

**An-Najah National University
Faculty of Graduate Studies**

**Photocatalytic Degradation of 2-Chlorophenol
in Water with Direct Solar Light using Pristine
and Kaolinite Supported ZnO**

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the Degree of Master of Chemistry, Faculty of Graduate Studies, An-
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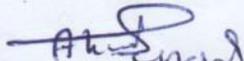
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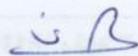
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III **Dedication**

I dedicate this thesis to my parents, my brothers (Tamer & Ahmed), to my sister (Diala) and especially to my beloved husband (Mohammad), to my baby (Merna) and to my mother in law for their continuous support.

Acknowledgement

Before every thing, I thank God who enabled me to complete my thesis. I would like to thank with full gratitude and appreciation my supervisors, Prof. Hikmat Hilal for his guidance, support, advice and suggestions and Dr. Ahed Zyoud for his assistance in laboratory research, help throughout my work in lab and giving me ideas for interpreting experimental results. I also would like to thank the technical staff at the Department of Chemistry at An-Najah National University, especially Mr. Nafeth Dwekat.

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	أقر بأن ما اشتملت عليه هذه الرسالة هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذ الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى	
	<u>Declaration</u>	
	The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degrees or qualifications.	
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List of Abbreviations

Symbol	Abbreviation
UV	Ultra violet
E_g	Band Gap
e^-	Electron
h^+	Hole
VB	Valance Band
CB	Conduction Band
PL	Photoluminescence
T.F	Turnover Frequency
T.N	Turnover Number
QY	Quantum Yield
ppm	Part Per million (mg/L)
eV	Electron Volt
nm	Nanometer
a.u	Arbitrary Unit
w/cm^2	Watt per square centimeter

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Abstract

The photocatalytic degradation of 2-chlorophenol in water under direct sun light was studied using ZnO as semiconductor photocatalyst. Different forms of catalyst were used, namely commercial ZnO, synthetic ZnO and for the first time using composite of ZnO/Kaolinite. These forms were characterized by photoluminescence and UV-visible spectra and the results indicate that the ZnO particles varied in size as: ZnO/Kaolinite < synthetic ZnO < commercial ZnO. The photodegradation of 2-chlorophenol was investigated under different conditions including effect of contaminant concentration, effect of catalyst amount and effect of pH. To study catalyst efficiency, values of overall rate, turnover number (T.N.), turnover frequency (T.F.), degradation percentage and quantum yield (Q.Y.) were all calculated.

Under neutral conditions, different ZnO forms catalyzed the photodegradation of 2-chlorophenol in water. The results were compared between ZnO forms, synthetic ZnO showed higher efficiency than commercial ZnO. Commercial ZnO/Kaolinite composite showed higher efficiency than commercial ZnO and synthetic ZnO. The order of efficiency using different form of ZnO system is commercial ZnO<

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synthetic ZnO < commercial ZnO/Kaolinite. Increasing contaminant concentration, catalyst amount and pH increased photodegradation rates. A mechanism is provided to explain how the photodegradation occurs.

Chapter One

Introduction

1.1 Overview

A pollutant is a hazardous substance, introduced into the environment, that has undesired effects. Pollution occurs in air, water and soil. It may cause long- or short-term damage by affecting growth rate of plants, animals or human health and many cause diseases. The development in our lives increased pollution significantly, giving rise to human illness and affect in environment balance. [1-3].

Water pollution involves any contamination that affects the water's purity and quality. There is many type of water contamination involves chemical pollutants (organic contamination, heavy elements, insecticides, herbicides, dyes, pesticides ... etc), biological pollutants (fungi, bacteria and viruses) and radiation pollutants. Pollution may occur in surface waters (rivers, lakes and oceans) or underground reservoirs [3,4].

Organic pollution occurs when large amounts of organic compounds, which serve as substrates for microorganisms, enter the water [5, 6]. Phenol and its derivatives are the most common organic pollutant [7].

Water purification and recycling are used to decrease the concentration of contaminants. Different methods are used to lower water contaminant concentrations. Many of these are expensive or less efficient. Recently solar energy has been widely investigated in a self-cleaning technology and photocatalysis [8-10].

1.2 Phenol and chlorophenol contaminations

1.2.1 Phenol

Phenol, sometimes called carboic acid, is an aromatic organic compound with the molecular formula C_6H_5OH . It is a white volatile crystalline solid.

It may exist in surface and tap waters for long periods of time, and in aqueous effluents from various manufacturing processes, phenol is moderately soluble in water [8-10]. Phenol and its derivatives are toxic pollutants known as human carcinogen, even at low concentrations [11, 12].

1.2.2 2-Chlorophenol

2-chlorophenol (C_6H_5ClO), or 2-Hydroxychlorobenzene, is an organic derivative of phenol. It is produced by reacting chlorine with phenol in presence of acidic catalyst. 2-Chlorophenol is a weakly acidic colorless to slightly amber liquid with an unpleasant odor [13, 14].

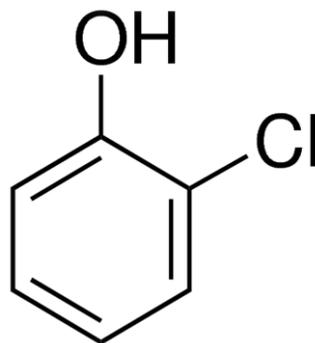


Figure (1.1): 2-Chlorophenol structural formula [15].

Chlorophenols can enter the environment when used as pesticides, dyes, bactericide ...etc [16, 17]. Most chlorophenol released to the environment goes into water. It is present in drinking-water as a result of the chlorination of phenols. It sticks to sediments and soil at the bottoms of rivers, lakes and streams [18, 19].

2-chlorophenol is toxic to human being and aquatic organisms and may cause long-term effects in the environment. Exposure to high levels of 2-

chlorophenol can cause damage to the liver, kidney and immune system. It may also cause irritation of the digestive tract and may cause cancer [15, 20]. Phenols along with its chlorophenol derivatives are soluble in water. The solubilities and dipole moment values of phenol, o-chlorophenol, m-chlorophenol, p-chlorophenol, are shown in Table (1.1) [16].

Table (1): Solubility of phenol and its chloro in water [16, 21].

Compound	Solubility (g/100g)	Dipole moment values
Phenol	9.48	1.22 D
o-chlorophenol	2.04	1.33 D
m-chlorophenol	2.25	2.10 D
p-chlorophenol	2.77	2.22 D

The table shows that the solubility of chlorinated phenols in water solution is low compared to phenol due to new bond with Cl. But for (o/m/p)-chlorophenol the solubility increased with increasing dipole moment value.

Crystal structure of 2-chlorophenol is shown in Figure (1.2). Helices are consists of hydrogen bond formation from 3 axes OH...OH. The helices are linked between two hydrogen atoms of one chain and one atom chlorine of other chain. [18].

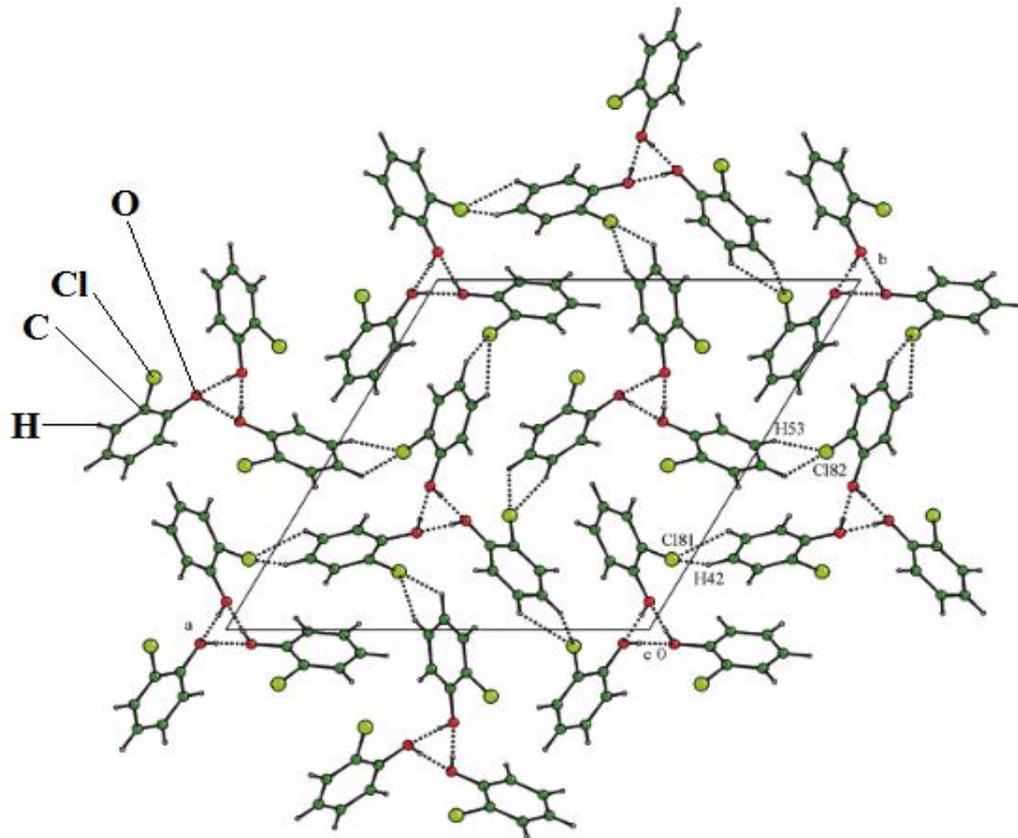


Figure (1.2): Crystal structure of 2-chlorophenol at ambient pressure and 100 K [18].

1.3 Semiconductor photocatalysis

During the recent decades, photocatalytic applications using semiconductors have received much attention to solve some environmental problems. Photocatalysis is a rapidly expanding technology for wastewater treatment [22]. A photocatalyst is a substance that increases the rate of a photo-chemical reaction without being consumed itself. Photocatalysis is an efficient process for complete degradation of organic compounds. It plays an important role in the degradation of toxic organic compounds from air and water into components that are safe [23-25].

In the photocatalytic process a semiconductor is commonly used, which is nontoxic, chemically stable and available at reasonable cost [26]. Photocatalysis is a process, which operates at room temperature on semiconductor materials and being used for the purification of polluted water and decomposition of toxic organic pollutants like phenol and its derivatives [16, 23].

Semiconductor photocatalysts accelerate chemical reactions upon light absorption, usually sunlight. Semiconductor photocatalysis is becoming an important technology for removal of organic contaminants in wastewater [27-29].

Semiconductor photocatalysts are more effective than other chemical oxidation methods, because these are inexpensive and can mineralize different organic compounds [30, 31]. A semiconductor is a solid material with electrical conductivity in between that of a conductor and an insulator (roughly in the range of 10^{-2} to 10^4 siemens per centimeter) [32, 33]. In semiconductors, the highest occupied energy band, the valence band (VB), is completely filled with electrons. The empty band is the conduction band (CB) [34]. The properties of a semiconductor are explained by quantum physics [35].

Semiconductor materials, such as ZnO, CdS, ZnS, TiO₂, SnO₂, LiNbO₃, Fe₂O₃, Al₂O₃, WO₃, are used as photocatalysts. Besides many tested photocatalysts, ZnO is widely used in different sectors and became the focus of recent research. Photocatalysis using zinc oxide is a safe, nonhazardous, and ecofriendly process which does not cause any harm to environment [26, 36].

1.4 Principles of photocatalysis

In the photocatalytic oxidation process, organic pollutants are destroyed in the presence of a semiconductor photocatalysts (e.g : ZnO), an oxidising agent such as oxygen or air, and radiation. Figure (1.3) summarizes the mode of action of ZnO as a photocatalyst.

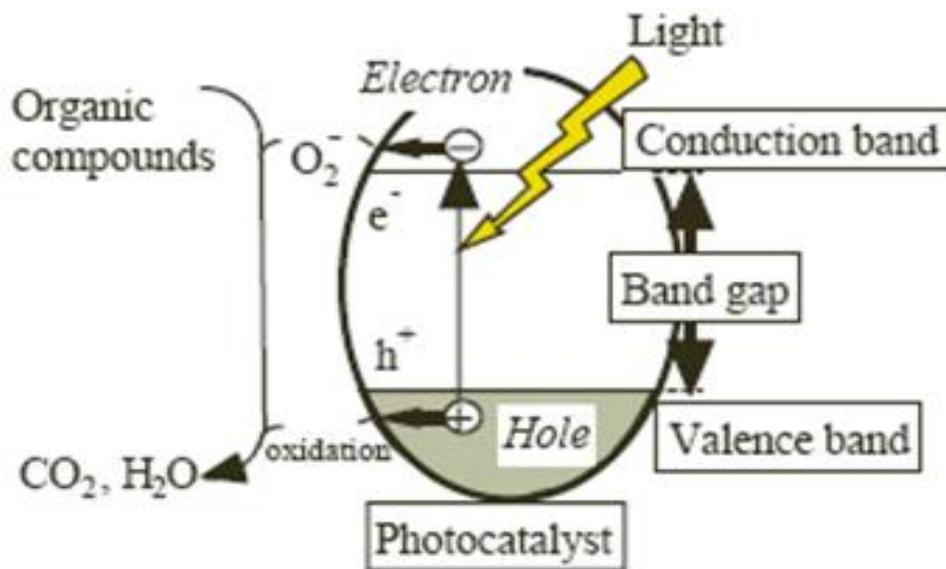
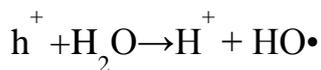
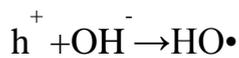
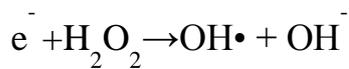
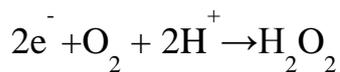
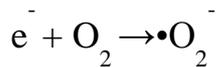
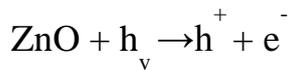


Figure (1.3): Schematic mechanism of photocatalysis [16].

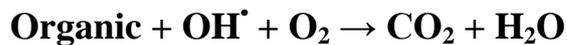
Each band has different energy levels, and the electrons fill the band from the lowest energy to the highest. The valence band (VB) is the highest energy filled band, which is analogous to the highest occupied molecular orbital (HOMO). The next higher band, which is analogous to the lowest unoccupied molecular orbital (LUMO), is called the conduction band (CB) [37].

The VB and the CB are separated by an energy bandgap (E_{bg}). The size of the bandgap and the filling of bands in a solid determine if a material is a conductor, a semiconductor, or an insulator [38].

