is estimated at 250 million cubic meters [4].


مقارنة بين الاستخدام الإسرائيلي - الفلسطيني لأحواض المياه الجوفية في الضفة الغربية (مليون متر مكعب سنوياً)

| الحوض الجوفي | إعادة التغذية السنوية | الاستخدام الإسرائيلي للمياه | استخدام المستوطنات للمياه | الاستخدام الفلسطيني للمياه | إجمالي استخدام المياه |
|---|---|---|---|---|---|
| الغربي | ٣٦٢ | ٣٤٠ | ١٠ | ٢٢ | ٣٧٢ |
| الشمالي الشرقي | ١٤٥ | ١٠٣ | ٥ | ٤٢ | ١٥٠ |
| الشرقي | ١٧٢ | ٤٠ من الآبار | ٥٠ | ٥٤ | ١٤٤ |
| الساحلي | ٢٥٠ | ٢٦٠ | ٠ | ٠ | ٢٦٠ |
| - بما فيه غزة | ٥٥ | ٠ | ٥-١٠ | ١١٠ | ١٢٠ |

Source: PASSIA, *Water - Special Bulletin*, p.3.

**Figure (1.1):** Aquariums in Palestine [5].

Given that Palestine is a beach party and a complete partner in this basin, the volume of our renewable water resources annually reaches an average of 1000 million cubic meters, and these quantities are sufficient to meet the Palestinians' need for the next fifty years without any problems, by dividing the total quantities of water consumed by the whole population, the average Palestinian per capita consumption is 87.3 liters of water per day. In the West Bank, this rate increased to 90.5 liters per day, an increase over prior years due to completed water projects that were able to develop existing resources and reduce waste. Because of the high contamination rate of water in Gaza, and calculating the amounts of water fit for human use from the available quantities, divided by the population, the per capita share of fresh water in Gaza reached 83.1 liters per day, a fall of 5.2 liters from the previous year. Given the disparity in per capita shares among governorates, establishing fairness in the distribution of resources among population centers is one of the State of Palestine's major issues. Because Israel controls more than 85 percent of Palestinian water supplies, the average Palestinian per capita water use remains below the internationally approved level [6]. It is also possible to expand the current irrigated areas to four times, noting that the agricultural sector in Palestine is one of the most important economic sectors. The water situation in the Gaza Strip has become more dangerous due to the expansion of salinity, and the increase in pollution areas [7].

The quantities of wastewater produced by the Palestinians are estimated at 106 million cubic meters annually, of which 50 million Cubic meters in the West Bank, in addition to 39 million cubic meters of settlements and their industrial zones in West Bank**.** According to data from the Palestinian Water Authority, wastewater treatment contributes significantly to the restoration of environmental systems; in 2019, the percentage of treated water inside Palestine was around 12% of total wastewater produced, and this percentage is expected to rise to 15% in 2021, from 12% in 2019. During the process of developing a wastewater treatment strategy, as well as increasing the efficiency of existing plants [8].

## 1.2 Location for main wastewater treatment plant according to surface catchments at the West Bank:

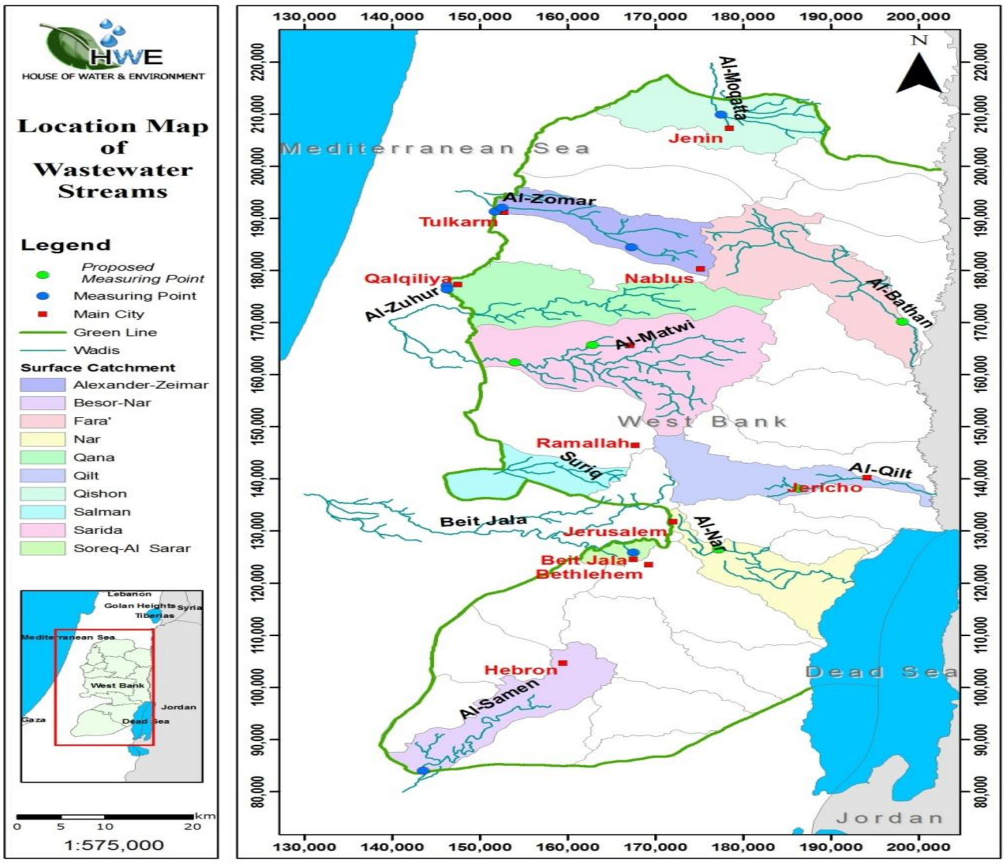


**Figure (1.2):** Location map of wastewater streams [9].

**Table (1.1): The Names of Waste Water Streames and their Governrate**

| No. | Stream (Wadi) | Governarat |
|---|---|---|
| 1 | Wadi Al-Moqatta | North Jenin |
| 2 | Wadi Al-Zomar | Nablus and Tulkarem |
| 3 | Wadi Al-Zuhur | Qalqilia |
| 4 | Wadi Suriq | West Ramallah |
| 5 | Wadi Beit Jala | Bethlehem |
| 6 | Wadi Al-Samen | South Hebron |

## 1.3 Secondary treatment:

### 1.3.1 What is secondary treatment?

Bacteria consume the organic parts of the wastes during secondary treatment, which is the second phase in most waste treatment systems. This is performed by the use of trickling filters or an activated sludge method to combine sewage, bacteria, and oxygen. All floating and settleable solids, as well as around 90% of oxygen-demanding compounds and suspended solids, are removed during secondary treatment. The final stage of the secondary treatment procedure is chlorination-based disinfection. [10]

### 1.3.2 Why is it important to concentrate on secondary processed water?

The focus of our research was on treated water because it causes health problems if it is not treated properly, due to the presence of different types of organic matter that are not removed in the different stages of treatment, which may cause damage to plants. This water is polluted. One of the advantages of using treated wastewater is to preserve water reserves, as its use in agriculture or any other uses instead of potable water leads to the provision of this water and the expansion of agricultural areas to produce a variety of agricultural crops at a lower price. It also leads to a reduction in costs related to production, import and use. Fertilizers due to the presence of the necessary elements for the plant in that water and reducing the costs of obtaining water in agriculture, especially if the sources of that water are underground. [11]

### 1.3.3 Secondary treated water's environmental and economic impact:

The most important impact is on the environment and economy, and it must be taken into account that they meet the regular conditions that keep disease at bay if this treated water is used, as the World Health Organization recommended, emphasizing the need for studies on the impact on farms and consumers of these crops. Wastewater that has been processed and reused. Attention should be paid to its chemical and physical components, since some elements were accumulated in quantities beyond the permissible limit, limiting plant growth, and their accumulation in fruits could cause long-term health problems for humans and deteriorate soil quality. [11]

## 1.4 The national dimension and strategies for reusing treated water in agriculture:

Water crises in Palestine is felt most acutely than that in the middle east as the Palestinians suffer from both of water availability due to natural factors and from water accessibility due political restrictions. Climate change, over-pumping, low rainfall, rising demand for water due to the population growth, and the degradation of water quality are expected to complicate the current situation and therefore, to increase the competition for the shared and scarce water resources. The increasing competition for good-quality water among different water-use sectors has reduced allocation of freshwater for agriculture. [12]

The water sector is one of the most vital sectors in sustainable agricultural development process at the national level. The estimated total water used for agriculture does not exceed 150 million cubic meters (MCM) annually (60 MCM in the West Bank and 90 MCM in the Gaza Strip. This amount represents 45% of the total water consumption, which is reflected directly on the limited prospects for the development of irrigated agriculture that can have an important economic, social and political role in rebuilding the Palestinian economy [13]. In order to narrow the gap between freshwater demand and supply, farmers have to increasingly rely on use of non-conventional water (brackish water and treated wastewater) for crop production [12].

In Palestine, the escalating population growth of approximately 2.9% [14] has increased not only the total demand of fresh water but also wastewater production into the watercourses that poses harm to the human health and the environment [15]. This situation puts pressure on securing safe and reliable potable water supply. To secure safe and reliable potable water supply in Palestine, the mobilization of additional freshwater resources is necessary [16]. The use of treated (reclaimed water) for irrigation is viewed as a strategic alternative for the agricultural sector in the West Bank [17]. The Palestinian National Agricultural Sector Strategy 2014 - 2016 aims to increase the available water for agriculture by 30 MCM end of 2016, 15 MCM of which is from nonconventional water resources as RW [18]. This is also in line with the National Water and Wastewater Strategy for Palestine 2012-2032 considering treated water as a resource [17].

On the light of the above, and in line with Palestinian Agriculture Sector Strategy (2017 - 2022) “Resilience and Sustainable Development”, reuse of treated wastewater in irrigation becomes a key to success of the Palestinian agriculture sector. It is alien completely with the two main strategic objectives which stated [19]:

1- Natural and agricultural resources sustainably managed and better adapted to climate change.

2- Increased agricultural production, productivity, and competitiveness in local and international market, along with their contribution in gross domestic product and food security.

The total volume of wastewater generated in Palestine for the year 2015 was estimated at 114.35 MCM, from which 65.85 MCM are generated in the West Bank. Only two thirds of the generated wastewater collected in sewage networks is discharged into a wastewater treatment facility. The annual wastewater collected by sewage networks reaches 15 MCM / year in the West Bank, and around 10.3 MCM of it is treated or partially treated in 6 centralized wastewater treatment plants and in 16 collective wastewater treatment plants [20].