Absorption of photons with energies greater than the bandgap energy (ΔE) causes excitation of electrons from valance band (VB) to conduction band (CB) and yields electrons (e^-) and holes (h^+). The formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band (CB) is an important step. Figure (1.3) explains these processes [16]. Theseperated e^- and h^+ transfer to ZnO particle surface where they can react with other species as follow [16, 39, 40] :



Photocatalysis reaction is:



1.5 Zinc oxide

Zinc oxide is an inorganic compound with the formula ZnO. It is a white powder that is insoluble in water [33,41]. ZnO is used as photocatalyst in degradation processes for environmental pollutants [42]. Its

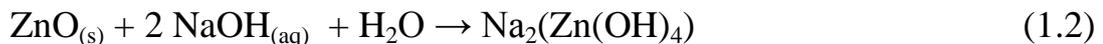
semiconducting (SC) characteristics are based on its wide band gap (3.2 eV) which absorbs in UV region (390 nm or shorter). Therefore, ZnO has been investigated as a catalyst for contaminant photo-degradation processes in water using UV or Solar light [43].

Zinc oxide is used as powder catalyst due to its oxidizing power with advantages over its competitors. It is relatively abundant, low cost [43], inexpensive, chemically stable, easy to prepare, non-hazardous, environmentally friendly, non-toxic substance [44] with photochemical activity [42]. ZnO can also be processed using various manufacturing processes. ZnO has other several advantages such as good transparency, high electron mobility, and strong room-temperature luminescence [45, 46].

Zinc oxide is an amphoteric oxide. It is nearly insoluble in water and organic solvents, but degrades by acids, such as hydrochloric acid to yield zinc ion, (eqn. 1.1) [47-49]:



Bases also degrade ZnO to give soluble zincates, (eqn. 1.2)



Zinc oxide occurs in three forms: hexagonal wurtzite, cubic zinblende, and the rarely observed cubic rocksalt. The wurtzite structure is most stable under ambient conditions and is most common form. The zinblende form can be stabilized by depositing ZnO on substrates with similar cubic lattice structure. Hexagonal and zinblende polymorphs have no inversion

symmetry element [50, 51]. Figure (1.4) summarizes crystal structures for ZnO types.

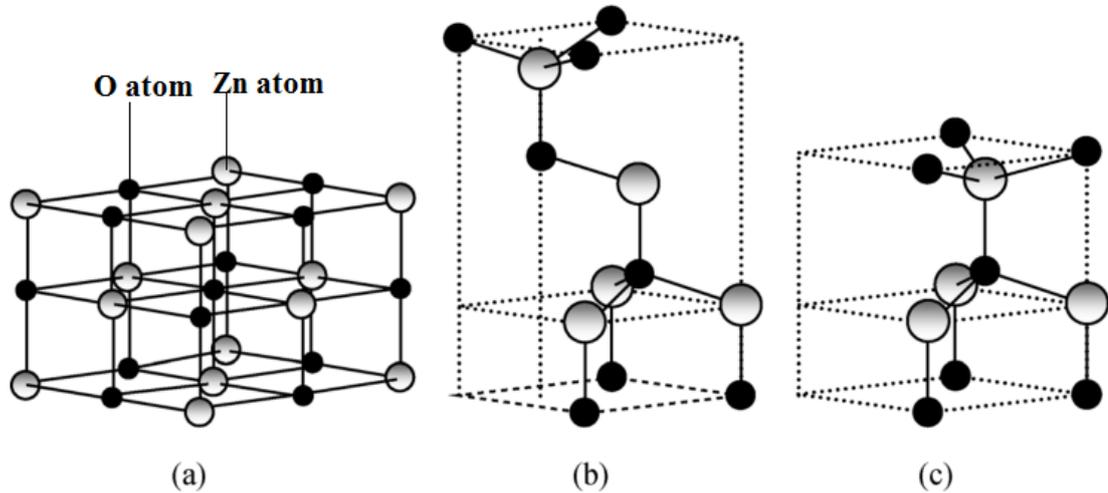


Figure (1.4): Stick and ball representation of ZnO crystal structure, (a): cubic rocksalt, (b): cubic zinc blend, (c): hexagonal wurtzite [50].

1.6 Clay

The term "clay" refers to naturally occurring materials involving additional minerals. It is a natural earthy material that is plastic when wet but hardens when dry, consisting primarily of hydrated silicates of aluminum. It also involves organic fragments and occurs as sedimentary rocks, soils, and other deposits. Clays become soft when moist but harden on heating and are used in bricks, cement, ceramics, etc [52, 53].

Clay minerals are hydrous aluminum silicates which may contain iron, alkali metals, or alkaline earths [52, 54]. Clays exist in different forms (Kaolinite, Illite, Montmorillonite and others) [55, 56].

1.6.1 Kaolinite

Kaolinite is the most common clay mineral with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is easily broken and can be re-shaped, especially when

wet [57]. Kaolinite is used for pottery and ceramic industry, especially in fine porcelains, because it can be easily molded with a fine texture, and becomes white when fired. It is used in the industry of paper, and in pharmaceuticals as an as important component in some medications [58,59].

Kaolinite involves repeated layers of one tetrahedral sheet (silica) and one octahedral sheet (alumina or magnesia) [60]. A tetrahedral sheet involves tetrahedral-shaped units. Each unit has a central atom surrounded by four oxygen atoms, linked nearby central atoms. An octahedral sheet involves octahedral units. Each unit has a central atom surrounded by six oxygen atoms, linked with other nearby central atoms. Figure (1.5) shows example of structures for clay minerals (tetrahedral and octahedral sheets). The tetrahedral sheet is bonded to an octahedral sheet. The tetrahedral sheet formula is $\text{Si}_4\text{O}_{10}^{-4}$. Octahedral sheets have tow types, Brucite $\text{Mg}_3(\text{OH})_6$, with all octahedrals occupied, and Gibbsite $\text{Al}_2(\text{OH})_6$, where $2/3$ of octahedral sites are occupied [61, 62].

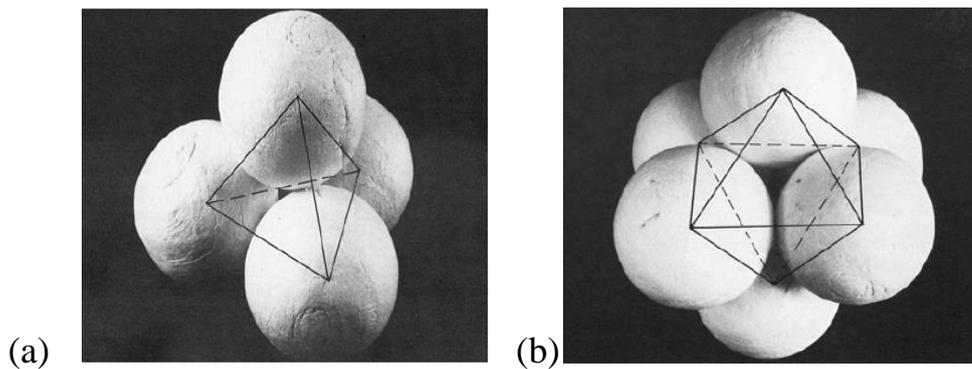
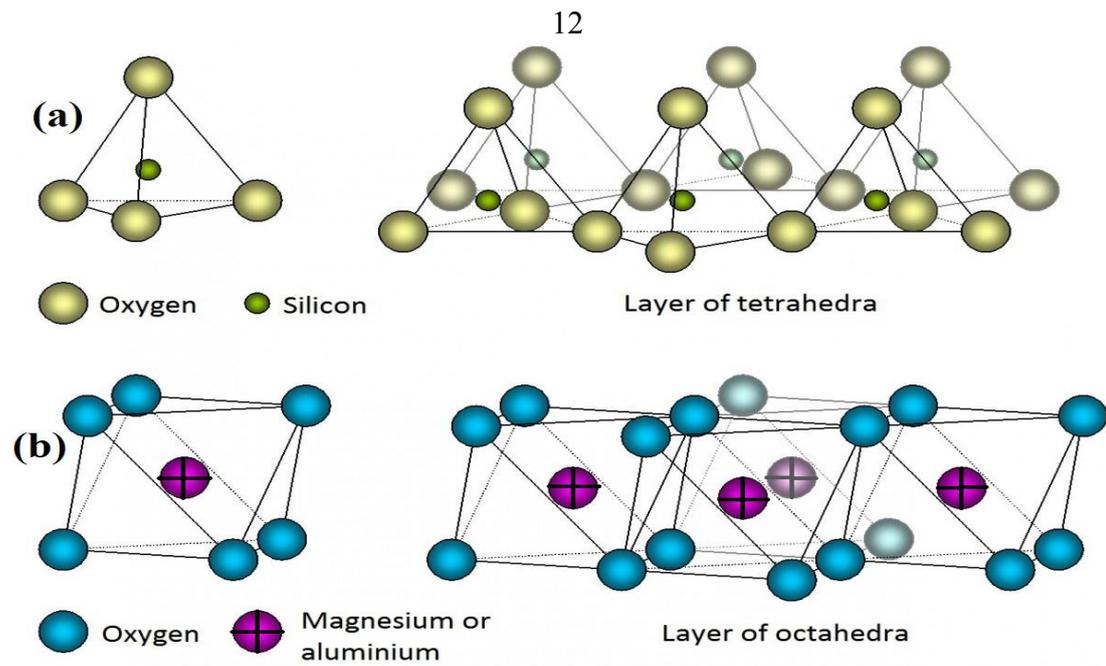


Figure (1.5): Basic structures of clay minerals (a) tetrahedral sheet (b) octahedral sheet [61].

Kaolinite is named a 1: 1 clay mineral [60,62] as it consists of one layer tetrahedral sheet and one layer octahedral sheet linked together, as shown in Figure (1.6). Kaolinite has a basal spacing of about 7.2\AA . The unshared oxygen is part of the octahedral sheet. Kaolinite is shown in Figure (1.7). It is insensitive to drying or moderate heating because it is non expandable. Kaolinite are damaged by heating at 500°C [63,64].

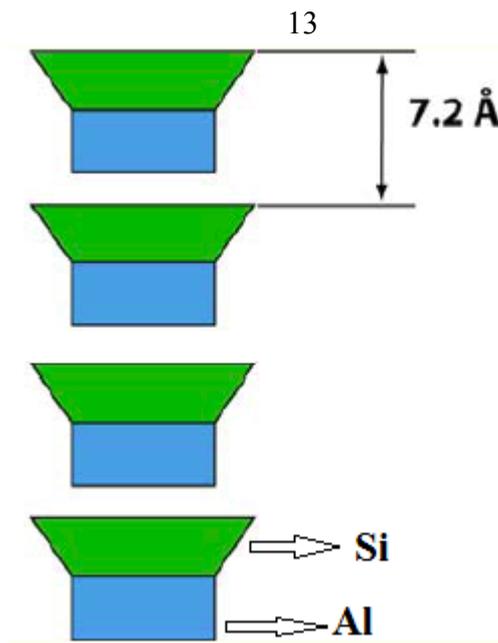


Figure (1.6): Layer structure of kaolinite [65].

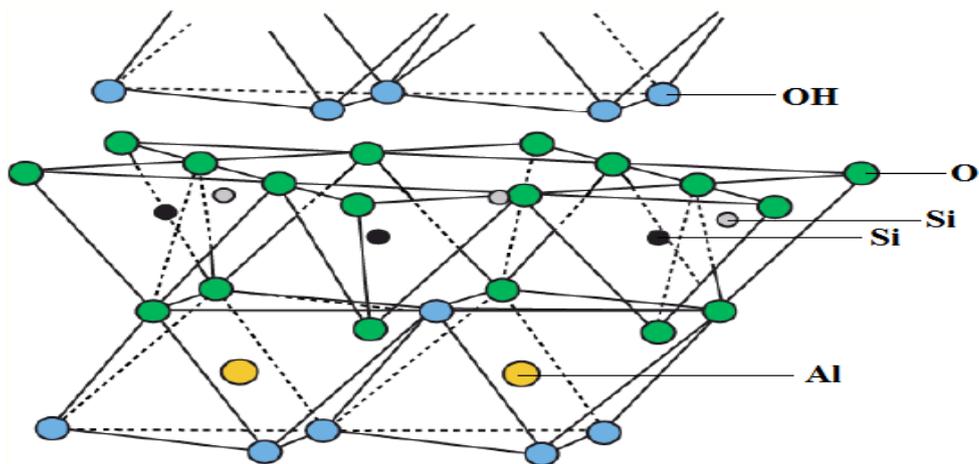


Figure (1.7): Simplest clay mineral kaolinite [61].

1.7 Objectives

The main purpose of this work was to find safe and economic processes (photo-degradation) to purify water and dispose organic contaminant (2-chlorophenol) from water using an inexpensive and non-toxic semiconducting material (ZnO) and solar energy. The nano-sized particles

of ZnO were used as commercial and prepared particles. Clay (kaolinite) was used to support nano-sized particles of ZnO. This work is expected to develop a new process that can be used in future water purification systems.

1.7.1 Technical objectives

The following technical objectives were achieved in this work:

- Characterize ZnO commercial using photoluminescence and UV/Visible spectra techniques.
- Use the ZnO commercial in direct solar light photodegradation of 2-chlorophenols in water.
- Prepare nano-sized particles of ZnO .
- Characterize the prepared ZnO using photoluminescence and UV/Visible spectra techniques.
- Use the prepared ZnO particles in direct solar light photodegradation of 2-chlorophenols in water.
- Support the nano-sized particles of ZnO on to insoluble solid surfaces (kaolinite) and characterize them using photoluminescence and UV/Visible spectra techniques.
- Use the supported catalyst (ZnO/kaolinite) in photodegradation of halophenols in water.
- Study different reaction parameters such as (effect of pH, contaminant concentration, catalyst concentration) on catalyst efficiency.
- Compare the result and characteristics of the forms of the catalyst efficiency in degradation of the contaminant.

1.8 Hypothesis

This work is based on the following assumptions:

- Halophenols are widely spread organic compounds and need to be completely removed from water by photocatalytic degradation.
- Using direct solar light in photodegradation studies may help completely degrade halophenols using UV region, into safe compounds.
- Supporting ZnO onto solid surfaces may increase efficiency of photocatalysts and makes it easier to recover after reaction steps.
- With its 3.2 eV band gaps, ZnO is known to absorb UV from solar light effectively. It may thus catalyze photodegradation of organic contaminants under direct solar light.

1.9 Novelty

Many research works were done on photocatalytic degradation using ZnO catalysts. Shadya Hejjawi[33] used TiO₂ and ZnO photocatalysts for degradation of widespread pharmaceutical wastes. Razan Khraim [66] studied purification of agricultural soil from halophenol contaminants by Photodegradation with ZnO nanoparticles. In this work we studied the ZnO photocatalytic degradation of halophenols in water using direct solar light. Nano-sized particles of ZnO were used in their pristine and supported forms. Clay particles were used as support. Such techniques have been described here in removing halophenols for the first time (to our knowledge). Effects of different parameters on catalyst efficiency were also studied.

Chapter Two
Materials and Methods

2.1 Materials

Commercial zinc oxide was purchased from Sigma Aldrich Co. and used as photo-catalyst for water purification. $ZnCl_2$ that was purchased from Chem. Samuel and NaOH from Frutarom Co. were used for synthetic ZnO preparation. Zinc acetate dihydrate [$Zn(OOCCH_3)_2(H_2O_2)$] from Sigma Aldrich (catalog no.25044) was used for composite catalyst preparation. Clay kaolinite (03584-250G) was purchased from Sigma Aldrich. The contaminant 2-chlorophenol was purchased from Sigma Aldrich.