In agreement with Palestinians sectors strategies discussed previously, A pilot agricultural treated wastewater projects were conducted. One of these projects was implemented by Agricultural Cooperative of Marj ibn Amer where treated wastewater of Jenin Municipality wastewater treatment plant, which is an aerated lagoons plant implemented in 2013, is used to irrigate 32.5 hectare of fodder crops and fruit trees in Marj ibn Amer. The project included installing a water distribution network of 20 Km of steel and polyethylene pipes that covers an area of 300 hectares. For the first time in Palestine, sub-surface irrigation networks were installed with drip lines buried at 20-25 centimeters underground [21].

## 1.5 Nanotechnology in Wastewater Treatment:

There are many methods to purify wastewater such as filtration [22], chlorination [23] and oxidation [24]. Nanotechnology has emerged as a novel and promising technology with an important role in treatment waste water. It has proven its ability to remove pollutants for reuse purposes [25]. Nanotechnology uses in wastewater treatment depends on its water quality properties. With scientific progress, this technology helps a lot in wastewater treatment, especially removing organic matter with the features: [26]

1- Low cost.

2- Easy to prepare and apply.

3- High surface area / volume.

4-Continuity and length of effect.

## 1.6 Catalysis:

### 1.6.1 What is a Catalyst?

The catalysis process depends on a substance that increases the rate of transformation of the reactants without being affected or being depleted. This substance is known as catalyst. It increases the rate of the reaction by lowering the activation energy [27].

### 1.6.2 Photo-catalyst:

The word photo catalysis is a two-part compound word, "photo" meaning light, and part two "catalysis" meaning stimulation. The photo catalytic process is a reaction in which light is used as an activator for the substance that will increase the rate of the chemical reaction without being consumed in the reaction itself, Figure (1.1). Photo catalysis is a physico-chemical process that has the following beneficial applications:

1-Water purification.

2-Pollution preventing.

3-Anti-bacterialactivity.

4-Removal of unpleasant odors.

5-Air purification. [28]

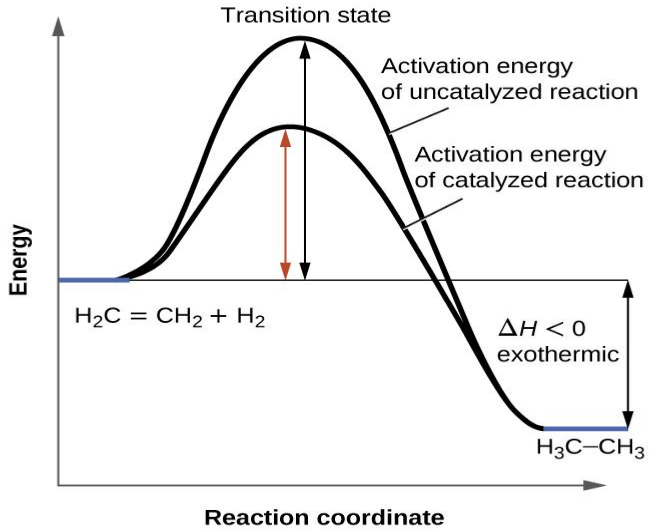


**Figure (1.3):** Activation energy for catalyzed and un-catalyzed reactions [27].

### 1.6.3 Semiconductors:

Semiconductors were chosen in photo-catalysis because semiconductor materials have moderate Energy gap($E_g$) values between the Valence Band (VB) and the Conduction Band(CB) [29]. Photo catalysis process can take place, when the semiconductor material absorbs energy from the irradiation sources that is at least equal to the $E_g$. Therefore, electrons move from the VB to the CB, leaving a positive hole (h+) in the VB. Positive (h+) acts as a strong oxidizer that can oxidize organic contaminant molecules [30].

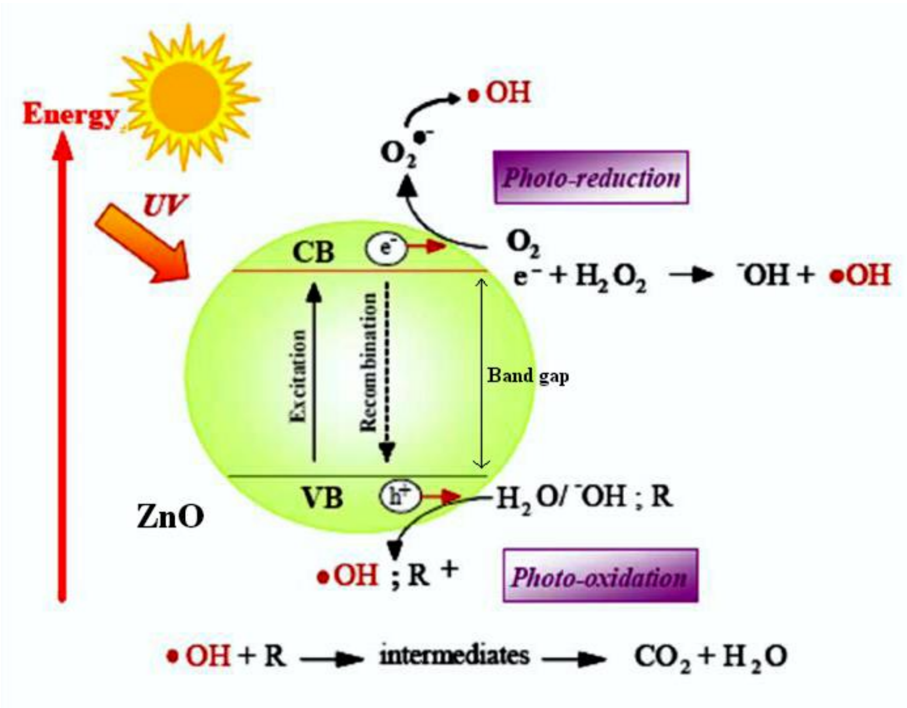


**Figure (1.4):** Mechanism of photo catalytic degradation [30]

### 1.7 Zinc Oxide (ZnO) Nanoparticles:

ZnO is a semiconductor photo-catalyst that is used to convert pollutants into safe products using solar light. This is due to the low cost of ZnO catalysts, which require mild reaction conditions and have high photo-catalytic activity

[31]. Because of its appropriate band gap (3.2 eV), ZnO is utilized as a semiconductor and can work in the ultraviolet tail of solar radiation. It is also beneficial in the photo-degradation of several organic pollutants by sun light [32]. In the UV zone, solar radiation has only a modest tail (5%) [33]. ZnO has relatively strong UV absorptivity, making it an effective photo-degradation catalyst [34]. In secondary treated waters, ZnO is employed as a probable catalyst for photo-degradation of several organic pollutants [35].

### 1.8 Total Organic Carbon (TOC):

Organic contamination in water is indicated by Total Organic Carbon in water. TOC measurement is used to determine the sources of organic pollutants in water. In general, high-precision measurements are obtained using instruments that use the catalytic oxidation technique of combustion at temperatures near 700 degrees [36].

### 1.9 Charcoal:

Charcoal is a solid, amorphous, highly porous substance containing fine grains of graphite, treated with special methods to make it porous. Heating process takes place at a temperature of 400-600 graphite, and this increases the effective surface in it [37].

### 1.10 Adsorption:

The association of different liquid, gaseous, solid, or even living, molecular or ionic substances with the surfaces of another substance that is often solid, these molecules or ions form a film or a thin layer on the surfaces of the adsorbent material by electrostatic forces [38].

The adsorption is used in different fields as industry, science and medicine, and active charcoal is usually used.

Coal miners use masks to protect against toxic gases; which relies on the purification of the air [39].

### 1.10.1 Mechanism of Adsorption:

Adsorption of any species (adsorbate) onto a solid surface only occurs at the surface atoms not at bulk atoms. This is because surface atoms are exposed to adsorbate. Moreover, the surface atoms are coordinatively unsaturated and can accommodate the adsorbate species. Under same conditions, larger adsorbent relative surface area should yield higher adsorption uptake [39].

### 1.11 Novelty:

The work described in this thesis has not been described before. Secondary treated waste waters are intended for only agricultural use, due to their remaining organic pollutants, and are not suitable for drinking. In this work we wish to purify the water (resulting from secondary treatment) by lowering the organic pollutants with photodegradation. This is a novel work which has not been described before, to our knowledge. We expect the ZnO and ZnO/Charcoal to catalyze the photo-degradation of organic pollutants, in water, with direct simulated solar light. The supported catalyst (ZnO/charcoal) is expected to show higher activity than the un-supported ZnO catalyst, due to ability of Graphite to absorb the contaminants. Therefore, we expect the project to show the feasibility of using solar energy processes in water purification at tertiary and quarterly levels where complete removal of organic contaminants is possible in safe and economic ways.

## 1.12 Objectives:

### 1.12.1 General Objective:

The main goal of this work is to further purify pre-treated water resulting from secondary treatment plants, by photo-catalytic degradation of any remaining organic pollutants and converting them into mineral gases.

### 1.12.2 Specific Objectives:

1. Prepare and characterize ZnO Nano-particles as possible photo-catalysts for water purification.
2. Support ZnO onto Charcoal to make its recovery easy.
3. Use the ZnO and the Charcoal/ZnO particles as photo-catalysts for further purification of waters coming out from secondary stage treatment plants of sewage in Jenin government.

# Chapter Two

# Chapter Two

# Materials and methods

## 2.1 Sample Collection:

The polluted water as stock solution was collected from secondary treated water from the wastewater treatment plant in Almuqata area at Jenin government. The collected stock solution at summer season was used in the photo degradation experiments. The experiments were performed in the laboratories of An-Najah National University, Nablus. We measured the organic content concentration, which was 45 ppm, before purification.

## 2.2 Materials and Equipment:

### 2.2.1. Materials:

Commercial Zinc oxide with a catalogue number 14439 was purchased from Sigma Aldrich and was used as the photo catalyst. Sodium hydroxide and hydrochloric acid were used to control the pH value. Olive stones (Jefet) was donated from local olive miller at Jenin government. The Jefet was carbonized and used as a charcoal substrate for ZnO supporting. Potassium Hydrogen Phthalate (KHP) was purchased from Sigma Aldrich.

### 2.2.2 Equipment:

A Jenway 3510 pH meter was used to measure and control the solution pH as desired. A Shimadzu UV-3101PC spectrophotometer, equipped with a thermal printer Model DPU-411-040, type 20BE, was used to study the absorbance of remaining organic carbon in solutions during photo degradation reactions. Lx -102 light meter was used to calculate the light intensity falling on the treated water sample. The accurate masses were measured by using a four-digit balance (S.N 330045/11). Oven, a heavy duty tubular regulated furnace (Lindberg 9001) at An-Najah University.

A SHIMADZU Total Organic Carbon analyzer (TOC-L) was used to measure the content of carbon of the organic compounds found in pure water and water–based systems in Palestine Technical University (Kadoorie). Irradiation from a solar simulated light source (Projection Lamp, type 7787XHP, 36 V, 400W) was used. The light intensity at the reaction mixture surface was 1000 lux light intensity, similar to natural sun light intensity at An-Najah University.

Crystal structures for ZnO catalysts were measured on Dispersive X-Ray (EDS), in the Department of Physics at the UAE, Al-Ain. Scanning Electron Microscopy (SEM) micrographs were measured in the Department of Physics at the UAE-Al-Ain University.

## 2.3 Setup of the model:

The adsorption experiment was performed by stirring secondary treated waste water samples with a specific amount of ZnO catalyst in a 250 mL beaker**.** A batch reactor system was used to conduct photo-degradation experiments using direct sunlight in magnetically stirred thermo-stated 250 ml beaker for an hour. The beaker was thermo stated at 25 ±5 ºC.

Direct sunlight with an average 1000 Lux with~ 4% UV fraction was applied to the top of the reaction mixture surface, After that, we took a sample and put it through the UV-VIS Spectrophotometer and TOC tests.

## 2.4 Preparation Methods.

### 2.4.1Solution Preparation:

#### 2.4.1.1 Potassium Hydrogen Phthalate (KHP) Solution:

0.2 gm of Potassium Hydrogen Phthalate was dissolved in water in 100 ml volumetric flask and the volume was completed with distilled water to give a solution of 0.1M. The solution was used to standardize sodium hydroxide (0.1 N) which will be used in the determination of the prepared charcoal surface area.

#### 2.4.1.2 Sodium Hydroxide and Hydrochloric Acid Solutions:

Dilute solutions of NaOH, 4 gm of powder sodium hydroxide was dissolved in water in 1000 ml volumetric flask and the volume was completed with distilled water to be 0.1M, and HCl were prepared for the purpose of controlling the pH of the solution of the catalytic experiments in An-Najah University.

### 2.4.2 Analysis of Total Organic Carbon:

After the degradation process, the total organic carbon was calculated by calculating the difference between the Total Carbon and the Total Inorganic

Carbon. (Total Organic Carbon (TOC) = Total Carbon (TC) – Total Inorganic Carbon (TIC)) [40]

### 2.4.3 Analysis of Absorption Spectrophotometry:

The samples were spectrophotometrically analyzed, at An-Najah National University labs, after each of photo degradation time period. The absorption spectrophotometry was scanned in the wavelength range of 200-800 nm, this is due to the fact that organic matter absorbs radiations in this range.

## 2.5 Photo-Catalyst Experiment.

### 2.5.1 Effect of pH values with and without AC:

The solution pH values were controlled by the addition of diluted solutions of sodium hydroxide and hydrochloric acid as required. The adjusted pH values were (3.0, 5.3, 7.0 and 10.0).

### 2.5.2 Effect of the Amount of ZnO:

In this part we examined the effect of different amounts of Zinc Oxide (0.0, 0.2, 0.4, 0.6gm) on degradation of Total Organic Carbon in 100 ml of secondary treated water under neutral pH for 60 min.

### 2.5.3 Effect of Irradiation Time on the Photo Degradation Rate:

Different time periods (15min,30min and 1 h) were used to study the effect of time on the photo degradation. Water aliquots, after each time period, were syringed out and characterized by different analysis techniques.

### 2.5.4 Charcoal Preparation:

The olive stone was washed several times and dried in an oven at 120 °C for 4 h. Then 100 gm of the dried sample was annealed at 600 °C inside a tube furnace under nitrogen for 3 h. This step was repeated because the device could not bear more than 100gm of olive stones. The percentage of yield was ~50%of charcoal.

### 2.5.5 Specific Surface Area Determination of Charcoal:

The Charcoal specific surface area was determined by a classical acetic acid adsorption method. A set of 100 ml acetic acid solutions with various concentrations (0.01, 0.05, 0.08, 0.10, 0.12 and 0.15 M) were prepared. The flasks were thermo-stated at 25 °C. A sample of the prepared AC (1.0 gm) was added to each flask. The flasks were shaken at constant Temperature (25 ºC) for an hour to achieve equilibrium. From each flask, a 25 ml of filtrate was titrated with 0.1 M NaOH standard to measure the remaining acid [41].

### 2.5.6 Preparing a Composite of ZnO and Charcoal:

A 10 gm of the commercial ZnO was mixed with 40 gm of the prepared charcoal and 100 mL of distilled water. The mixture was sonicated for an hour and then stirred for another hour. The mixture was left to settle, decanted and dried on a hotplate with continues magnetic stirring. The solid composite was kept dry for further uses.

# Chapter Three

# Chapter Three

# Results and discussion

### 3.1 Characterization:

The ZnO photo catalyst was characterized by XRD, SEM, EDS and surface area techniques.

### 3.1.1 X Ray Diffraction (XRD):

Cu $K_\alpha$ was used as a radiation source (λ = 1.5418 Å), to measure the XRD patterns. The particle sizes were measured by Scherrer equation [42].

$$\boldsymbol{d} = \frac{K\lambda}{B\cos\theta}$$

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

X-ray pattern for commercial ZnO nano-powder is shown in Figure (3.1). The figure shows distinguished peaks at 2Ө = 31.6°, 34.2°, 36°, 47.4°, 56.4°, 62.7°, 67.8° and 68.6. The peaks resemble those reported earlier for (100), (002), (101), (102), (110), (103), (112) and (201) crystal planes, respectively, with wurtzite-like structure. The pattern of carbon is observed at about 25° and 45°.Nano-ZnO particle size was calculated using Scherrer equation and found to be ~43nm.

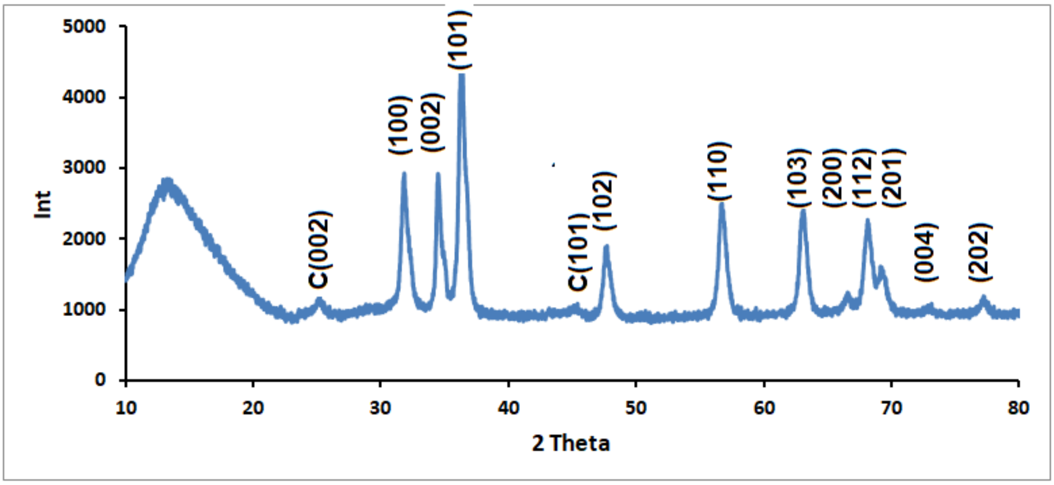


**Figure (3.1):** XRD-pattern measured for commercial ZnOnano-particles.

### 3.1.2 Scanning Electron Microscopy (SEM):

The SEM was used to study the surface morphologies and surface contrast of ZnO and ZnO/Charcoal. Figure (3.2) shows the SEM micrograph to the Commercial ZnO catalyst is a uniform spherical. The SEM photograph shows an agglomeration (~2µm) of Nanoparticles of ZnO (~40 nm) Fig (3.2).

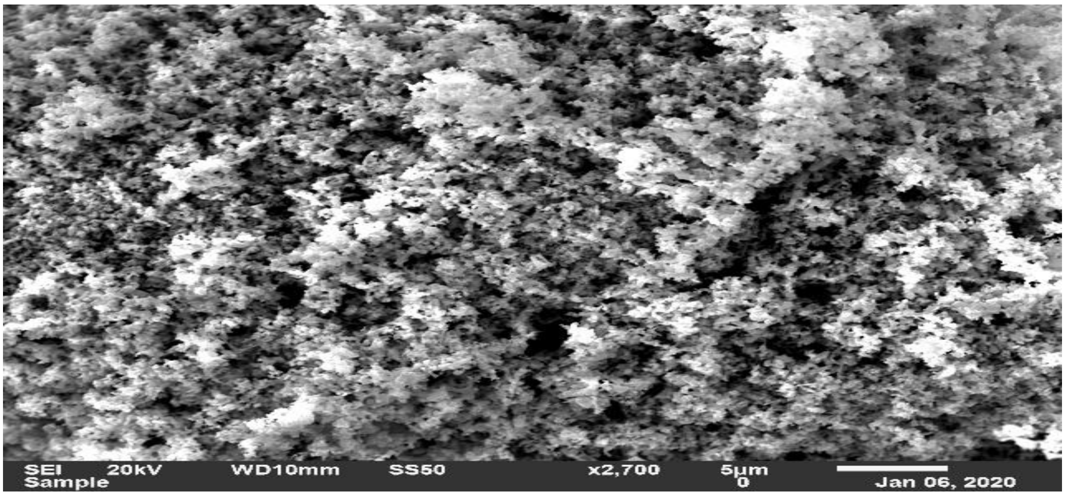


**Figure (3.2):** SEM micrographs measured for commercial ZnO catalyst.

Figure (3.3) shows the SEM micrograph to the ZnO/charcoal catalyst is a uniform spherical. The SEM photograph of the composite ZnO/charcoal shows smaller agglomerates (2.647 μm) of ZnO dispersed on the charcoal surfaces, Fig (3.3).