2.2 Equipments

A Shimadzu UV-1601 spectrophotometer, equipped with a DPU-411-040/20BE printer, was used to study the absorbance of remaining 2-chlorophenol in solutions, using a calibration curve, the band at 280 nm was used for this purpose. A Perkin-Elmer (LS50) Luminescence Spectrometer was used to study the maximum absorbance of each ZnO form. A Lux-meter (Lx-102 light meter) was used to determine the intensity that reaches the water sample in the photo-catalytic purification experiments.

Centrifuge a Scientific Ltd model 1020 D.E. centrifuge was used to separate contaminant solution from solid materials. A Jenway 3510 pH meter was used to adjust the reaction mixture pH as desired. A mercury thermometer was used to measure temperature.

2.3 Preparation of solutions

- Stock solution preparation : 2-Chlorophenol stock solution (1000 ppm) was prepared by dissolving 0.100 g 2-chlorophenol in distilled water and then diluting it to 100 ml. The solution was kept in the

dark. Different concentrations (5, 10, 20, 40, 60, 80 ppm) were prepared using the stock solution.

- Dilute solutions (0.05 M) of both HCl and NaOH were prepared for the purpose of controlling the pH in the catalytic reaction mixtures.

2.4 Catalyst preparation

2.4.1 Preparation of ZnO nanoparticles

The precipitation method was used to prepare ZnO nanoparticles [33]. A 250 ml solution (0.45 M) of ZnCl_2 was prepared by dissolving 15.230 g of ZnCl_2 in 200 mL distilled water. The volume was then completed to 250 ml in a 250 mL volumetric flask. A solution (0.9 M) of NaOH was prepared by dissolving 9.000 g of NaOH in 200 mL distilled water. The volume was then completed to 250 ml in a 250 mL volumetric flask. The NaOH solution was placed in 500 ml beaker and heated to about 55°C. Then the 250ml of 0.45 M Zinc chloride solution was added slowly dropwise to the heated solution of 0.9 M NaOH under high speed magnetic stirring. Finally the resulting powder was decanted and washed with distilled water until the solution became neutral. The powder was then separated from the mixture using a centrifuge (speed 500 rounds per minute, for 6 min).

2.4.2 Supporting ZnO particles onto Kaolinite clay

0.39 M solution of Zinc acetate dihydrate, $\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2(\text{H}_2\text{O})$, was prepared by dissolving 8.5 g Zinc acetate in 100 mL solution. A 0.9 M solution of NaOH was prepared by dissolving 9.000 g of NaOH in 250 mL solution. After that 10 g of Kaolinite clay was placed in a 250 ml of 0.9 M

sodium hydroxide. The mixture was heated at 55°C under stirring for 120 minute with gradual addition of zinc acetate dihydrate solution (0.39 M) dropwise. The resulting powder was filtered and washed with distilled water until the mother liquid became neutral. The powder was then dried in an oven at 250°C for 1 hour and then stored.

2.4.3 Photo-catalytic experiments

The photo-degradation reaction was conducted in a 100 ml beaker containing aqueous reaction mixtures of known concentrations of contaminant and catalyst. The catalytic experiments were carried out in a magnetically stirred thermostated beaker. The reaction mixture was continuously stirred magnetically to make a good distribution of the catalyst through the mixture and the beaker was placed in a thermostated water-bath to prevent the change of temperature. The temperature was measured throughout reaction time and kept constant by manipulating the water bath when needed.

Direct solar light (which contains about 5% UV) was applied vertically to the photo-catalytic mixture surface. Small aliquots of solution were syringed out, from the reaction container at different reaction times, and double centrifuged (500 round/minute for 3 minutes each time). The resulting clear solution was then taken and placed in a quartz cell. The absorbance was measured for all sample aliquots at different times using UV/visible spectrophotometry. The default temperature for the catalytic experiment was 25°C and the default pH was 7. The pH was controlled as

required when studying the effect of pH by adding drops of NaOH or HCl dilute solutions.

2.5 Control Experiments

- In the absence of any catalyst, 2-chlorophenol solution (100 ml) was placed in the reactor under direct sun light with stirring for 60 min. Absorption was measured before and after exposure to sun light. The 2-chlorophenol concentration did not change under direct sun light with time. This means that the 2-chlorophenol did not photodegrade in the absence of catalysts.
- 100 ml of 2-chlorophenol were stirred with ZnO catalyst of the three forms each one separately (0.1 g commercial ZnO, 0.1 g synthetic ZnO and 0.42 g composite commercial ZnO/Kaolinite) was kept in the dark for 60 min. The absorption spectrum was measured with time. The contaminant concentration did not change. This indicate that no effect of photodegradation of three forms of ZnO catalyst in dark place, and no observable lose by adsorption because ZnO and kaolinite have low surface area ($\sim 25 \text{ m}^2/\text{g}$ for ZnO and $7 \text{ m}^2/\text{g}$ for kaolinite).

2.6 Calibration Curve

Different concentrations of 2-chlorophenol (5, 10, 20, 40, 60 and 80 ppm) were prepared. The electronic absorption spectra were measured for different concentrations at λ_{max} 280 nm. Figure (2.1) shows the absorption spectrum for 2-chlorophenol. A Calibration curve was constructed by measuring the absorbance vs. 2-chlorophenol concentration. as shown in Figure (2.2).

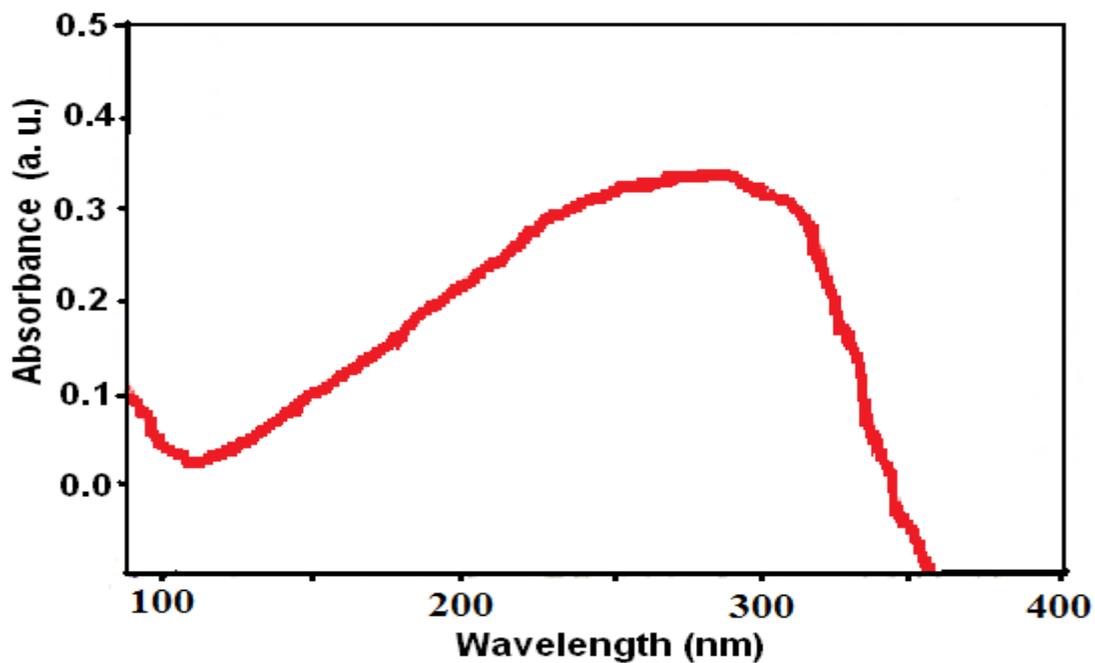


Figure (2.1): UV-visible spectrum for 2-chlorophenol.

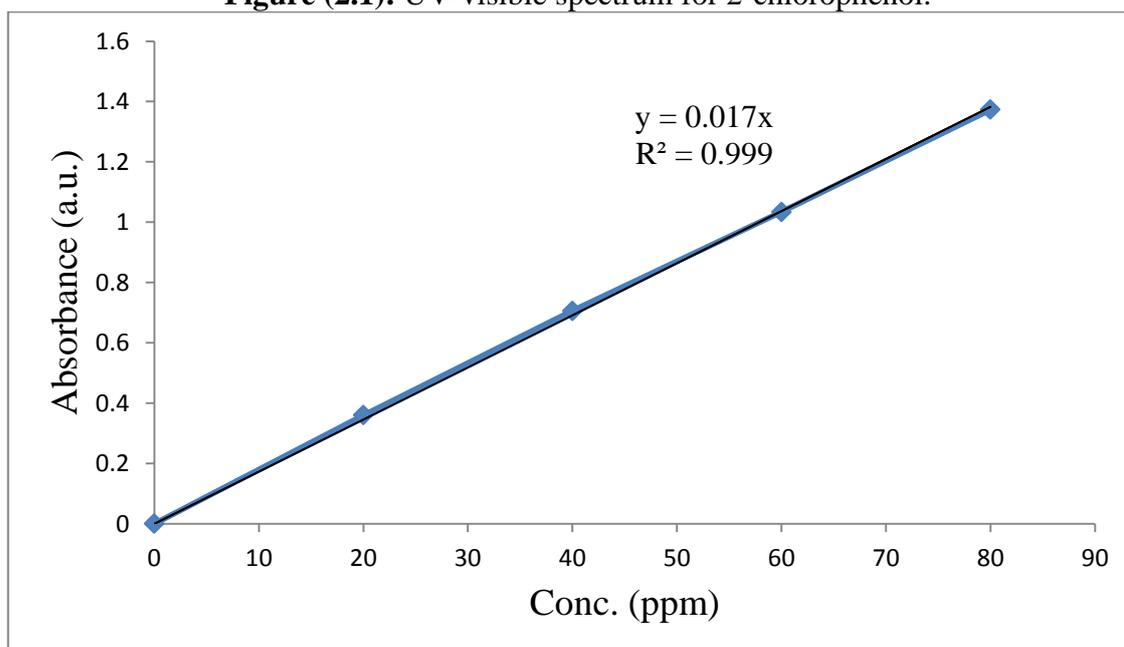


Figure (2.2): A calibration curve showing a plot of electronic absorbance vs. 2-chlorophenol concentration (ppm) in water, at room temperature. The maximum wavelength was 280 nm.

Chapter Three

Results and Discussion

3.1 Photocatalyst characterization results and discussion

Commercial ZnO, synthetic ZnO and ZnO/Kaolinite powders were characterized by using UV-visible absorption spectrophotometry and photoluminescence spectra.

3.1.1 Photoluminescence (PL) spectra characterization

Photoluminescence emission spectra were studied for commercial ZnO, synthetic ZnO and ZnO/Kaolinite powder. Small amount of each powder was suspended in distilled water and placed in a quartz cell. Each suspension was characterized using (PL) using excitation $\lambda = 340$ nm.

3.1.1.1 Photoluminescence (PL) Spectra of unsupported ZnO

The photoluminescence spectra of commercial and synthetic ZnO powders were measured as shown in Figure (3.1). The emission peak of commercial ZnO in the photoluminescence spectrum is 387 nm whereas for synthetic ZnO is 385 at room temperature. From the relation E_g (eV) = $1240/\lambda_{max}$ (nm) [32] the band gap values were calculated as 3.20 for commercial and 3.22 for synthetic ZnO powders. Figure (3.1) also shows a broad peaks around 500 nm and 420 nm.

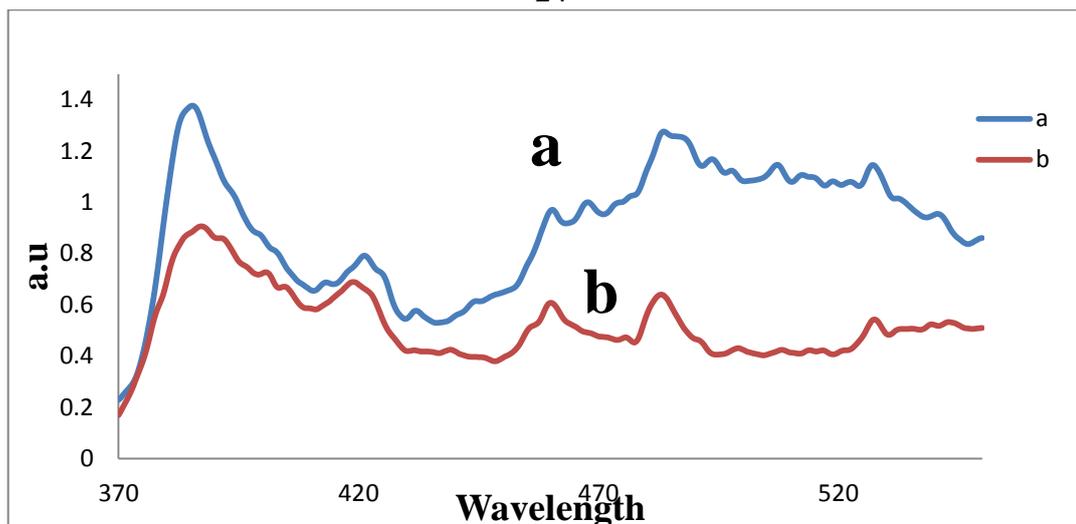


Figure (3.1): Photoluminescence emission spectra for (a) commercial ZnO, (b) synthetic ZnO at excitation $\lambda = 340$ nm.

The emission peak of commercial ZnO in the photoluminescence spectrum has longer wavelength than the synthetic ZnO. This indicates that the synthetic ZnO powder has smaller particle size than the commercial ZnO powder [66]. The additional emission peaks observed around 500 and 420 are due to the presence of ionized oxygen vacancies [67].

3.1.1.2 Photoluminescence (PL) Spectra of kaolinite and ZnO/kaolinite

The photoluminescence spectra of kaolinite and ZnO/kaolinite were measured as shown in Figure (3.2). For naked kaolinite there is no important PL peak, whereas a peak at 380 for composite ZnO/kaolinite is observed. A peak around 450 nm for ZnO/kaolinite composite material and naked kaolinite is observed.