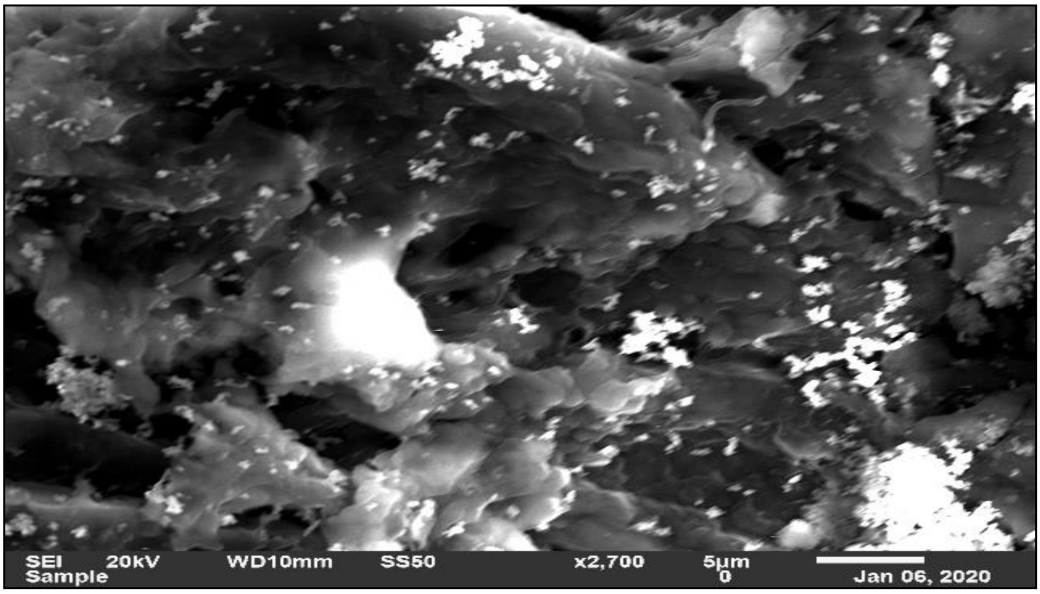


**Figure (3.3):** SEM micrographs measured for ZnO/charcoal catalyst.

Figure (3.4) shows the SEM micrograph to the charcoal catalyst is a uniform spherical.

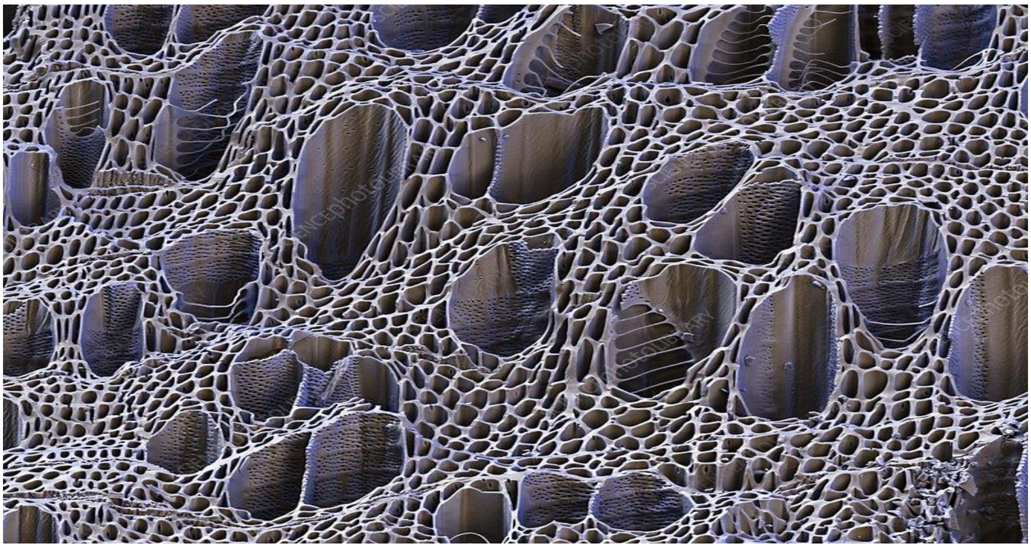

**Figure (3.4):** SEM micrograph charcoal [43].

### 3.1.3 Energy Dispersive X-ray Spectrometer (EDS):

The EDS was used to study the elemental analysis of ZnO and ZnO/charcoal. It is generated by any atom in the sample that is sufficiently excited by the incoming beam.

Table (3.1) and Figure (3.5) give the results of EDS analysis for the commercial ZnO. Different atomic ratios for Zn, C, and O (Zn: C: O 43.37: 17.49: 39.15 respectively) can be seen. The Zn is the dominant element in the sample.

**Table (3.1): EDS atomic analysis for composite ZnO.**

| Formula | Mass% | Atom% | Sigma |
|---:|---:|---:|---:|
| C | 5.72 | 17.49 | 0.04 |
| O | 17.06 | 39.15 | 0.07 |
| Zn | 77.22 | 43.37 | 0.31 |

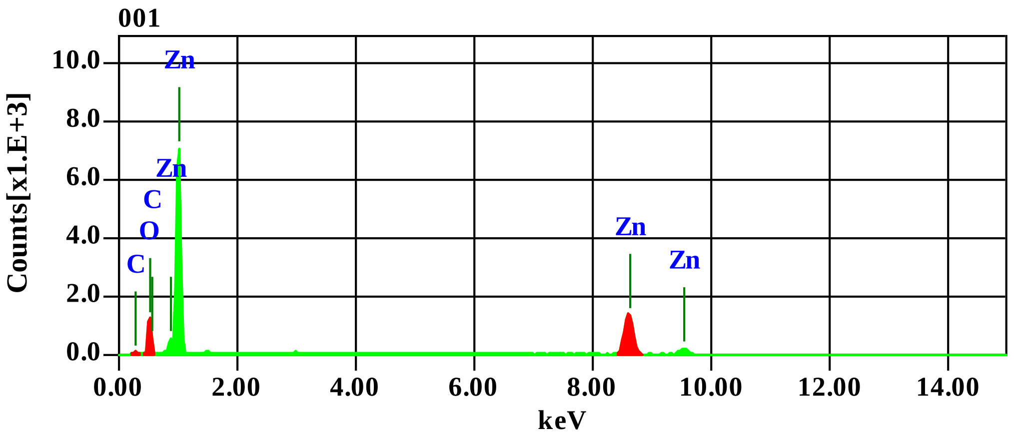


**Figure (3.5):** EDS patterns for commercial ZnO.

### 3.1.4 Specific Surface Area of ZnO/charcoal:

**Table (3.2): ZnO/charcoal surface area result:**

| Ci | V(NaOH) | C eq | N= (Ci - Ceq) *0.1 | Ceq/N |
|---|---|---|---|---|
| **0.01** | 2.1 | 0.048 | 0.00016 | 52.5 |
| **0.05** | 10.8 | 0.0432 | 0.00068 | 63.52 |
| **0.1** | 22.5 | 0.09 | 0.001 | 90 |
| **0.15** | 34.5 | 0.138 | 0.0012 | 115 |

Ci: initial concentration of acetic acid.

V: volume of 0.1 M NaOH titrated 25 ml.

C eq: equilibrium acetic acid conc. = 0.1 * V (NaOH) / 25.

N: total number of moles.

α: sectional area.

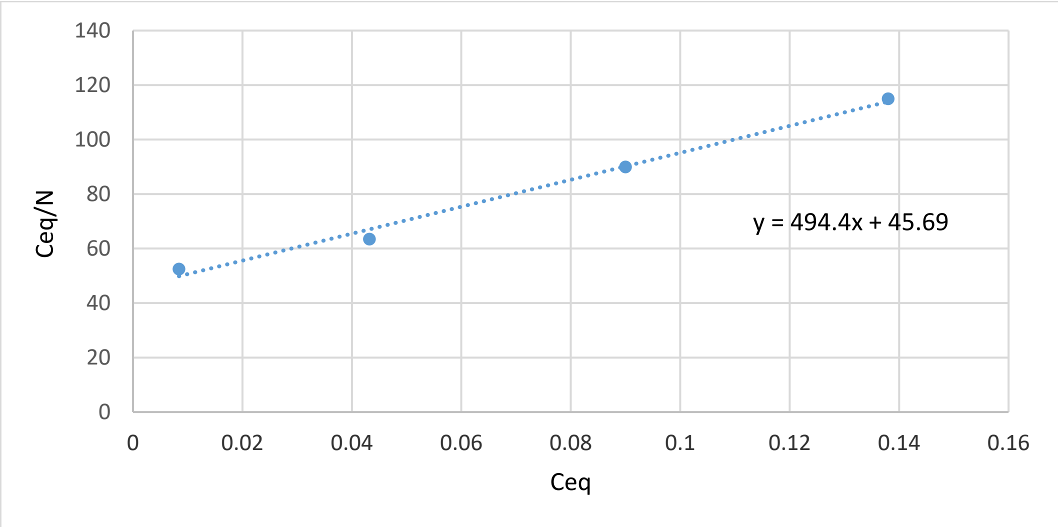


**Figure (3.6):** ZnO/Charcoal Surface Area Curve

Slope = 494.483

Nm = 1/ slope = 0.00202

Area = Nm * Na * α

= 0.00202 * 6.022 * $10^{23}$ * 21 *$10^{-20}$ = 255.745 $m^2/g$

ZnO has a specific surface area of (∼ 17 $m^2/g$) [44]. From literature the specific surface area for ZnO/charcoal is in the range 200-500$m^2/g$ [45]. In our experiment, it is 255.745 $m^2/g$ for the ZnO/charcoal specific surface area.

## 3.2 Organic Contents Photo Degradation:

Effects of different parameters (pH value, catalyst concentration and time) on organic content removal by photo degradation were studied. Degradation percentage of the organic contents was also studied. The results are discussed below.

### 3.2.1 Removal of Organic Contents Using ZnO:

#### 3.2.1.1 Effect of pH:

In this study, the effect of different pH(3.0, 5.3, 7.0 and10.0) on purification of 100ml of water sample mixed with 0.2 gm ZnO or 1.0 gm ZnO/charcoal was investigated. The mixture exposed to light for 60 min.

The impact of pH on the adsorption capacity is very critical in efficiency of removal of organic contents by changing the chemistry of adsorbent-adsorbate. In this experiment we used various pH values (3.0, 5.3, 7.0 and10.0) with different photo-catalysts (ZnO, ZnO/Charcoal). The adjustment of pH was carried out by using 0.1 M HCl and 0.1M NaOH. The spectroscopic analysis for organic was made by absorption peak at 263nm.

Figure (3.7) shows the pH effect on removal of organic contents using ZnO. The highest purification activity was shown at higher pH.