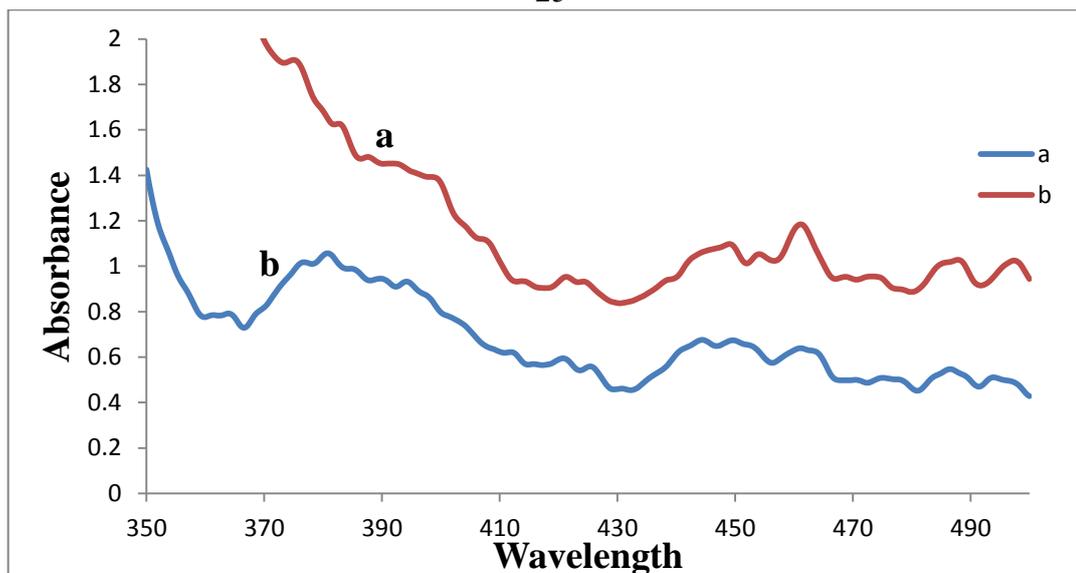


Figure (3.2): Photoluminescence emission spectra for (a) Kaolinite, (b) ZnO/Kaolinite at excitation $\lambda = 340$ nm.

The PL emission peak measured for the composite commercial ZnO/kaolinite is shorter than the emission peak for the commercial ZnO. This is because the supported ZnO particles can not combine together into larger particles. Their sizes remain small, whereas the commercial ZnO particles may combine together to form larger ones with longer λ as they are left aside. The peaks around 450 nm for ZnO/kaolinite composite material and kaolinite also due to presence of oxygen vacancies [68]. The results indicate that the ZnO particles varied in size as: ZnO/Kaolinite < synthetic ZnO < commercial ZnO. These differences can be useful in explaining differences in catalyst activities, as shown later.

3.1.2 UV-visible spectra characterization

UV-Visible spectra were measured for commercial ZnO, synthetic ZnO, kaolinite and ZnO/Kaolinite materials. A small amount of each powder

was individually suspended in distilled water and placed in a quartz cell. The maximum absorption wavelength was then measured.

3.1.2.1 UV-visible spectra for nonsupported ZnO

UV-visible spectra for commercial and synthetic ZnO powders were measured as shown in Figure (3.3). Spectrum for commercial ZnO showed a non clear maximum absorbance at 377 nm, whereas spectrum for synthetic ZnO showed a clear maximum absorbance at 371 nm.

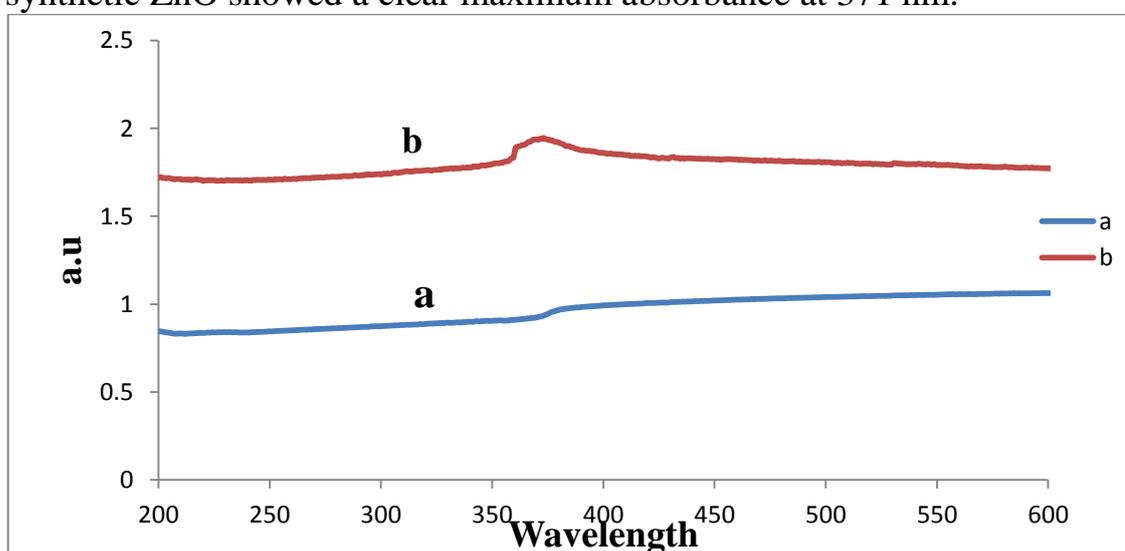


Figure (3.3): Solid state electronic absorption spectra measured for (a) commercial ZnO, (b) synthetic ZnO, the spectra were measured as aqueous suspensions.

Spectrum for commercial ZnO showed a maximum absorbance at wavelength (377) longer than that for synthetic ZnO (371). This is because synthetic ZnO has smaller particles size than commercial particles [66]

3.1.2.2 UV-visible spectra for ZnO/Kaolinite and naked kaolinite

UV-visible spectra for ZnO commercial/Kaolinite and kaolinite were measured as shown in Figure (3.4). Kaolinite has showed no specific

maximum absorbance, whereas the ZnO/kaolinite showed a maximum absorbance at 370 nm.

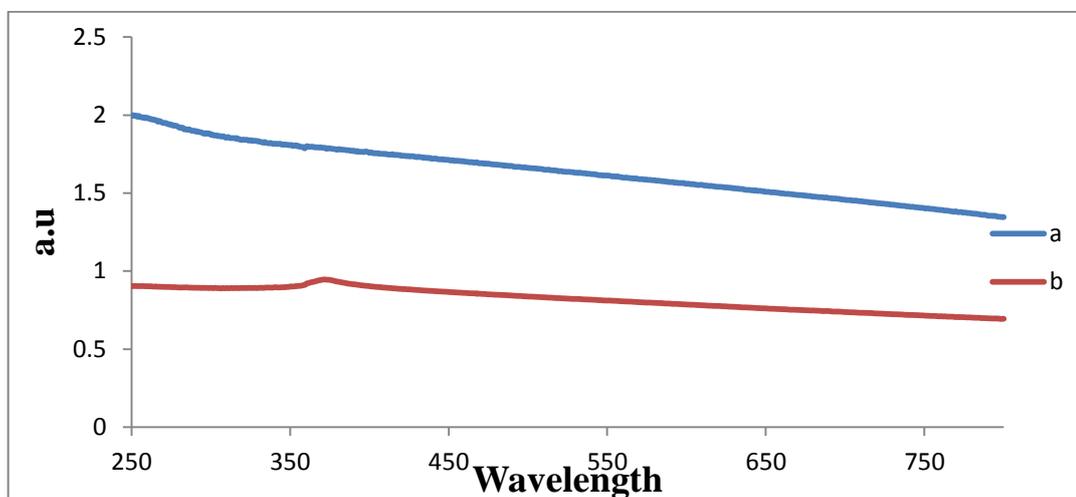


Figure (3.4): Solid state electronic absorption spectra measured for (a) kaolinite, (b) commercial ZnO/Kaolinite, as aqueous suspensions.

The maximum absorbance wavelength for composite ZnO/kaolinite has shorter wavelength than other ZnO powders. This indicates that supported ZnO particles have smaller size than other ores. The UV-visible spectral results are consistent with the PL spectra results.

3.2 Photocatalytic degradation of 2-chlorophenol

Effect of 2-chlorophenol concentration, ZnO photocatalyst concentration and pH on photodegradation reaction, were all studied.

3.2.1 Effect of contaminant concentration

Different concentrations of 2-chlorophenol (5, 10, 20, 40, 60 and 80 ppm) were prepared to study the effect of its concentrations on photodegradation process. Every concentration was mixed with 0.1 g of ZnO and placed in beaker under direct sun light for 60 min at the default temperature and pH.

A small amount from reaction mixture was taken every 15 min, centrifuged and then measured for absorbance.

3.2.2 Effect of catalyst concentration

Different amounts of ZnO catalyst (0.05, 0.1, 0.15 and 0.2) were used to study the effect of catalyst concentration on photodegradation process. Each amount of ZnO was mixed with 100 ml solution of 2-chlorophenol (50 ppm) and placed in a beaker under direct sun light for 60 min at the default temperature and pH. A small amount from the reaction mixture was taken individually every 15 min and then centrifuged and measured for absorbance.

3.2.3 Effect of pH

Photodegradation process was studied at different values of pH (acidic=3.5, neutral=7 and basic=11). The solutions were prepared using 50 ml solution of 2-chlorophenol and 0.1 g ZnO catalyst for each pH value. The pH value was controlled by adding drops of hydrochloric acid and sodium hydroxide. The experiment was then conducted as described earlier.

3.3 Photocatalytic reaction results and discussion

3.3.1 Commercial ZnO catalyst system

ZnO Commercial systems was used to catalyze photodegradation of 2-chlorophenol contaminant in water using direct solar light. The following reaction parameters were studied for this catalyst system.

3.3.1.1 Effect of 2-chlorophenol concentration

The effect of contaminant concentration on degradation of 2-chlorophenol was studied under neutral conditions. The concentration of 2-chlorophenol was varied from 5 ppm to 80 ppm with constant catalyst amount (0.10 g) of commercial ZnO catalyst in 100 mL distilled water. Figure (3.5) shows that the ZnO catalyzes the photodegradation process. The overall photodegradation reaction increases with increasing contaminant concentration. In addition the degradation for 10 ppm 2-chlorophenol was completed after 38 min and 5 ppm was completed after 25 min.

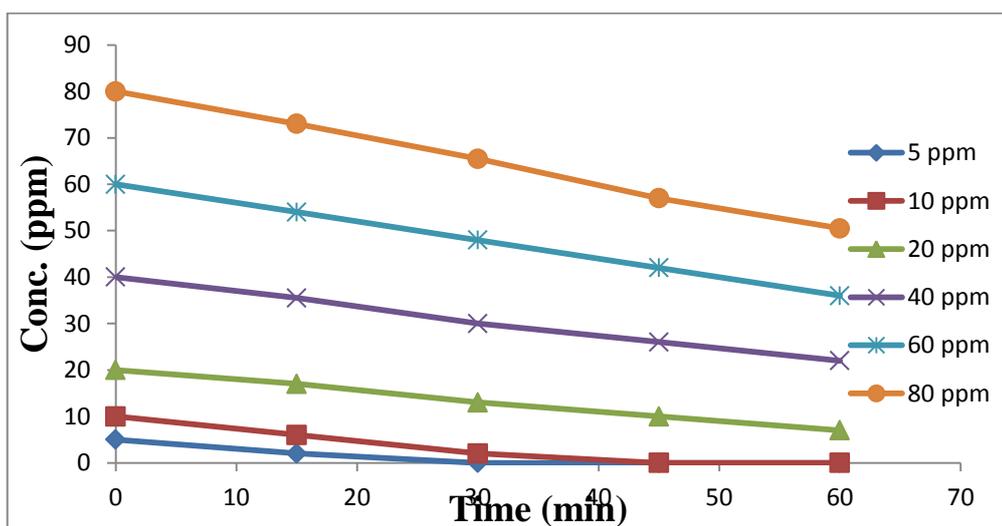


Figure (3.5): Effect of contaminant concentration on photodegradation of 2-chlorophenol using commercial ZnO catalyst under direct solar light under neutral conditions.

Values of overall rate, turnover number (T.N.), turnover frequency (T.F.) degradation percentage and quantum yield (Q.Y.) were all calculated after 60 minutes for different concentrations of 2-chlorophenol (5, 10, 20, 40, 60 and 80 ppm) as shown in Table (3.1).

Table (3.1): Effect of contaminant concentration on values of overall rate, turnover number, turnover frequency, % degradation and quantum yield for 2-chlorophenol degradation after 60 minutes, using commercial ZnO under direct sun light at default temperature.

2-cp Concentration (ppm)	Overall rate (ppm/min)	% Degradation	T.N. ($\times 10^{-3}$)	T.F. (min^{-1}) ($\times 10^{-3}$)	Q.Y.
5	0.08	100	1.58	0.03	0.05
10	0.17	100	3.16	0.05	0.11
20	0.22	65	4.11	0.07	0.14
40	0.30	45	5.70	0.10	0.19
60	0.40	40	7.60	0.13	0.26
80	0.50	37	11.47	0.19	0.31

Figure (3.6) shows plots of values of T.N. and Q.Y. vs. contaminant concentration.

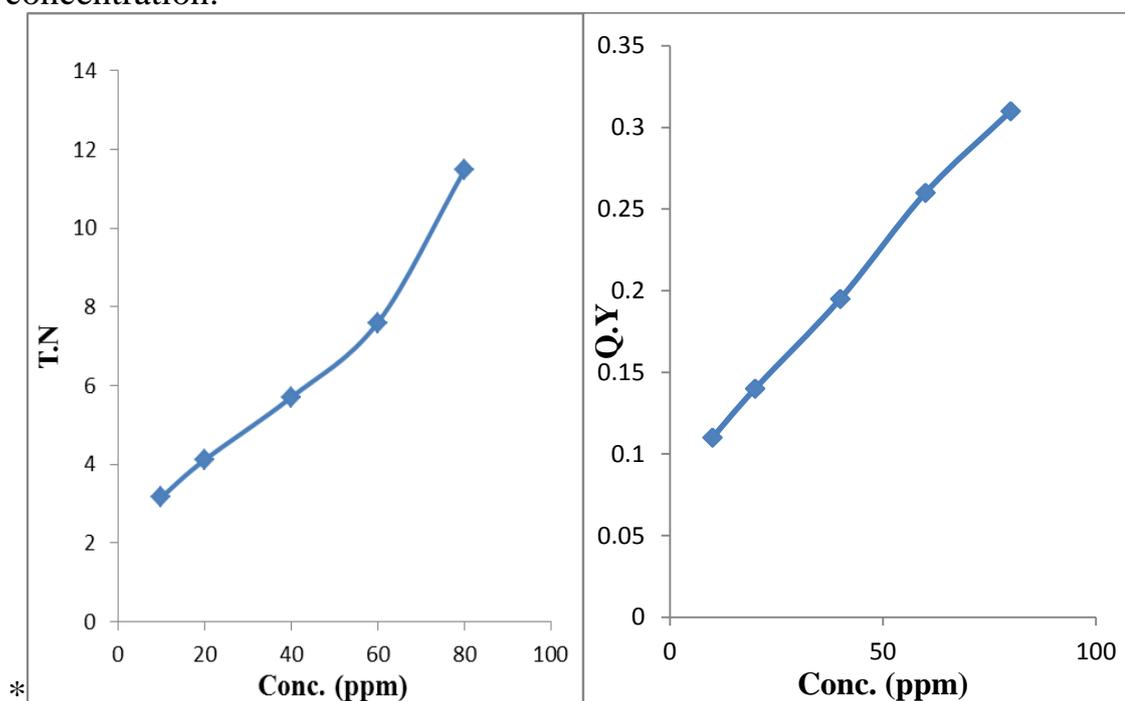


Figure (3.6): Effect of 2-chlorophenol concentration on T.N. and Q.Y. values using 0.1 g of ZnO commercial in 100 ml neutral solution under direct solar light at default temperature after 60 min.