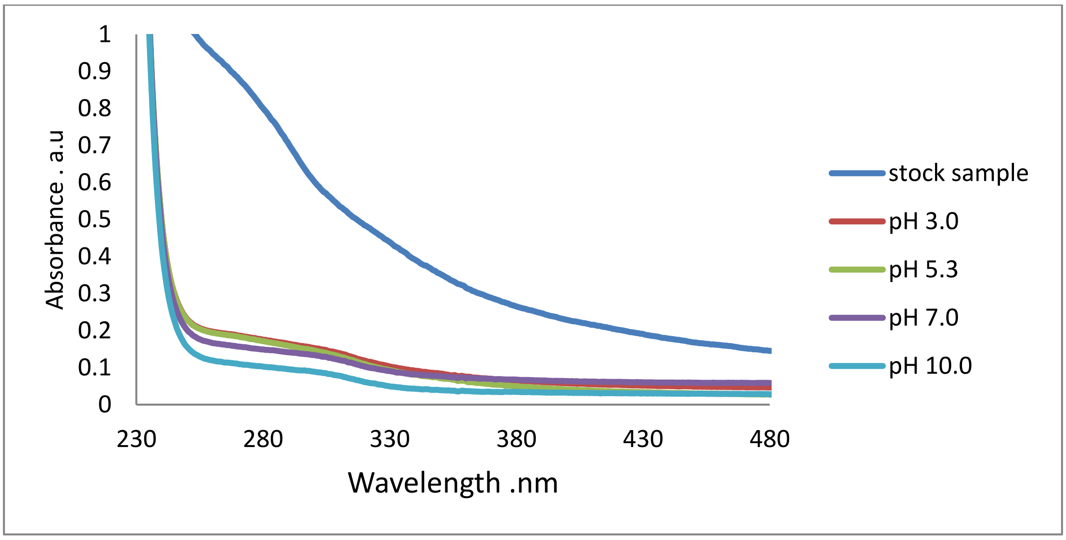


**Figure (3.7):** UV-Vis absorbance spectra measured for organic content at various pH values. Experiments were conducted using 0.2 g ZnO for 1 h without Charcoal in 100 ml solution at 25 ºC.

Figure (3.8) shows the percentage of removal of pollutants. Within the studied pH range, the photo-degradation process reaches higher degradation percentage. For example, at pH = 10.0 (alkaline solution), the organic compound removal slightly increased up to 87.52% degradation percentage with time. Results indicated that, at pH 7.0, the degradation percentage removal reached 82.23 % in 60 min. In acidic solutions (pH 3.0 and 5.3) the organic content removal percentage was 79.12% and 79.45%, respectively. However, as naturally polluted waters normally have pH values in the range 4-8, the results indicate the applicability of the process to purify polluted waters. This is because under neutral conditions, up more the degradation percentage is higher than 82% within only 1 h. At alkaline solution (pH 10.0) the organic content removal percentage was 87.52%.

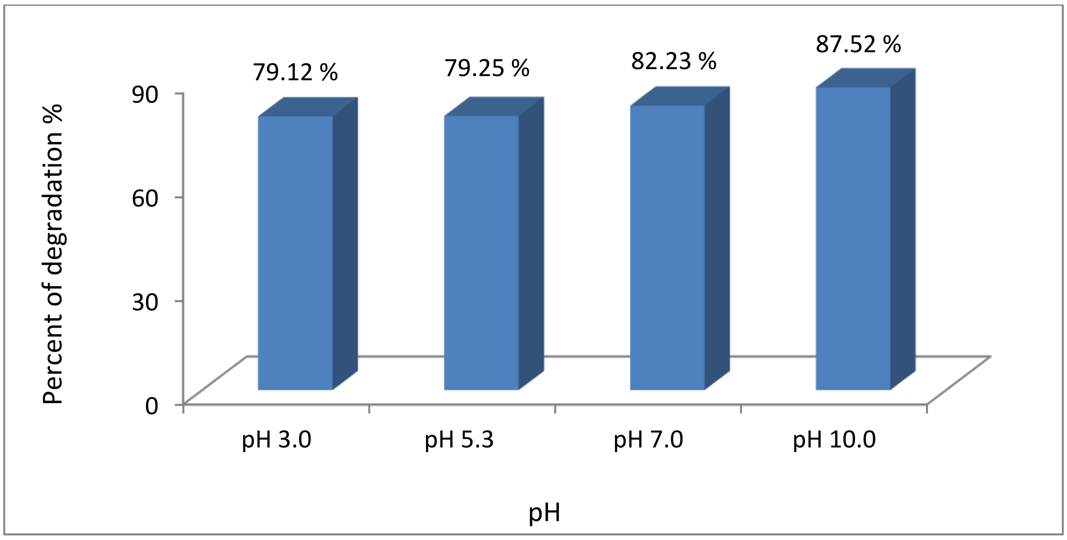


**Figure (3.8):** Degradation percentage of organic content by ZnO at different pH values. Experiments were conducted using 0.2 gm ZnO for 1 h without Charcoal in 100 ml sample at 25 ºC.

### 3.2.1.2 Effect of Time:

In this study, the effect of time (15 min, 30 min and 1h) on organic removal percentage using photo catalysts ZnO (0.2 gm).

Figure (3.9) shows the time effect on purification of organic contents using ZnO. Most (~60%) of organic contaminants disappeared within 15 min of illumination.

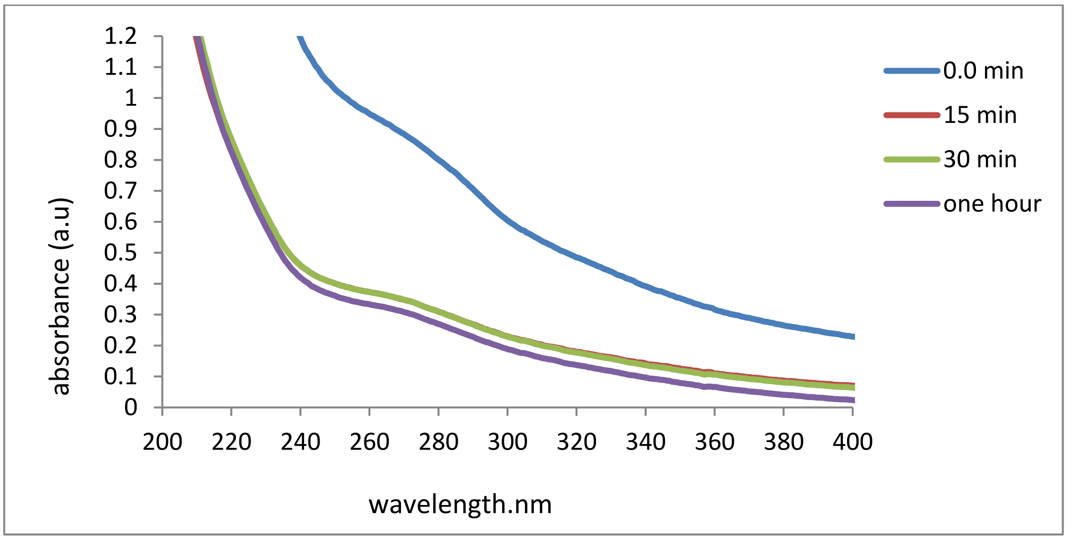


**Figure (3.9):** Electronic absorption spectra measured for organic content at various times. Experiments were conducted using 0.2 gm ZnO at neutral pH without Charcoal in 100 ml sample at 25 ºC.

After that the removal percentage showed only slight increase with time, as described in Figure (3.10).

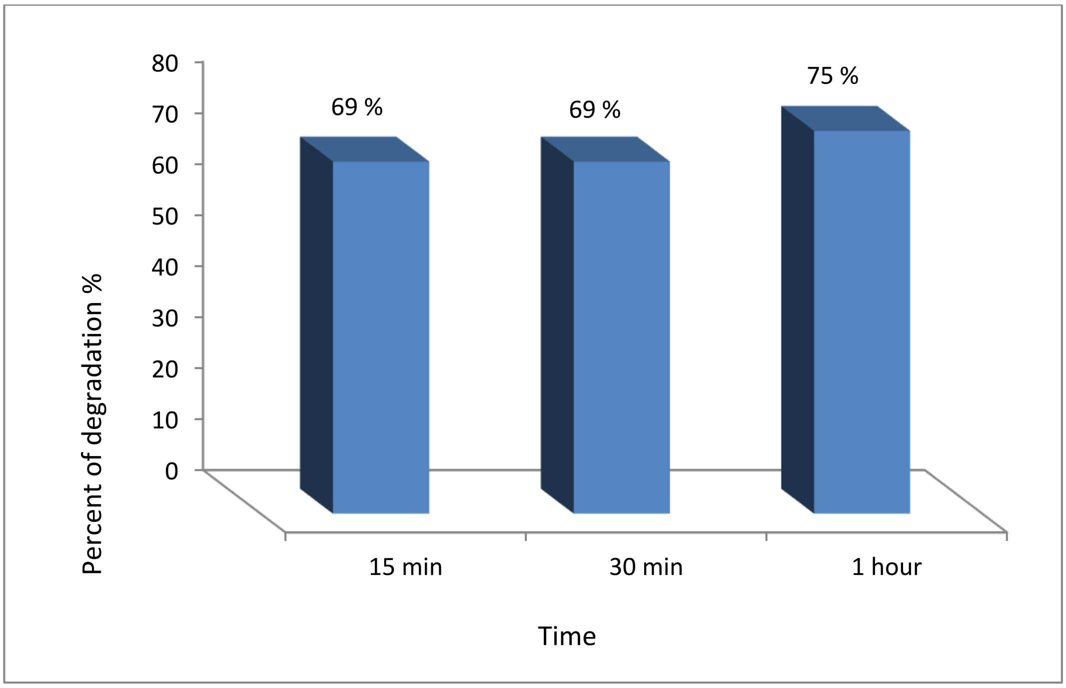


**Figure (3.10):** Organic removal percentage values by ZnO at different times. experiments were conducted using 0.2 gm ZnO at pH is neutral without Charcoal in 100 ml sample at 25 ºC.

### 3.2.1.3. Effect of amount of ZnO:

In this study, the effect of different amounts of ZnO Nanoparticles (0.0, 0.2, 0.4, and 0.6gm) on purification of 100ml of water sample at fixed pH were studied.