The results show that the values of overall reaction, T.N., T.F. and Q.Y. increased with increasing contaminant concentration. The degradation percentage was higher at lower contaminant concentration. Table (3.2) shows how values of T.N., T.F., %degradation and Q.Y. were measured.

Table (3.2): How to calculate turnover number, turnover frequency, %degradation and quantum yield.

* Turnover Number (T. N.) =

$$\frac{\text{No. of moles of reacted contaminant (2 - chlorophenol)}}{\text{No. of moles of catalyst}}$$

Number of contaminant moles reacted =

$$\frac{(\text{Initial concentration} - \text{Final concentration}) \text{ in ppm} \times (50 \times 10^{-6})}{\text{Molecular weight of contaminant}}$$

$$\text{Moles of catalyst (ZnO)} = \frac{\text{Weight of catalyst}}{\text{Molecular weight}}$$

$$* \text{ Turnover Frequency (T. F.)} = \frac{\text{Turnover Number}}{\text{Time (min.)}}$$

* Percent Degradation =

$$\frac{(\text{Initial concentration} - \text{Final concentration})}{\text{Initial concentration}} \times 100\%$$

$$* \text{ Quantum yield (Q. Y.)} = \frac{\text{No. of contaminant molecules reacted}}{\text{Total number of photons}}$$

$$E \text{ (J)} = \text{Incident power per unit area} \times \text{Total area (cm}^2\text{)} \times \text{Exposure time}$$

(s)

Assuming average wavelength of incident light is 385 nm, then:

$$v = \frac{c}{\lambda}$$

$$E (J) = nhv \quad (\text{Plank's equation})$$

$$n = \frac{J}{hv}$$

Where:

M.wt of 2-chlorophenol = 128.56 g/mole.

M.wt of ZnO = 81.408 g/mole.

Incident power per unit area for solar light = 0.0146 w/cm².

Total area or incider power = 21.6 cm².

Time = 60 min.

$$c = 3 \times 10^8.$$

$$h = 6.62 \times 10^{-34}.$$

Average wavelength of incident light for UV light = 385 nm.

n = number of photons

3.3.1.2 Effect of catalyst concentration

The effect of commercial ZnO amount (0.05, 0.1, 0.15, 0.2 g) on photodegradation of 2-chlorophenol was studied under direct solar light and neutral condition at in 100 ml solution, and constant concentration of 2-chlorophenol (50 ppm). At default temperature Figure (3.7) shows that

increasing amount of commercial ZnO photocatalyst under direct sun light, increased the degradation percentage.

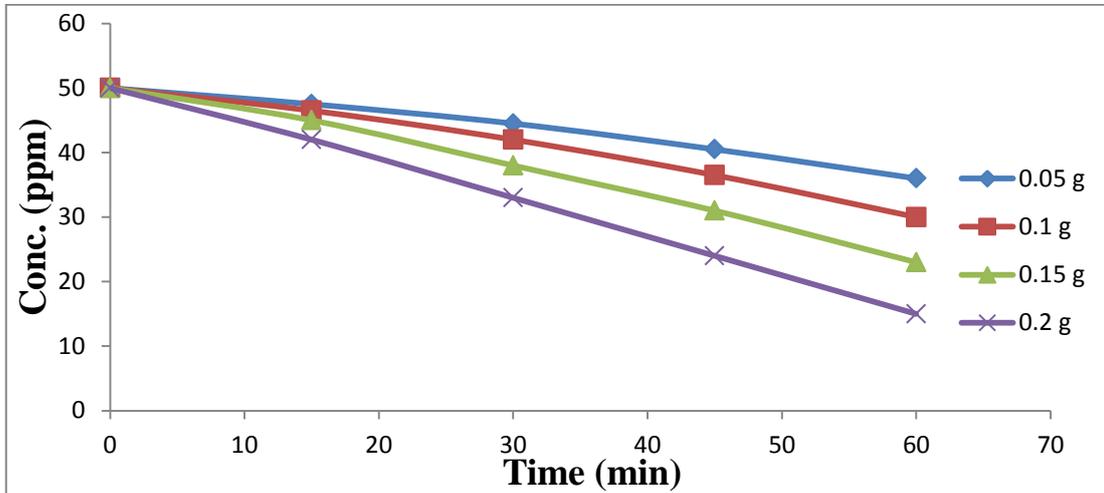


Figure (3.7): Effect of concentration of commercial ZnO on photodegradation of 2-chlorophenol under direct solar light and neutral conditions.

Values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage were calculated after 60 minutes for different amounts of catalyst (0.05, 0.1, 0.15 and 0.2 g) as shown in Table (3.3).

Table (3.3): Effect of catalyst concentration on values of overall rate, turnover number, turnover frequency, % degradation and quantum yield for 2-chlorophenol degradation after 60 minutes, using commercial ZnO under direct sun light.

Catalyst weight (g)	Overall rate (ppm/min)	%Degradation	T.N ($\times 10^{-3}$)	T.F (min^{-1}) ($\times 10^{-3}$)	Q.Y
0.05	0.23	28	9	0.15	0.15
0.1	0.33	40	6.3	0.11	0.21
0.15	0.45	54	5.7	0.095	0.29
0.2	0.58	70	5.5	0.09	0.37

Figure (3.8) shows plots of T.N and Q.Y values vs. mass of ZnO

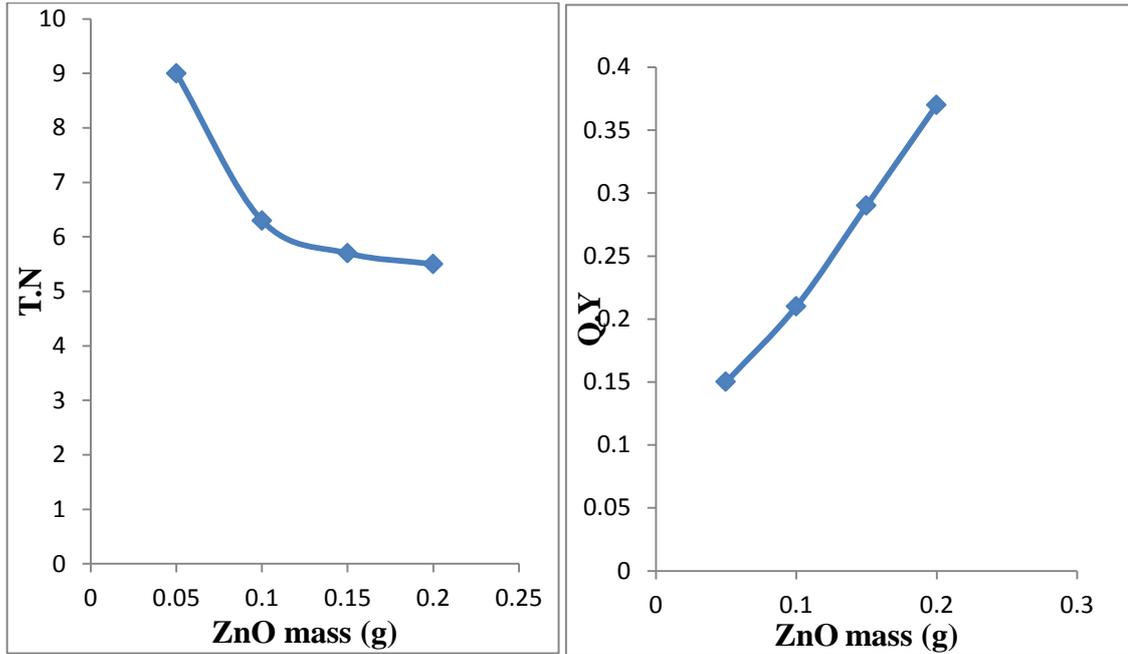


Figure (3.8): Effect of commercial ZnO loading on T.N. and Q.Y. values using 5 ml of 2-chlorophenol in 100 ml neutral solution under direct solar light.

The results show that the T.N. and T.F. values decreased with increasing catalyst amount, while the overall rate of reaction, degradation percentage and Q.Y. were higher with higher catalyst amounts.

3.3.1.3 Effect of pH

Effect of pH of 2-chlorophenol photodegradation was studied under direct solar light at different pH values (Neutral pH=7, Acidic pH=3.5 and Basic pH=10) using constant amount (0.10 g) of commercial ZnO in 50ml solution). Figure (3.9) shows that the photodegradation is faster under basic conditions.

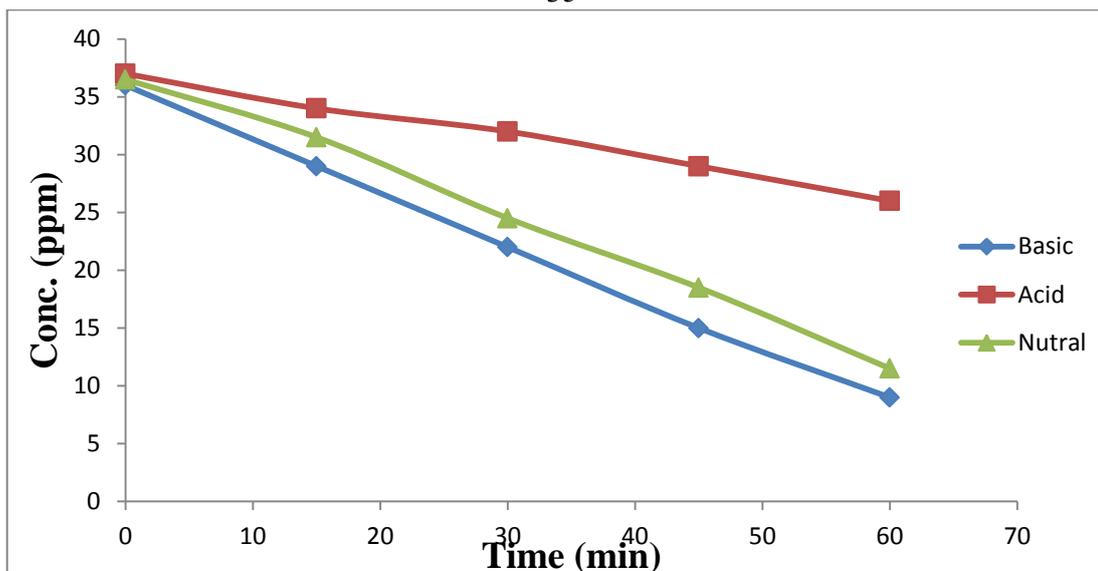


Figure (3.9): Effect of pH of 2-chlorophenol photodegradation using commercial ZnO under direct solar light at default temperature.

Values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage were calculated after 60 minutes as shown in Table (3.4).

Table (3.4): Effect of pH on values of overall rate, turnover number, turnover frequency, % degradation and quantum yield for 2-chlorophenol degradation after 60 minutes under direct sun light using 0.1 g commercial ZnO.

pH	Overall rate (ppm/min)	% Degradation	T.N (X 10 ⁻³)	T.F (min ⁻¹) (X 10 ⁻³)	Q.Y
Basic	0.45	75	8.5	0.14	0.29
Neutral	0.42	68.5	7.9	0.13	0.27
Acidic	0.18	30	3.5	0.06	0.12

Figure (3.10) shows the effect of pH on T.N. and Q.Y. values.

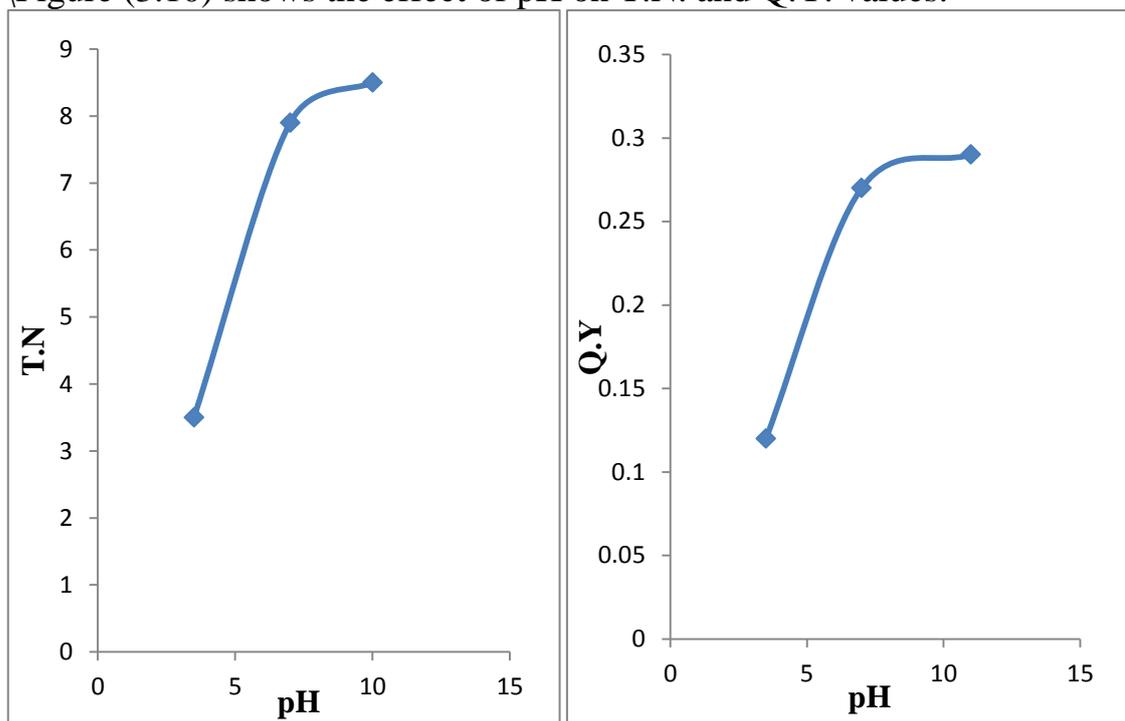


Figure (3.10): Effect of pH on T.N. and Q.Y. values under direct solar light for 60 min.

The results show that the values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage in basic medium are higher than in neutral and acidic media.

3.3.2 Synthetic ZnO catalyst system

Synthetic ZnO system was prepared in the lab and used to catalyze photodegradation of 2-chlorophenol contaminant in water using direct solar light under different conditions.

3.3.2.1 Effect of 2-chlorophenol concentration

The synthetic ZnO was used to study the effect of contaminant concentration on degradation of 2-chlorophenol under neutral conditions. The concentration of 2-chlorophenol (5, 10, 20, 40, 60 and 80 ppm) were

used with constant catalyst (0.10 g ZnO) in 100 mL distilled water. Figure (3.11) shows that the synthetic ZnO catalyzes the photodegradation process.

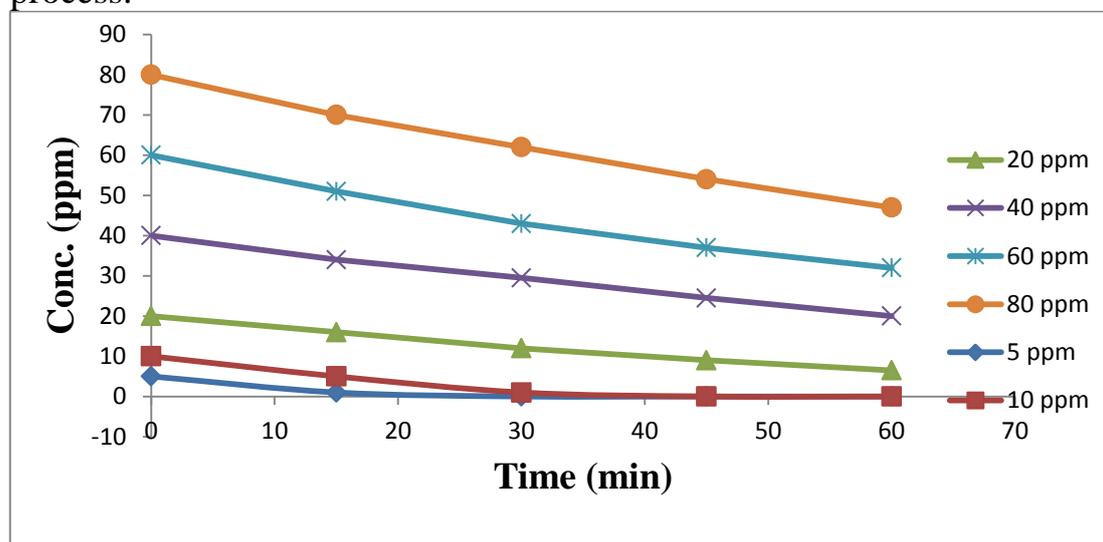


Figure (3.11): Effect of contaminant concentration on photodegradation of 2-chlorophenol using synthetic ZnO photocatalyst under direct solar light and neutral conditions at default temperature.

Figure (3.11) shows that the photodegradation increased by increasing contaminant concentration. Also the degradation was completed for 10 ppm after 30 min. and after 15 min for 5 ppm.

The photodegradation reaction was faster with increasing initial contaminant concentration by using both form of ZnO (commercial and synthetic). This is due to higher probability of contaminant molecules to reach the active sites of photocatalyst surface. Therefore, the reactive species ($\bullet\text{OH}$ and $\bullet\text{O}^{2-}$) have higher probability to react with 2-chlorophenol at higher concentrations. The following equations (4.1- 4.3) summarize how the reactive species are formed by activation of the catalyst surface [69]:



The reactive species are responsible for activating the contaminant molecules. Therefore, with higher contaminant concentration the reaction must go faster as more reactant molecules are exposed to the reactive species. This result is consistent with other results reported earlier showing that contaminant concentration increases the rate of photodegradation reactions of 2,4-dichlorophenol or phenolic of 4-chlorophenol contaminants in Kaolinite Catalysts [70-72].

In Table (3.5) values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage were calculated after 60 min using synthetic ZnO at different concentrations of 2-chlorophenol (5, 10, 20, 40, 60 and 80 ppm).

Table (3.5): Effect of contaminant concentration on values of overall rate, turnover number, turnover frequency, %degradation and quantum yield for 2-chlorophenol degradation after 60 minutes, using synthetic ZnO under direct sun light neutral conditions and default temperature.

2-cp Concentration (ppm)	Overall rate (ppm/min)	%Degradation	T.N. ($\times 10^{-3}$)	T.F. (min^{-1}) ($\times 10^{-3}$)	Q.Y.
5	0.08	100	1.58	0.03	0.05
10	0.17	100	3.16	0.05	0.11
20	0.23	67.5	4.3	0.07	0.20
40	0.33	50	6.3	0.11	0.23
60	0.47	47	8.9	0.15	0.31
80	0.55	41	10.4	0.17	0.40

The effect of 2-chlorophenol concentration on T.N. and Q.Y. values is shown in Figure (3.12).

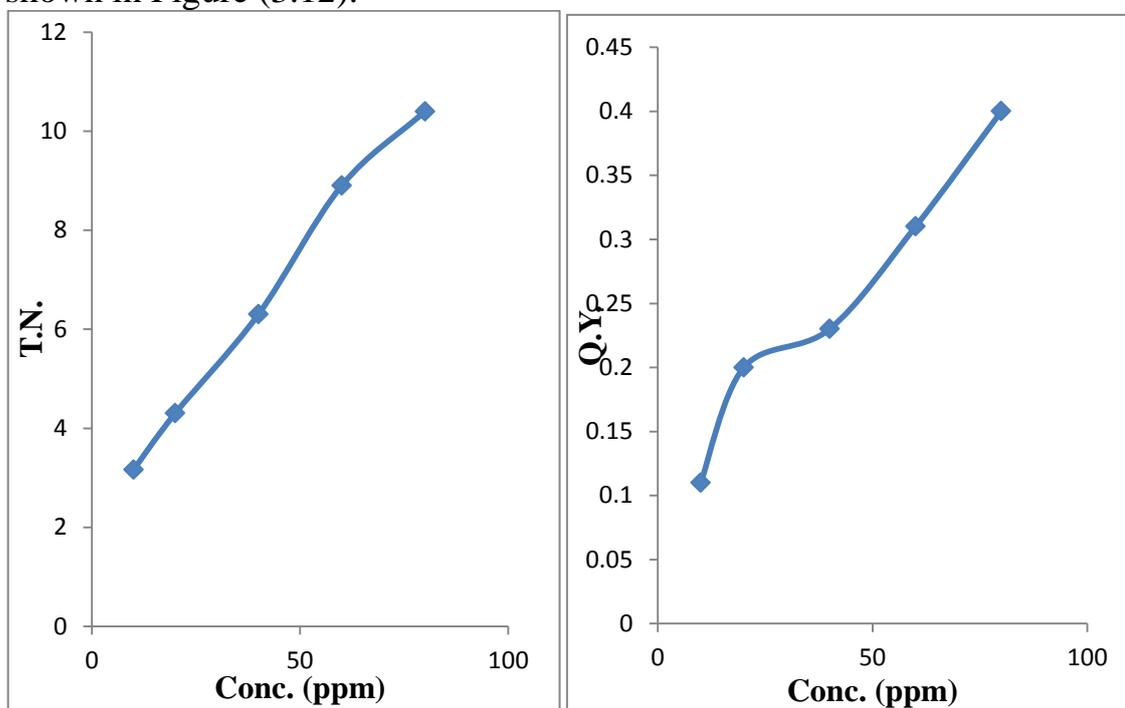


Figure (3.12): Effect of 2-chlorophenol concentration on T.N. and Q.Y. values using 0.1 g of synthetic ZnO in 100 ml neutral solution under direct solar light.

The results show that the values of overall reaction rate, T.N., T.F. and Q.Y. increased by increasing the concentration of contaminant. Therefore the efficiency of synthetic ZnO catalyst is higher with higher initial contaminant concentration.

For two forms of ZnO (commercial and synthetic) the degradation percentage was higher at lower contaminant concentration. Values of T.N., T.F. and Q.Y. increased with increasing 2-chlorophenol concentration. These results indicate that the efficiency of ZnO catalyst is higher with higher initial concentration of 2-chlorophenol. T.N. and Q.Y. values increased with increase of contaminant concentration due to increasing

number of reacted contaminant molecules, while keeping other conditions the same. T.N. is the number of moles of reacted 2-chlorophenol/number of moles of ZnO catalyst and Q.Y. is the number of molecules of 2-chlorophenol reacted/total number of photon. Value of T.F. ($TF = TN/\text{time}$) also increased with increasing contaminant concentration. The results indicate that the reaction was faster in case of higher contaminant concentration.

3.3.2.2 Effect of catalyst concentration

The effect of concentration of synthetic ZnO on photodegradation of 2-chlorophenol was also studied under direct solar light and neutral condition using different amount of ZnO (0.05, 0.1, 0.15, 0.2 g) in 100ml solution, and constant concentration of 2-chlorophenol (50 ppm). Figure (3.13) shows that the reaction goes faster with higher catalyst amount.

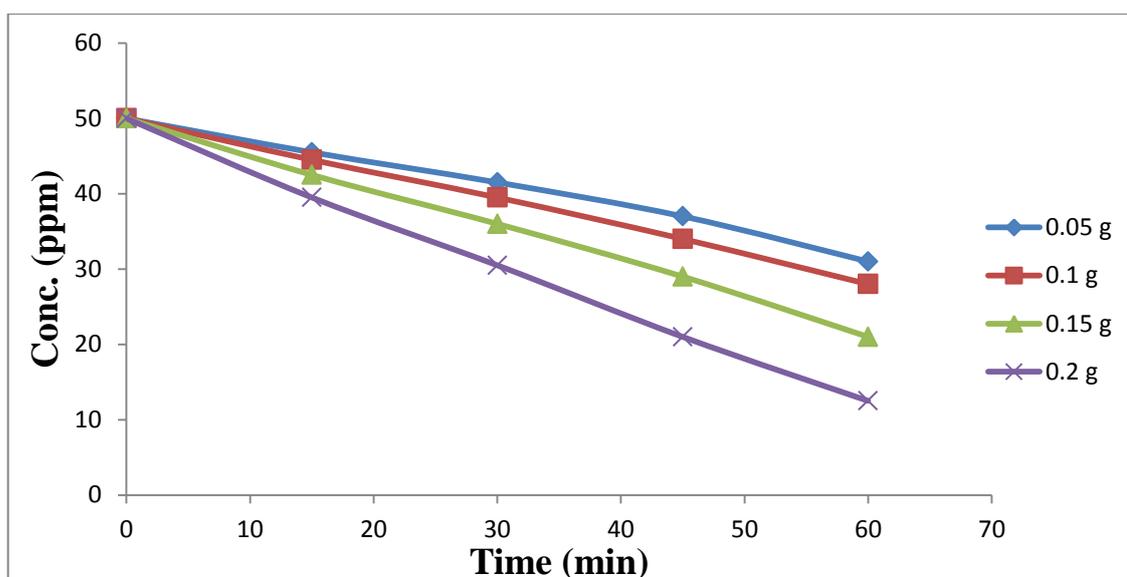


Figure (3.13): Effect of concentration of synthetic ZnO on photodegradation of 2-chlorophenol under direct solar light and neutral conditions.

Photodegradation of 2-chlorophenol was faster with higher catalyst concentration for both commercial and synthetic ZnO catalyst. With more ZnO particles, there will be higher numbers of active catalyst sites. Therefore, the reactant molecules will have higher chance to interact with the catalyst sites in case of higher concentrations. These results are consistent with earlier studies where higher ZnO or Kaolinite catalyst amounts increased the photodegradation rates of chlorophenols [72-75].

Values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage were calculated after 60 minutes for different amounts of catalyst (0.05, 0.1, 0.15 and 0.2 g) as shown in Table (3.6). The T.N. and T.F. values decreased with increasing catalyst amount, while the overall rate of reaction, degradation percentage and Q.Y. increased with increasing catalyst amounts.

Table (3.6):Effect of catalyst concentration on values of overall rate, turnover number, turnover frequency, %degradation and quantum yield for 2-chlorophenol degradation after 60 minutes, using synthetic ZnO under direct sun light.

Catalyst weight (g)	Overall rate (ppm/min)	%Degradation	T.N. ($\times 10^{-3}$)	T.F. (min^{-1}) ($\times 10^{-3}$)	Q.Y.
0.05	0.31	38	12.3	0.21	0.20
0.1	0.37	44	7.0	0.15	0.23
0.15	0.48	58	6.1	0.10	0.31
0.2	0.63	75	5.9	0.098	0.40

Figure (3.14) shows the effect of synthetic ZnO on T.N. and Q.Y.

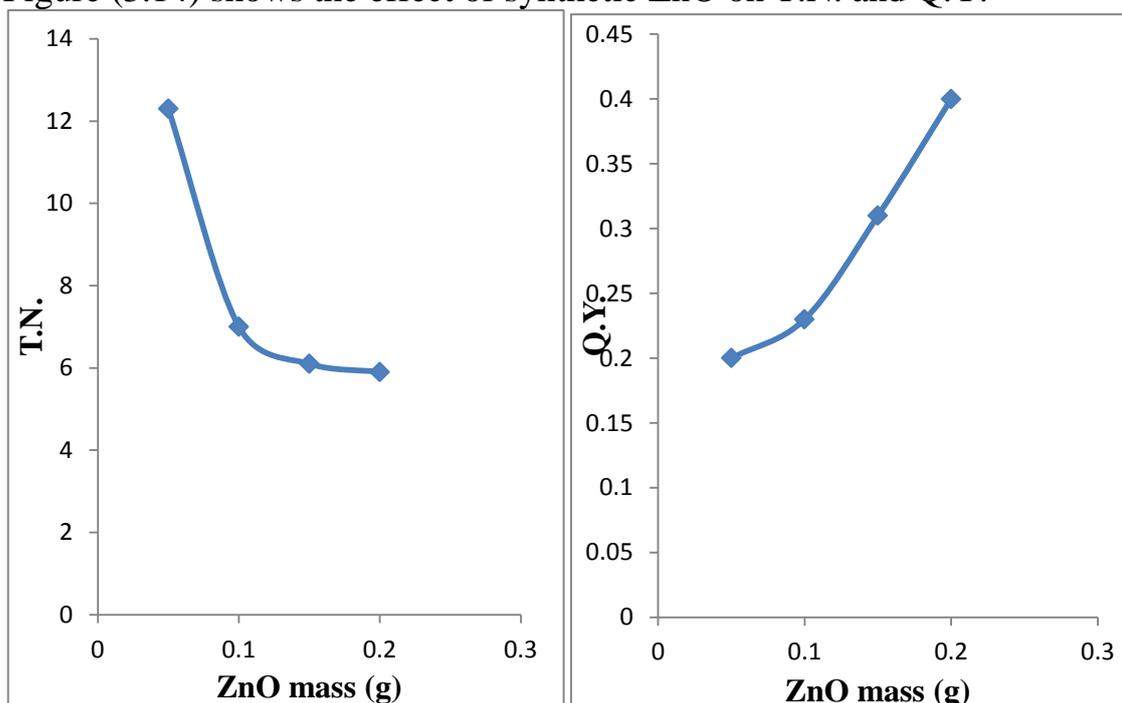


Figure (3.14): Effect of synthetic ZnO loading on T.N. and Q.Y. values using 5 ml of 2-chlorophenol in 100 ml neutral solution under direct solar light.

The results show that T.N. and T.F. values decreased with increasing catalyst amount, while the overall rate of reaction, degradation percentage and Q.Y. increased with increasing catalyst amounts.