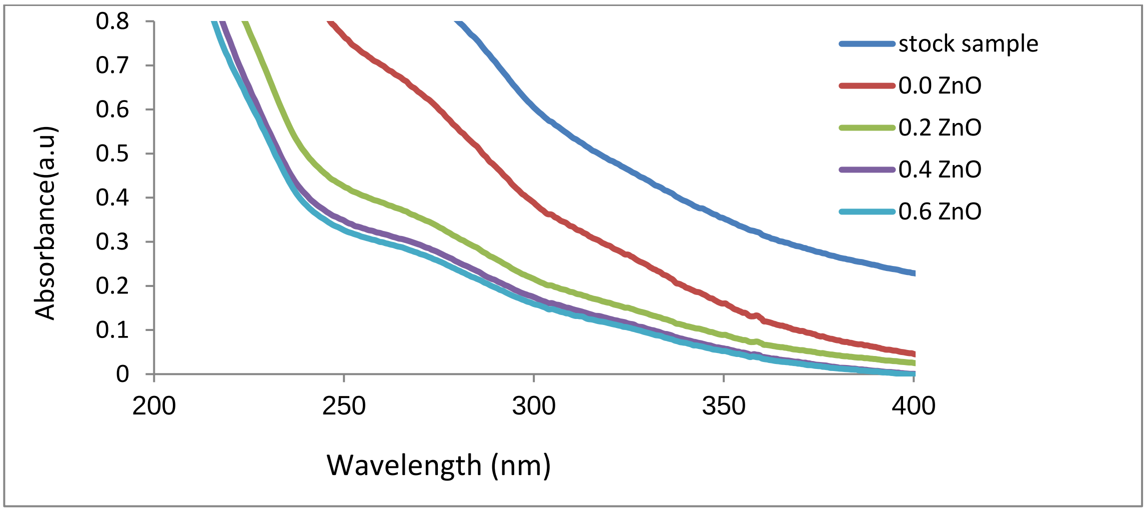


**Figure (3.11):** UV-Vis absorbance spectra measured for organic content at various amount of ZnO, experiments were conducted using pH is neutral at 1h in 100 ml sample at 25ºC.

Figure (3.11) shows the amount of ZnO effect on photo- degradation rate of organic content. The rate of water purification was increased with increasing the amount of used ZnO. The maximum water purification was achieved when using 0.4 gm of ZnO, no significant increases was shown when using 0.6 gm of ZnO. The percentage of water purification at different ZnO amount is presented in Figure (3.12).

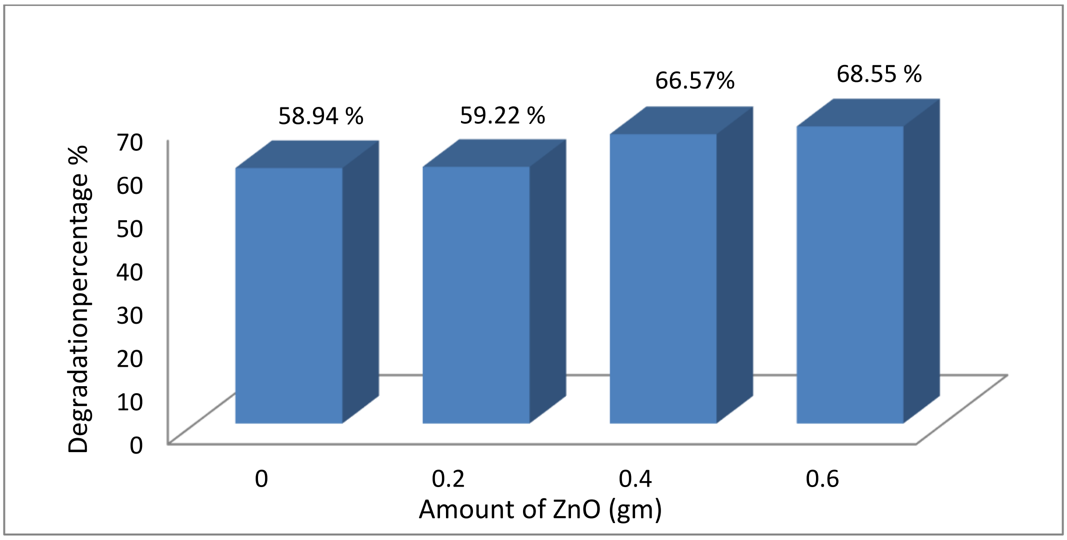


**Figure (3.12):** Organic removal percentage values using various amounts of ZnO. Experiments were conducted using neutral pH for 1 h in 100 ml sample at 25 ºC.

### 3.2.2 Removal Organic Content Using ZnO/Charcoal.

#### 3.2.2.1 Effect of pH:

The pH effect on the photo-degradation of organic content using 1.0 gm of ZnO/Charcoal (containing 0.2 gm ZnO) as catalyst is shown in Figure (3.13).The figure shows that the highest removal rate was at pH of 10. The presence of Charcoal, even at high acidic solution enhanced the removal of the Organic Contents. Using alkaline solution of high pH values showed highest removal efficiency. The results indicate that the Charcoal supported ZnO catalyst is more efficient than the ZnO.

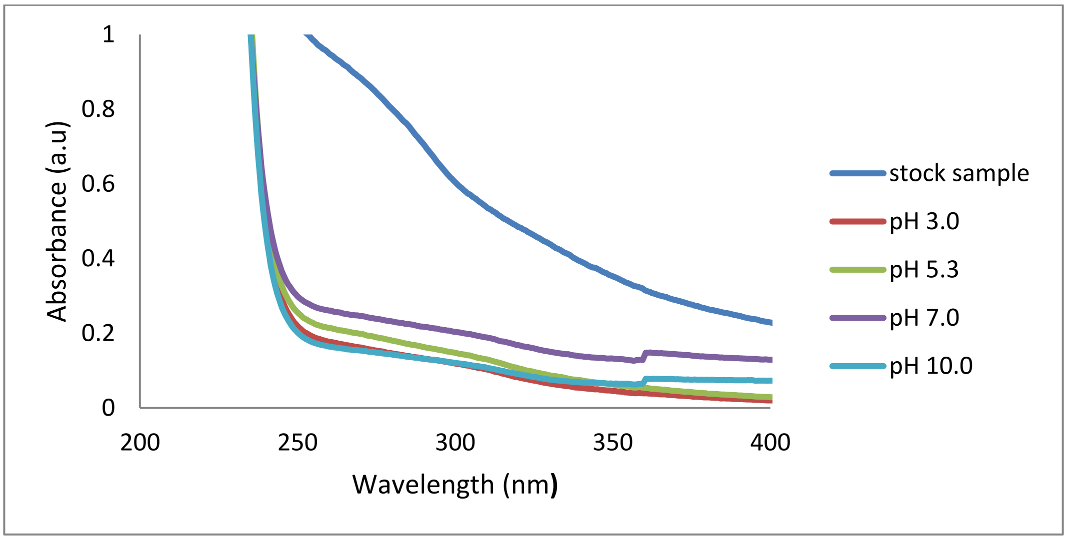


**Figure (3.13):** Effect of pH on organic content removal by Charcoal supported ZnO photo catalyst. UV-Vis absorbance spectra are shown for organic content at various pH. Experiments were conducted using 1 gm ZnO/Charcoal for 1 h in 100 ml sample at 25 ºC.

The organic contaminant removal percentage as a function of time at various pH values was investigated. Figure (3.14) shows the removal percentage of organic content from water by photo-degradation with ZnO/Charcoal. At alkaline solution (pH 10.0) the organic content removal percentage increased to ~89.15%. At the neutralpH7.0 the removal percentage reached~84.54% in 60 min of photo-catalytic reaction. At lower pH values, 3.0 and 5.3, the organic removal percentage values were 81.47% and 81.60%, respectively.

Results showed that the removal efficiency increased with increasing pH due to adsorption onto the Charcoal, which has a high specific surface area which can increases the adsorption of organic molecules on the ZnO/Charcoal catalyst surface. Therefore, carbon keeps the contaminant molecules closer to the hydroxyl radicals that result from excitation of catalytic ZnO particles under illumination with radiation.

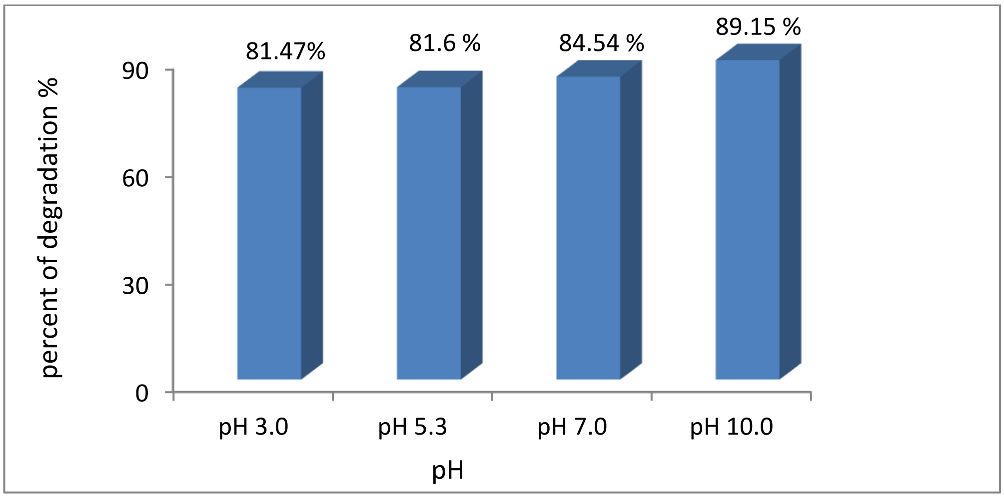


**Figure (3.14):** Purification percentage of organic content by ZnO/Charcoal at different pH values. Experiments were conducted using 1 g ZnO/Charcoal (containing 0.2 g ZnO) for 1 h in 100 ml sample at 25 ºC.

### 3.2.2.2 Effect of Time:

In this study, the effect of time (15 min, 30 min and 1h) on organic removal percentage using photo catalysts ZnO/Charcoal (1.0 gm, containing 0.2 gm ZnO).

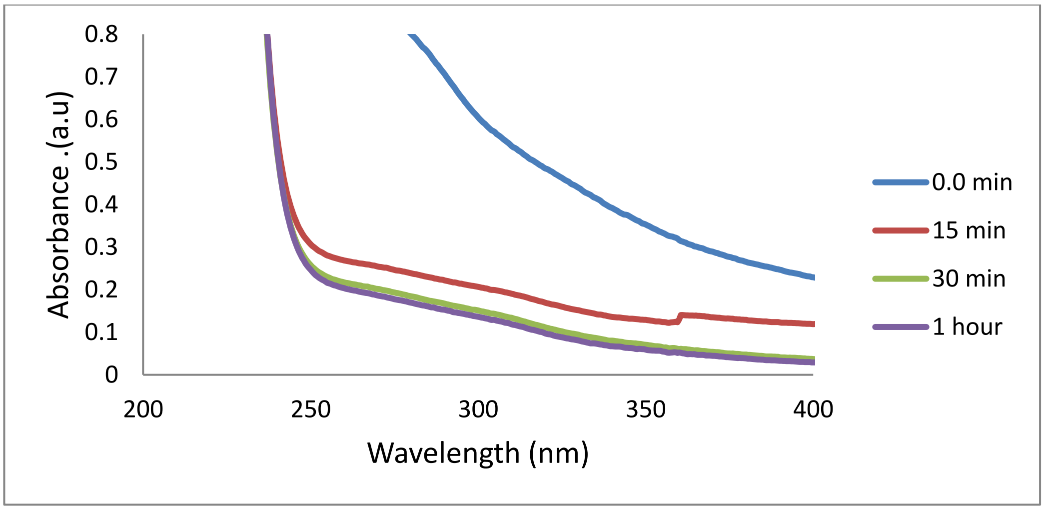


**Figure (3.15):** UV-Vis absorbance spectra measured for organic content at various time, experiments were conducted using 1 gm ZnO/Charcoal at pH is neutral in 100 ml sample at 25ºC.

Figure (3.15) shows the time effect on photo-degradation rate of organic content using ZnO/Charcoal as catalyst. After thirty minutes, removal rate was noticeable, and no significant increase was shown at 60 min of irradiation. The maximum water pollutants removal was ~ 80%. The superiority of water purification of water in ZnO/Charcoal system is due to capability of Charcoal to adsorb contaminant species. The adsorbed pollutant molecules are close to the photocatalyst sites which increases the photo-degradation.

The percentage of water contaminant removal by using ZnO/Charcoal at different time periods is presented in Figure (3.16).

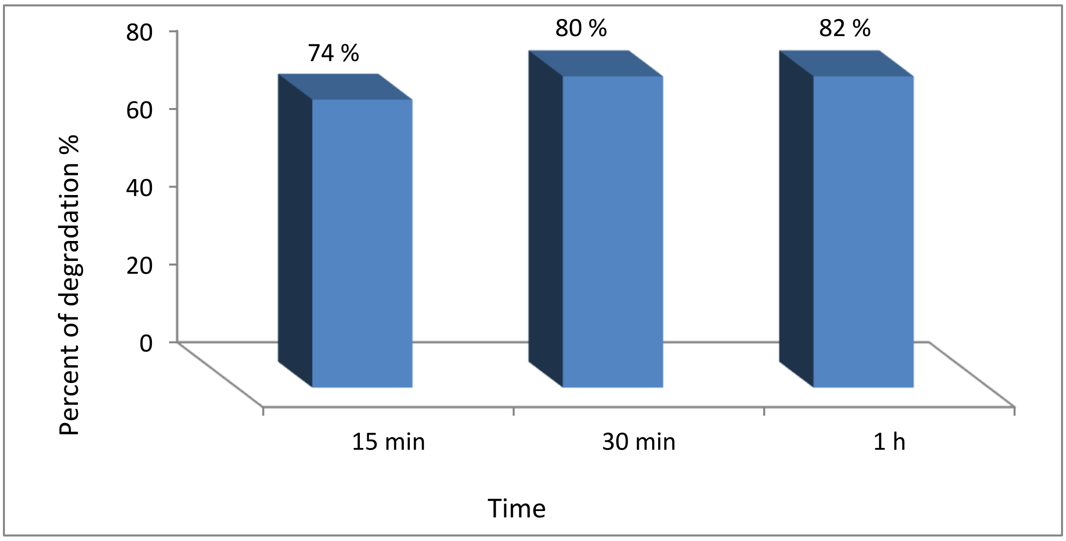


**Figure (3.16):** Degradation percentage of organic content by ZnO/ Charcoal at different time. Experiments were conducted using 1 gm ZnO/Charcoal at pH is neutral in 100 ml sample at 25 °C.

### 3.3.3 Organic Removal Percentage Values with ZnO and ZnO/Charcoal at Different pH Values:

Figure (3.17) shows removal percentage values using the two different catalyst types at various pH values. The Figure (3.17) shows that removal percentage increases at higher pH. The ZnO/Charcoal is also more efficient catalyst than ZnO.

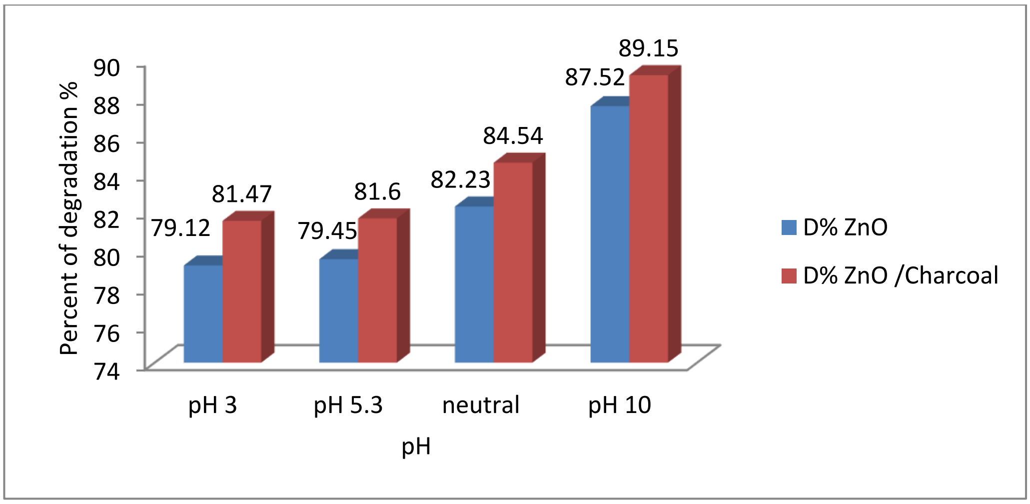


**Figure (3.17):** Organic removal percentage values using photo catalysts ZnO (0.2 gm) and ZnO/Charcoal (1.0 gm, containing 0.2 gm ZnO) at various pH values.

## 3.3 TOC Results After Photo- Degradation:

The results of TOC analysis show that the amount of total organic carbons removal with different parameters (pH value, and catalyst amount) were studied.

### 3.3.1 TOC of purified water using ZnO at different pH values.

Figure (3.18) shows the amount of Total Organic Carbon residual in the sample after organic removal at different pH values. The minimum amount of residual organic carbon was shown when using pH of 10, Figure (3.18). The TOC contents at pH 10 was 15 ppm, this value is still higher than the threshold limit of safe uses water (5 ppm).

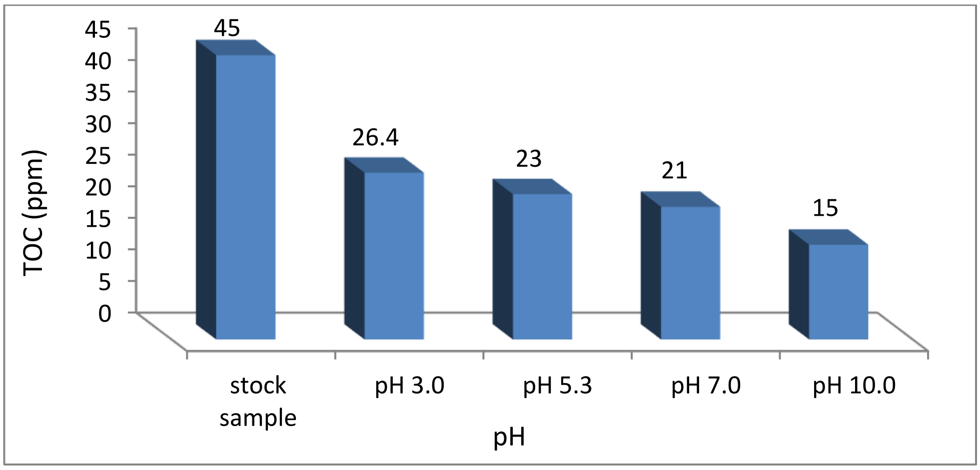


**Figure (3.18):** TOC of organic content by use ZnO at different pH values compared with the stock sample, experiments were conducted using 0.2 gm ZnO at 1 h in 100 ml sample at 25°C.

### 3.3.2 TOC for experiments performed using ZnO/Charcoal.

The amount of Total Organic Carbon after removal when using ZnO/Charcoal catalyst was studied. The maximum removal value was achieved at pH of 10. The value of presence organic carbon was 5 ppm; this value is in the range of recommended safe value of water TOC value. The results of TOC values at different pH values are presented in Figure (3.19).

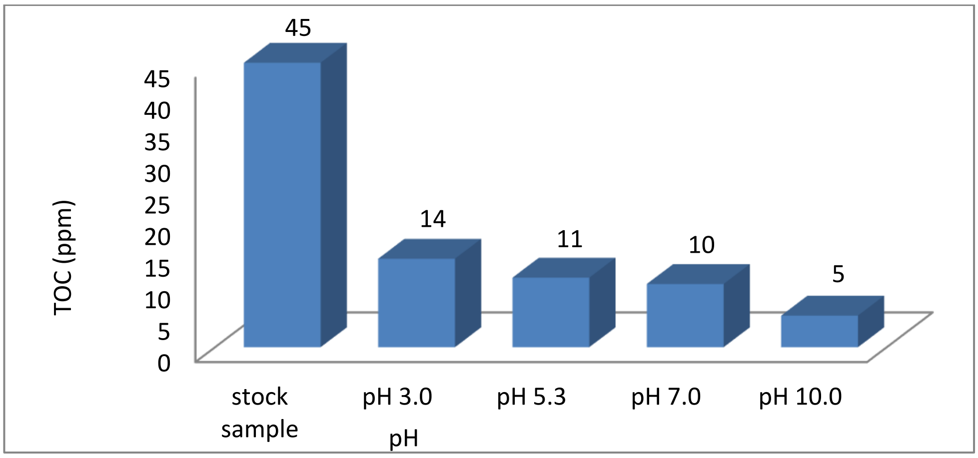


**Figure (3.19):** TOC of organic content by use ZnO/Charcoal at different pH values compared with the stock sample, experiments were conducted using 1 gm ZnO/Charcoal at 1h in 100 ml sample at 25°C.

### 3.3.3 TOC for experiments performed using ZnO at different amount:

The TOC analysis of treated water sample after using different ZnO catalyst amount was studied. Figure (3.20) shows the amount of TOC amount in the sample after degradation with different amount of ZnO. The minimum amount of TOC was observed when using 0.6 gm of ZnO.