For tow forms of ZnO (commercial and synthetic) values of T.N. and T.F. decreased with increasing catalyst amount. This means that the relative catalyst efficiency is lowered in case of higher catalyst amounts. This is because with higher amounts the ZnO particles will screen more light from entering the reaction mixture. The value of Q.Y. decreased with increasing catalyst concentration, again because light screening occurs more with higher catalyst concentration [76].

3.3.2.3 Effect of pH

At constant amount of synthetic ZnO (0.1 g ZnO /50ml solution), the effect of pH on 2-chlorophenol photodegradation was studied under direct solar light at different pH values (Neutral pH=7, Acidic pH=3.5 and Basic pH=10). Figure (3.15) shows that the photodegradation is faster in basic medium.

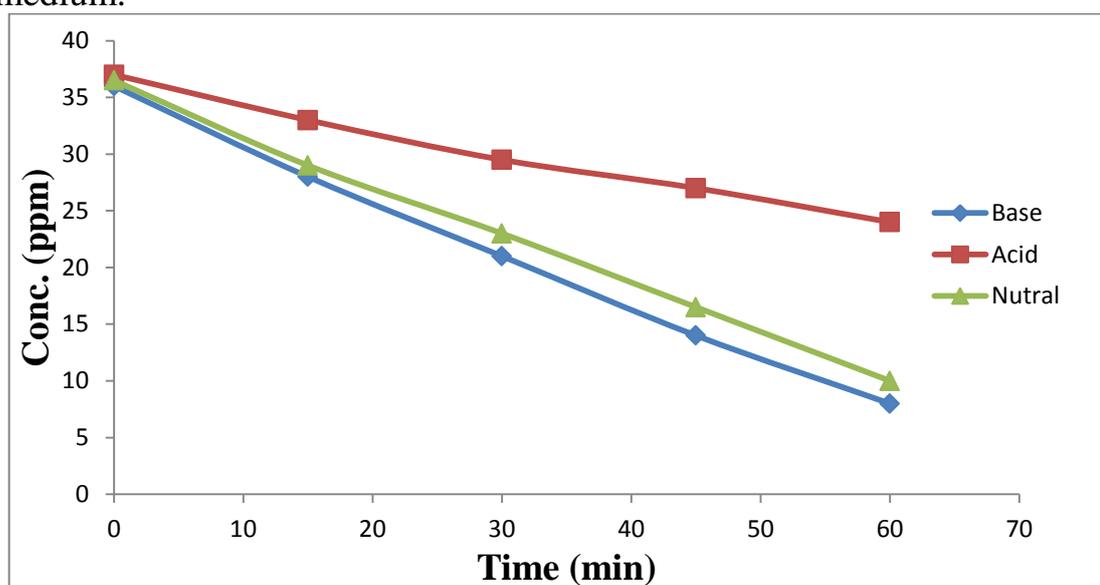


Figure (3.15): Effect of pH of 2-chlorophenol degradation using synthetic ZnO under direct sun light using ZnO.

The photodegradation reaction rate increased with increasing pH values for both forms commercial and synthetic ZnO. Increasing of pH value cause increase of hydroxyl radicals ($\bullet\text{OH}$) that are required for the degradation of the 2-chlorophenol. The hydroxyl radicals increase with values of pH because more OH^- ions exist at higher pH. The concentration of hydroxyl radicals depends on the pH at zero point charge (pH_{zpc}). The value of pH_{zpc} for ZnO is 9. Therefore, if pH value < 9 the catalyst surface is in the H^+ form while if pH value > 9 the catalyst surface is negatively charged, and the chlorophenol is also negatively charge. This indicates that when the

surface of the catalyst is negative at higher pH, large quantity of OH⁻ exists. Therefore, holes transfer to surface and the oxidation OH⁻ ions to yield •OH species increases which enhances photodegradation efficiency [77]. Similar results were reported by other researchers who reported increased of photodegradation at higher pH values [71,78].

Values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage were calculated after 60 minutes. as shown in Table (3.7).

Table (3.7): Effect of pH on values of overall rate, turnover number, turnover frequency, %degradation and quantum yield for 2-chlorophenol degradation after 60 minutes, using synthetic ZnO under direct sun light.

pH	Overall rate (ppm/min)	% Degradation	T.N. (X 10 ⁻³)	T.F. (min ⁻¹) (X 10 ⁻³)	Q.Y.
Basic	0.47	78	8.9	0.15	0.31
Neutral	0.44	72.5	8.4	0.14	0.28
Acidic	0.33	35	4.1	0.07	0.14

Figure (3.16) shows the effect of pH on T.N. and Q.Y. on photodegradation of 2-chlorophenol.

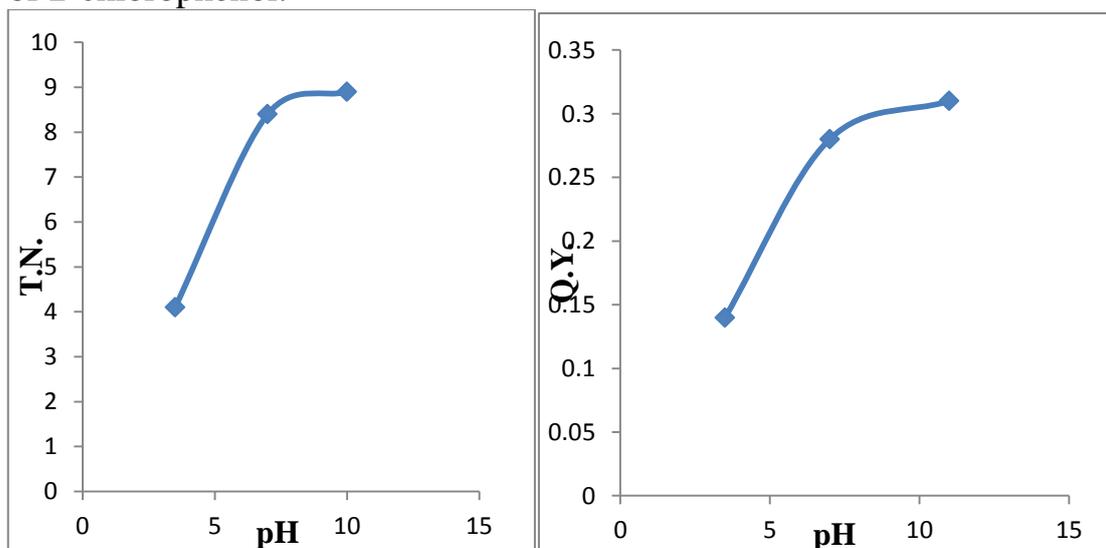


Figure (3.16): Effect of pH on T.N. and Q.Y. values under direct solar light.

The results show that the values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage are higher in basic medium than in neutral medium. The neutral medium shows higher rate than acidic medium. This indicates that the photo-degradation efficiency increased as the pH value increased. Same result for commercial ZnO that T.N., T.F. and Q.Y. values increased at higher pH value due to easy generation of hydroxyl radicals on photocatalyst surface at higher pH [79].

3.3.3 Effect of ZnO type

Commercial and synthetic ZnO powders were compared as catalysts for photodegradation 2-chlorophenol at 10 ppm under direct sun light.

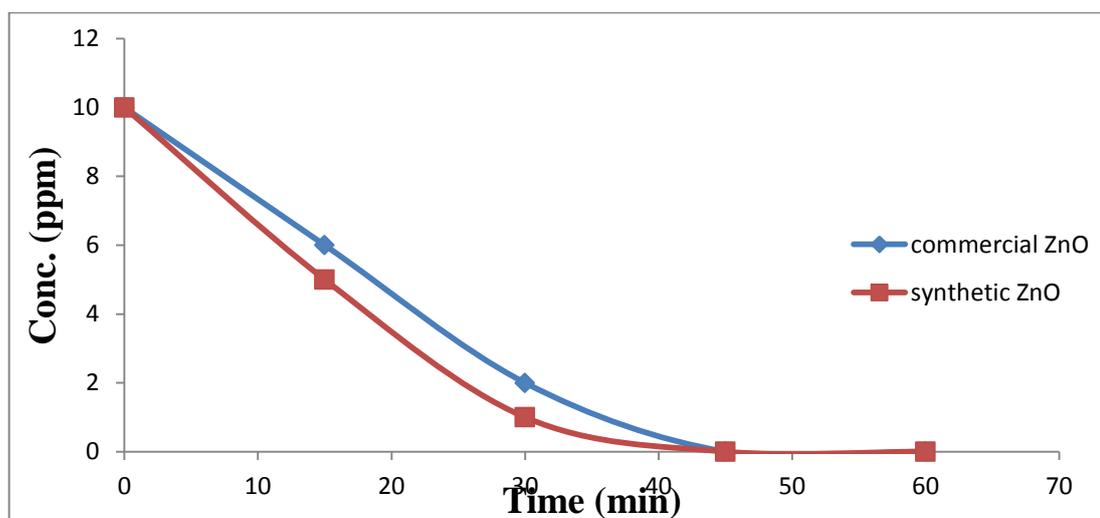


Figure (3.17): Synthetic ZnO and commercial ZnO powders as catalysts in photodegradation of 2-chlorophenol at 10 ppm under direct sun light and neutral conditions.

Figure (3.17) shows that synthetic ZnO is slightly more effective than commercial ZnO in 2-chlorophenol photodegradation. The two powders have different particle sizes, where the synthetic ZnO has smaller sizes.

This means that the relative surface area in synthetic ZnO is larger than that for commercial ZnO. With higher surface area the degradation reaction using synthetic ZnO should be faster [33]. Moreover, with smaller particles, the synthetic ZnO has larger band gap. This makes it more effective catalyst in the UV light that reaches Earth.

3.3.4 ZnO/kaolonite Photocatalysis System

Kaolonite was used to support commercial ZnO particles to catalyze photodegradation of 2-chlorophenol contaminant in water using direct solar light.

3.3.4.1 Effect of contaminant concentration

Under neutral conditions the effect of contaminant concentration was studied by using comoposit ZnO/Kaolinite. Different concentrations of 2-chlorophenol (20, 40, 60 and 80) were prepared and mixed with 0.42 g of ZnO/Kaolinite in 100 ml solution (0.42 g from ZnO/Kaolinite contain 0.1 g of ZnO). Figure (3.18) shows that composite ZnO/Kaolinite catalyzed the photodegradation process.

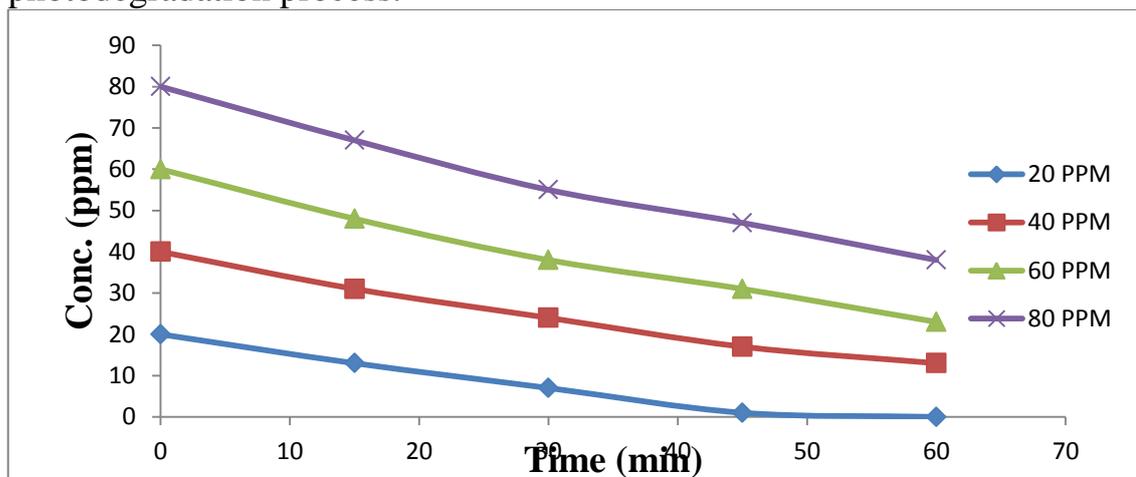


Figure (3.18): Effect of contaminant concentration on photodegradation of 2-chlorophenol using ZnO/Kaolinite under direct solar light and neutral conditions at default temperature.

The Figure (3.8) shows that contaminant concentration increased, the photodegradation reaction rate increased. The contaminant was completely degraded incase of 20 ppm 2-chlorophenol after 50 min.

In Table (3.8) values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage were calculated after 60 minutes using ZnO/Kaolinite for different concentrations of 2-chlorophenol (20, 40, 60 and 80 ppm).

Table (3.8): Effect of contaminant concentration on values of overall rate, turnover number, turnover frequency, %degradation and quantum yield for 2-chlorophenol degradation after 60 minutes, using ZnO/Kaolinite under direct sun light.

2-cp Concentration (ppm)	Overall rate (ppm/min)	%Degradation	T.N. ($\times 10^{-3}$)	T.F. (min^{-1}) ($\times 10^{-3}$)	Q.Y.
20	0.33	100	6.3	0.10	0.21
40	0.45	67.5	8.5	0.14	0.29
60	0.62	61.5	11.7	0.19	0.40
80	0.70	52.5	13.3	0.22	0.45

The effect of contaminant concentration on T.N. and Q.Y. are shown in Figure (3.19).

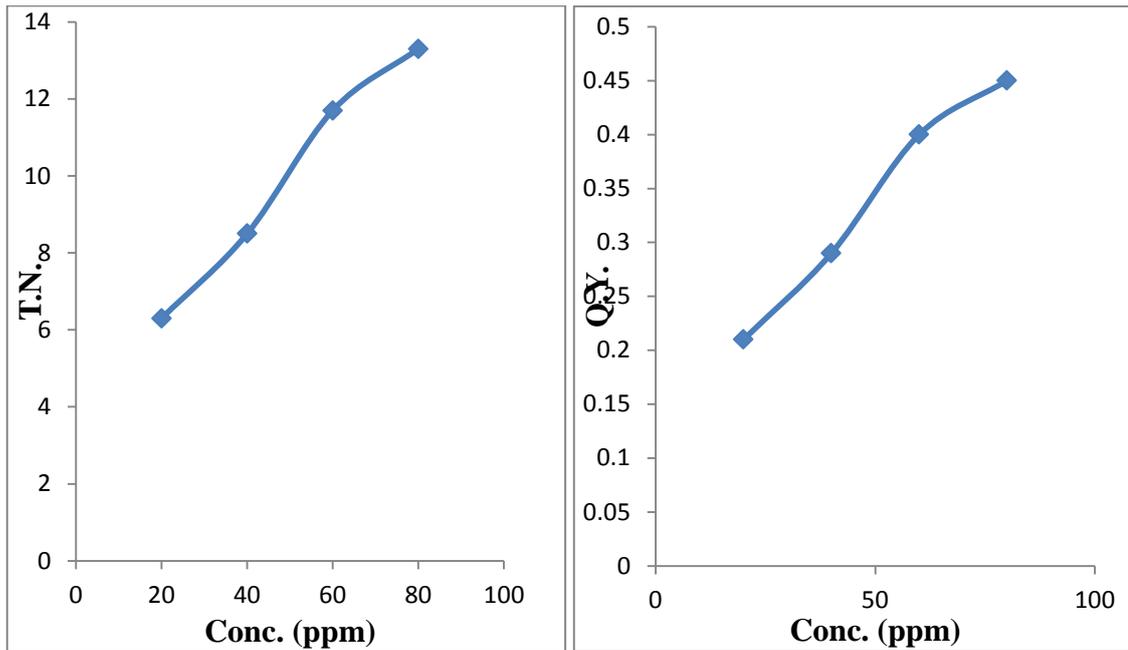


Figure (3.19): Effect of 2-chlorophenol concentration on T.N. and Q.Y. values using 0.42 g of ZnO/Kaolinite composite in 100 ml neutral solution under direct solar light.