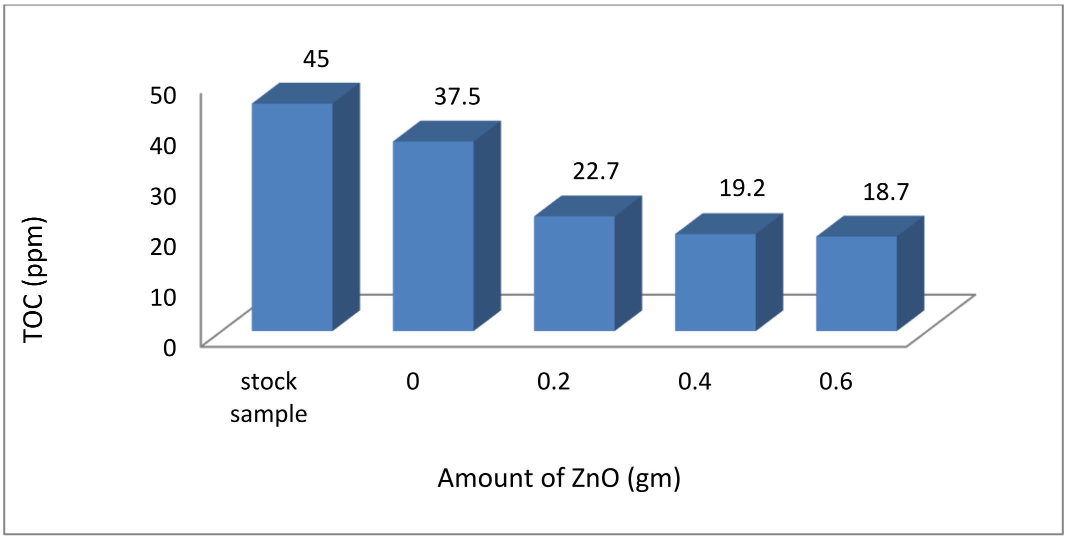


**Figure (3.20):** TOC of organic content by various amount of ZnO compared with the spike sample, experiments were conducted using pH is neutral at 1h in 100 ml spike sample at 25 $^{o}$**C.**

### 3.4 Control Experiments of ZnO/Charcoal Catalysis:

In photo-catalytic experiments we studied the effect of light and catalyst on purifying water from organic content. Three control experiments were conducted for this purpose. The first experiment was conducted by exposing a beaker containing 100 mL sample to the light for an hour in absence of catalyst. The sample was then spectrophotometrically analyzed for removing of organic contents. The second control experiment was performed by mixing a 100 mL water sample with 0.6 gm of ZnO/Charcoal catalyst composite. The mixture was continuously stirred in dark for an hour, and then analyzed for any losses of organic contaminants by adsorption. The third control experiment was performed by exposing a mixture of 100 mL water stock sample and 0.6 gm ZnO/Charcoal catalyst composite to light with stirring for an hour. The sample was then spectrophotometrically analyzed. The absorption spectral profiles are shown in Figure (3.21).

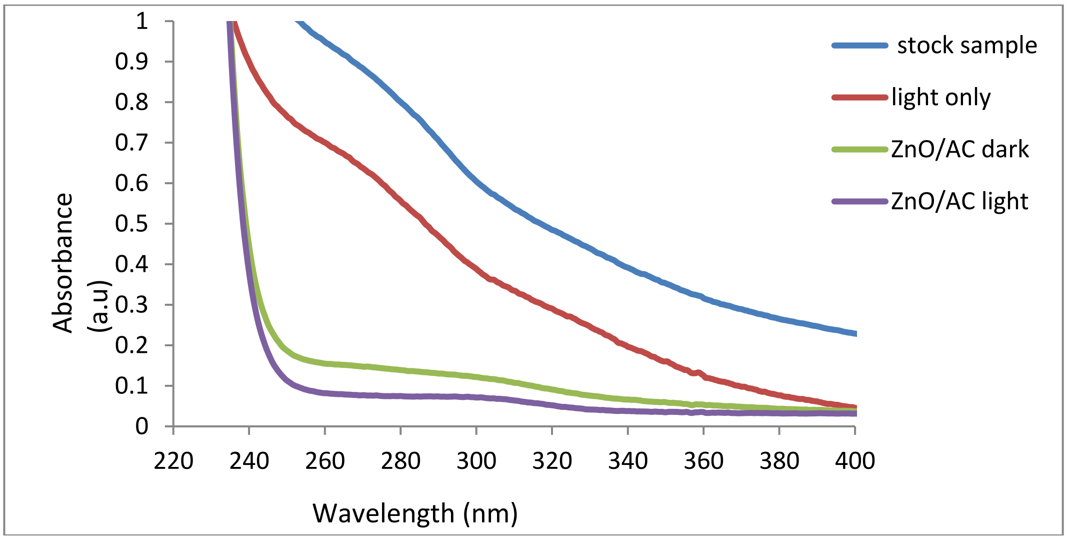


**Figure (3.21):** UV-Vis absorbance spectra measured for organic content at various light and catalyst, experiments were conducted using 0.6 gm ZnO/Charcoal for1 h in 100 ml stock sample at 25$^{o}$C.

Figure (3.22) shows by exposing the treated water to light, in the presence of catalyst, the percentage of purification of the sample was higher than in the dark.

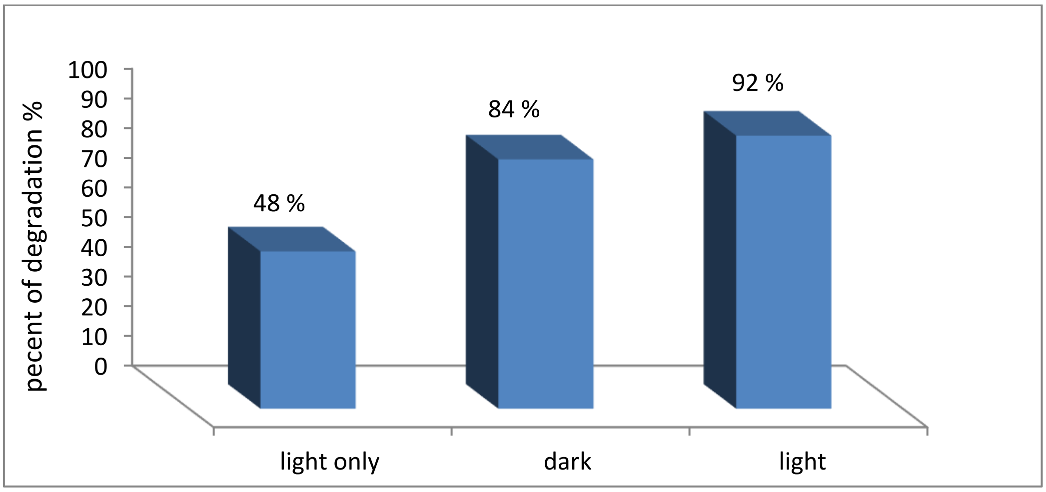


**Figure (3.22):** Degradation percentage of organic content with light and catalyst. Experiments were conducted using 0.6 gm ZnO/Charcoal for 1 h in 100 ml solution (the concentration of the organic contents before purification is 45 ppm at 25 ºC.

# Chapter Four

# Chapter Four

# Conclusions and Recommendations

## 4.1 Conclusions

Photo-degradation of organic pollutants in secondary pre-treated water by batch system has been investigated under solar simulated light using commercial ZnO and ZnO/Charcoal as catalysts. The following can be concluded:

1. Photo-degradation of organic pollutants occurred under solar simulation light using ZnO and ZnO/Charcoal were catalyst. In case of ZnO/Charcoal, the TOC decreased from 45 ppm to ~5 ppm within 15 min?
2. The supported catalyst (ZnO/Charcoal) shows higher activity than the un-supported ZnO catalyst, due to ability of Graphite to adsorb the contaminants.
3. Adsorption and photo-degradation process of organic contaminants with both catalyst systems was affected by conditions such as pH, time and catalyst loading.

## 4.2 Recommendations for future work:

1. Study the possibility to recover and re-use the ZnO/Charcoal for several times in water purification.

2. Use the catalyst system to degrade other organic pollutants with direct solar light.

3. Use different types of photo catalysts to compare their efficiency in organic contaminant solution.

4. Investigate continuous flow reaction technique in purifying recycled water for the safe drinking levels

5. Investigate the applicability of photo-degradation processes in purifying waters recycled waters by using a pilot-plant scale study.

6. Need to apply the search to a wider area and be closer to the ideal in Palestine.

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كلية الدراسات العليا

# التحلل الضوئي للملوثات العضوية من المياه المعالجة الثانوية باستخدام ضوء الشمسي المحاكي

إعداد

بتول هاشم محمود نور

إشراف

أ.د. حكمت هلال

د.عاهد زيود

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

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## الملخص

ويجري تنقية مياه الصرف الصحي في فلسطين على نطاق واسع في محطات المعالجة في مناطق مختلفة. تستخدم المحطات العلاجات الثانوية للمياه، وقد لا تزال المياه الناتجة تشمل أنواعا مختلفة من الملوثات العضوية القابلة للذوبان. المياه المعالجة يتبعها أساليب مختلفة مثل الكلورة، والبيروكسيد، والأوزون والأشعة فوق البنفسجية يستخدم عادة على الصعيد العالمي، ومع ذلك، كل هذه مكلفة. في العمل الحالي استخدمنا الضوء الشمسي المباشر لتحلل الملوثات العضوية من المياه المعالجة الثانوية. استخدام ZnO المدعومة بالفحم (الفحم / ZnO) هو محفز تدهور الصورة. هذه الطريقة آمنة حيث من المتوقع أن يتم تحويل المواد الملوثة العضوية إلى مركبات معدنية آمنة. لقد شهدنا نتائج واعدة باستخدام 0.6g ZnO لكل 100ml من مياه الصرف الصحي، في pH 10 لمدة 1 ساعة. وجدنا أن المركبات العضوية TOC موجودة في المياه المطالب بها بتركيزات تصل إلى 45 ppm قبل التنقية.

من هذه المواد العضوية، 80٪ قد تدهورت تماما ترك أي آثار عضوية، كما أكد تحليل إجمالي الكربون العضوي (TOC)، تم تحسين إزالة المحتويات العضوية عندما استخدمنا ZnO / الفحم، وكان وصول جدول المحتويات 5 جزء في المليون، وهو حد آمن وفقا لمنظمة الصحة العالمية (WHO).

لقد درسنا خصائص المحفز (أكسيد الزنك التجاري) والفحم المدعوم ZnO (ZnO / الفحم) باستخدام المجهر الإلكتروني المسح الضوئي (SEM)، الأشعة السينية الحيود (XRD) والطاقة التشتت الأشعة السينية الطيفي (EDS). لقد درسنا معلمات مختلفة (مثل تحميل المحفز، درجة الحموضة والوقت) لتحديد الحالة المثلى للمعلمات المدروسة. تظهر النتائج أن استخدام ZnO0.6 g لكل 100 مل من مياه الصرف الصحي، عند pH 10 لمدة 1 ساعة يعطي أفضل النتائج.