The results show that the values of overall reaction rate, T.N., T.F. and Q.Y. increased by increasing the concentration of contaminant. The degradation percentage was higher for lower contaminant concentration. Results of effect of 2-chlorophenol using composite are consistent with commercial and synthetic ZnO results.

3.3.4.2 Effect of pH

The effect of pH on 2-chlorophenol photodegradation was studied under direct solar light under different pH values (Neutral pH=7, Acidic pH=3.5 and Basic pH=10) by using constant amount of ZnO/Kaolinite (0.1 g composite /50ml solution). Figure (3.20) shows that the photodegradation is faster in basic medium.

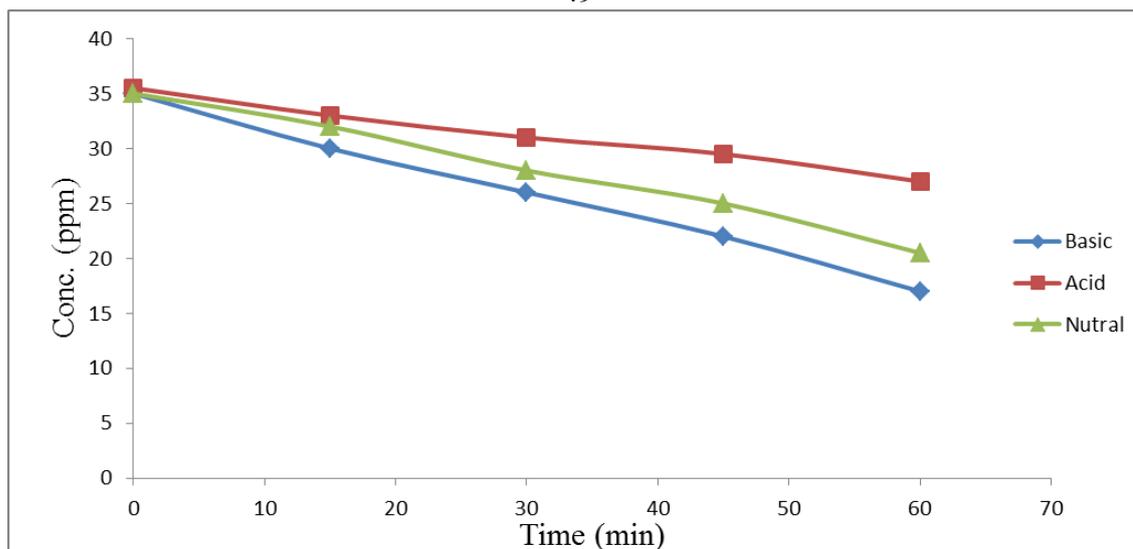


Figure (3.20): Effect of pH of 2-chlorophenol degradation under direct sun light using ZnO/Kaolinite.

Values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage were calculated after 60 minutes. The result show that the values in basic medium are higher than in neutral and acidic media, as shown in Table (3.9).

Table (3.9): Effect of pH on values of overall rate, turnover number, turnover frequency, %degradation and quantum yield for 2-chlorophenol degradation after 60 minutes, using ZnO/Kaolinite under direct sun light.

pH	Overall rate (ppm/min)	%Degradation	Turnover number	Turnover frequency (min^{-1})	Quantum yield
Basic	0.30	51	5.7	0.10	0.19
Neutral	0.24	41	4.6	0.08	0.15
acidic	0.13	23	2.5	0.04	0.085

The effect of pH on T.N. and Q.Y. are shown in Figure (3.21).

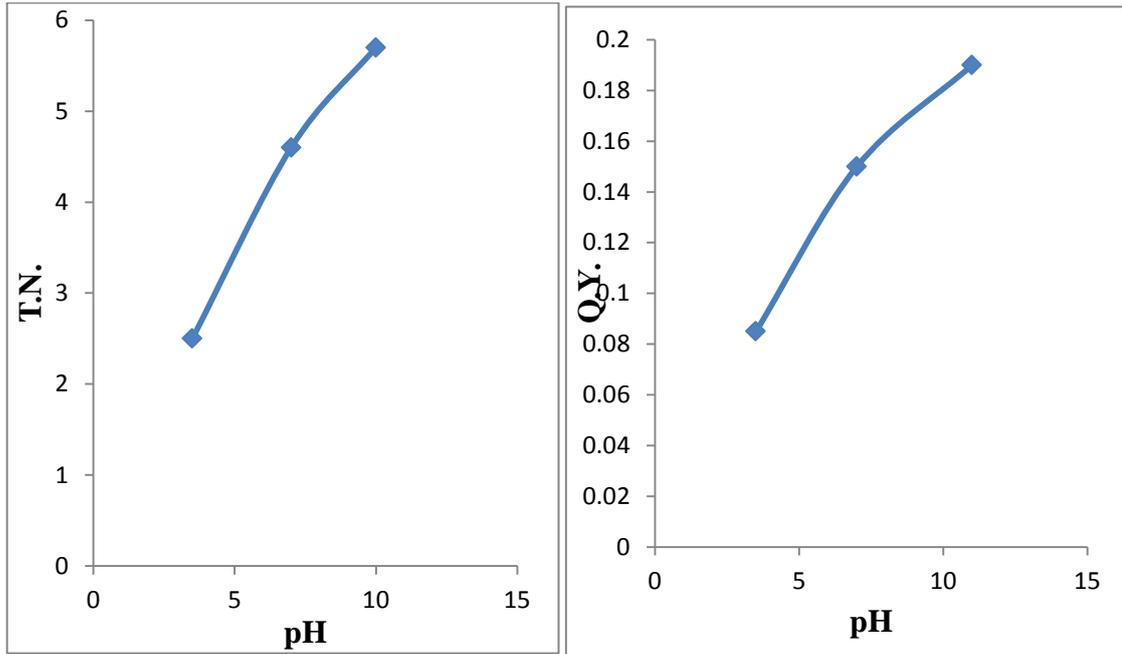


Figure (3.21): Effect of pH on T.N. and Q.Y. values using ZnO/Kaolinite under direct solar light and neutral condition.

The results show the values of T.N., T.F., Q.Y., overall rate reaction and degradation percentage are higher in basic medium than in neutral medium. The neutral medium shows higher rate than acidic medium. This indicates that the photo-degradation efficiency increased as the pH value increased due to same result of using commercial and synthetic ZnO that mentioned previously.

3.3.5 Commercial ZnO vs. synthetic ZnO vs. ZnO/Kaolinite composite catalysts

Commercial ZnO, synthetic ZnO and ZnO/Kaolinite were compared for photodegradation of 2-chlorophenol at 20 ppm under direct sun light and neutral condition. Figure (3.22) shows the degradation percentage values for commercial ZnO, synthetic ZnO and ZnO/Kaolinite systems at 20 ppm with time. The results show that the ZnO/Kaolinite is more effective than commercial ZnO and synthetic ZnO for photodegradation of 2-

chlorophenol in water. The order of efficiency are commercial ZnO < synthetic ZnO < ZnO/Kaolinite.

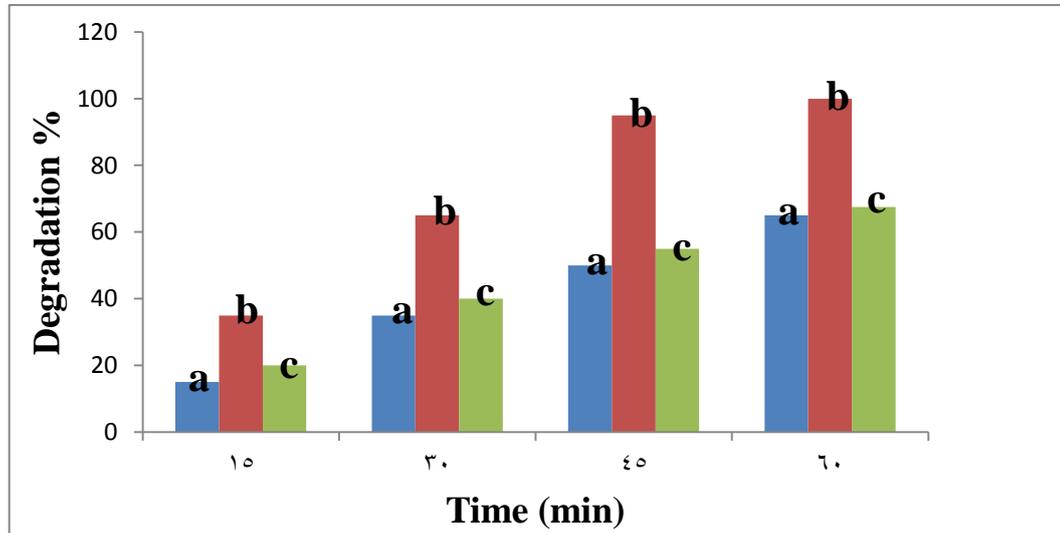


Figure (3.22): Degradation percentage of 20 ppm 2-chlorophenol for 60 min a) commercial ZnO and (b) ZnO/Kaolinite composite (c) synthetic ZnO.

Figure (3.22) shows that after 60 min the degradation was completed in case of ZnO/Kaolinite composite, whereas for commercial ZnO and synthetic ZnO was not completed. That means that the ZnO/Kaolinite is more effective than synthetic ZnO and commercial ZnO for photodegradation of 2-chlorophenol in water.

The results show that commercial ZnO/Kaolinite has higher efficiency than commercial ZnO because the commercial ZnO particles combine together and the sun does not reach to each particles that's make a lot of particles of commercial ZnO do not enter in the interaction. But in the case of ZnO/Kaolinite each particle of ZnO combine with particle of kaolinite that's make all the particles reached by the sun and enter into interaction. Moreover in case ZnO/Kaolinite no growth particle as commercial ZnO, relative surface area smaller and higher E_g . This cause enhances the absorption capacities which increase the photodegradation process.

Chapter Four
Conclusions and Recommendations for Future
Work

4.1 Conclusions

Photodegradation of 2-chlorophenol has been investigated using commercial ZnO, synthetic ZnO and commercial ZnO/Kaolinite. The following conclusions could be deduced:

1. Photodegradation of 2-chlorophenol was successfully investigated under direct sun light using commercial and synthetic ZnO powders as photocatalysts.
2. Photodegradation of 2-chlorophenol was successfully investigated under direct sun light using commercial ZnO/Kaolinite composite for the first time.
3. Photodegradation increased with increasing initial 2-chlorophenol concentration in all catalyst system under direct sun light under neutral condition.
4. Photodegradation increased by increasing the catalyst amount under direct sun light under neutral condition.
5. Photodegradation of 2-chlorophenol with all catalyst systems was affected by the value of pH of the medium.
6. Photoluminescence and UV-visible spectral studies showed that synthetic ZnO powder has smaller size of particles than commercial ZnO powder.
7. Synthetic ZnO powder showed higher photodegradation efficiency than the commercial ZnO.
8. Commercial ZnO/Kaolinite composite showed higher photodegradation efficiency than the commercial ZnO.

9. ZnO/Kaolinite composite showed higher photodegradation efficiency than the synthetic ZnO.

4.2 Recommendations for future work

Based on the study presented in this Thesis, it is strongly advisable to pursue further study in the area of direct solar light degradation of aqueous 2-chlorophenol, with special focus on the following points:

1. Using other of types of photocatalysts systems in photodegradation of 2-chlorophenol.
2. Using other methods to prepare ZnO powder and ZnO/Kaolinite systems to with smaller particle sizes to give higher efficiency.
3. Using other kinds of clay such as montmorillonite or illite clays or using other materials to support ZnO powders such as sand or graphite and study the effect of the support on 2-chlorophenol photodegradation.
4. Study the effect of different parameters for longer times and for reuse of the catalyst systems.
5. Study the effect of photodegradation of chlorophenol under UV lamp instead direct sun light.
6. Study the effect of ZnO/Kaolinite on other phenolic contaminant.
7. Study stability of different catalyst systems and their ability to recover and reuse.
8. Study the effect of pH by using other concentrations of 2-chlorophenol.

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إعداد

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

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ب

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الملخص

لقد تم دراسة التحطيم الضوئي ل 2-كلوروفينول في الماء تحت اشعة الشمس المباشرة باستخدام شبه الموصل أكسيد الزنك كحفاز ضوئي. استخدمت أشكال مختلفة من المحفز وهي أكسيد الزنك التجاري، أكسيد الزنك الاصطناعي ولأول مرة استخدام مركب أكسيد الزنك المثبت على الفخار (كالونايت). هذه الانواع تم تشخيصها باستخدام الوميض الضوئي والامتصاص الضوئي وأشارت النتائج الى ان جزيئات أكسيد الزنك تختلف في الحجم كما يلي: أكسيد الزنك/كالونايت > أكسيد الزنك الصناعي > أكسيد الزنك التجاري. وقد تم تحقيق التحلل الضوئي ل 2-كلوروفينول في ظل ظروف مختلفة تشمل تأثير تركيز الملوثات، تأثير كمية المحفز، وتأثير درجة الحموضة. لدراسة كفاءة المحفز تم حساب المعدل العام والمعطائية والمعطائية الزمنية ونسبة التحلل والعائد العام للنتائج.

في ظل الظروف العادية، تم تحفيز أشكال أكسيد الزنك المختلفة باستخدام التحلل الضوئي لل 2-كلوروفينول في المياء. تم مقارنة النتائج بين أشكال أكسيد الزنك وكانت كفاءة أكسيد الزنك الاصطناعي أعلى من أكسيد الزنك التجاري. و مركب اكسيد الزنك التجاري/كالونايت أعلى كفاءة من اكسيد الزنك التجاري وايضاً مركب اكسيد الزنك التجاري/كالونايت اكثر كفاءة من اكسيد الزنك الصناعي. وبالتالي كان ترتيب الكفاءة باستخدام أشكال مختلفة من أكسيد الزنك هو أكسيد الزنك التجاري > أكسيد الزنك الاصطناعي > أكسيد الزنك التجاري/كالونايت. زيادة تركيز الملوثات، وكمية المحفز ودرجة الحموضة تزيد من معدلات التحلل الضوئي. هذا وقد تم مناقشة ميكانيكية مناسبة لتفاعل التحطيم بالحفاز الضوئي المستخدم.