An-Najah National University

Faculty of Graduate studies

Clay-supported sensitized nano-ZnO in photocatalytic degradation of aqueous halophenols using direct solar light

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A Thesis Submitted in Partial Fulfillment of the Requirements for **Degree of Master** in Chemistry

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Dedication

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

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Praise to Allah who guided my steps in all my work till the very end.

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الإقرار

انا الموقعة ادناه مقدمة الرسالة التي تحمل العنوان:

Clay-supported sensitized nano-ZnO in photocatalytic degradation of aqueous halophenols using direct solar light

إستخدام دقائق اكسيد الزنك النانونية المثبتة على الفخار الطبيعي لتنقية المياه من الهالوفينولات تحت أشعة الشمس

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الاشارة اليه حيثما ورد، وأن هذه الرسالة ككل أو جزء منها لم يقدم من قبل لنيل أي درجة أو بحث علمي أو بحثي لدى أي مؤسسة تعليمية او 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 of qualification.

اسم الطالبة: Student's name:

التوقيع: Signature:

Date: التاريخ:

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List of Abbreviations

°C	Celsius
2CP	2-Chlorophenol
CB	Conduction band
Cl^-	Chloride ion
CO_2	Carbon dioxide
E_g	Energy band gap
eV	Electron volt
Fe_2O_3	Iron(III) oxide
FT-IR	Fourier transform infrared
h^+	Holes
HOMO	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
KCl	Potassium chloride
LUMO	Lowest Unoccupied Molecular Orbital
M	Molarity
OH•	Hydroxyl radical
ppm	Part per million
Q.Y	Quantum yield
rpm	Round per minute
SEM	Scanning Electron Microscopy
T.F	Turnover frequency
T.N	Turnover number
TiO_2	Titanium dioxide
t_R	Retention time
UV-Vis	Ultraviolet-Visible
VB	Valence band

XRD	X-Ray Diffraction
ZnO	Zinc oxide
λ_{EX}	Excitation wavelength

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Abstract

This work describes the adsorption and photo catalytic degradation of aqueous 2-chlorophenol (2CP) contaminant using nano sized ZnO semiconductor photo catalyst. The ZnO particles are trapped into solid natural clay particles, producing a new highly active and easy to recover ZnO catalyst system. The degradation was performed under direct sun light. This research investigates the effect of sensitization on the photocatalytic efficiency. The prepared ZnO and prepared ZnO/natural clay systems were characterized by several methods, such as FT-IR, UV-Visible, Photoluminiscence, SEM and XRD which confirmed the ZnO formation in the composite catalyst. High Performance liquid chromatography was used to study the 2-chlorophenol adsorption and

degradation. The results showed that the 2CP photo-degradation on the sensitized ZnO/clay occurred with highest activity (~64% $\pm$ 0.01) loss of 2CP compared with ZnO/Clay composite catalyst (~56% $\pm$ 0.01) loss of 2CP under direct sun light under natural conditions. Effects of different reaction parameters onto photo degradation reaction of 2CP by natural clay/ZnO catalyst have also been studied. The ability of catalyst recovery and reuse in photo-catalytic reactions was also studied, the recovered catalyst showed loss efficiency (~41%) of 2CP. Attempts were made to regenerate efficiency of recovered catalyst by adding new dye molecules. When calculating relative catalytic efficiency, in terms of turnover number, all recovered and regenerated catalysts maintained original efficiency of fresh samples.

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Chapter 1
Introduction

Chapter one

Introduction

1.1 Overview

Among the various known types of pollution, water pollution is of a great concern since water is the prime necessity of life. Only 0.02% of the total water on the earth surface is suitable for drinking. Increased industrial, agricultural and domestic activities have resulted in wastewater containing different of toxic pollutants [1-4].

There are many types of water contaminants including chemical pollutants, biological pollutants and radiation pollutants. Organic chemical pollutants

transfer to the environment then transport to the water supply, accumulate in large amounts and serve as substrates for many microorganisms [5].

A number of methodologies with varying degrees of success have been developed to manage water pollution. Some of them involve coagulation, filtration, ion exchange, sedimentation, electrolysis, disinfection and chemical precipitation. However, these methods have their own shortcomings and limitations [6-7].

Recently, application of advanced oxidation processes using solar energy has been established for the purification of water from many contaminants [8]. Such processes employ special photo catalyst systems in their strategy.

1.2 Catalysts

A catalyst is defined as "*a substance that increases the rate of a chemical reaction without being consumed in the reaction and without affecting its equilibrium*" [9-10]. Catalysts can be prepared by several operations such as decomposition, reduction, impregnation and precipitation [11]. Catalysts are used in most industrial chemical processes [12], and are classified as homogenous (such as most organometallics) or heterogeneous (such as pellets with high surface areas, nanoparticles of metal oxides TiO_2 and ZnO [13, 14] and layered structures-clay, and others) [15-17].

1.3 Clay

Clays are the class of phylosilicates with colloidal layered hydrous aluminosilicates [18]. Clay structure consists of multi-layers of octahedral and tetrahedral sheets [19, 20]. As shown in figure (1.1), the silica tetrahedral layer involves silicon atoms that are located in the centers of tetrahedral at equivalent distances from four oxygen atoms. As a result of arrangement of tetrahedrons, a hexagonal network appears infinitely in two directions to form silica tetrahedral sheet [19, 21]. Octahedral sheets involve closely packed oxygens and hydroxyls. Different types of cations in octahedral sheets produce many types of sheets. For example gibbsite sheets contain aluminum cations while in brucite sheets the cations are magnesium.
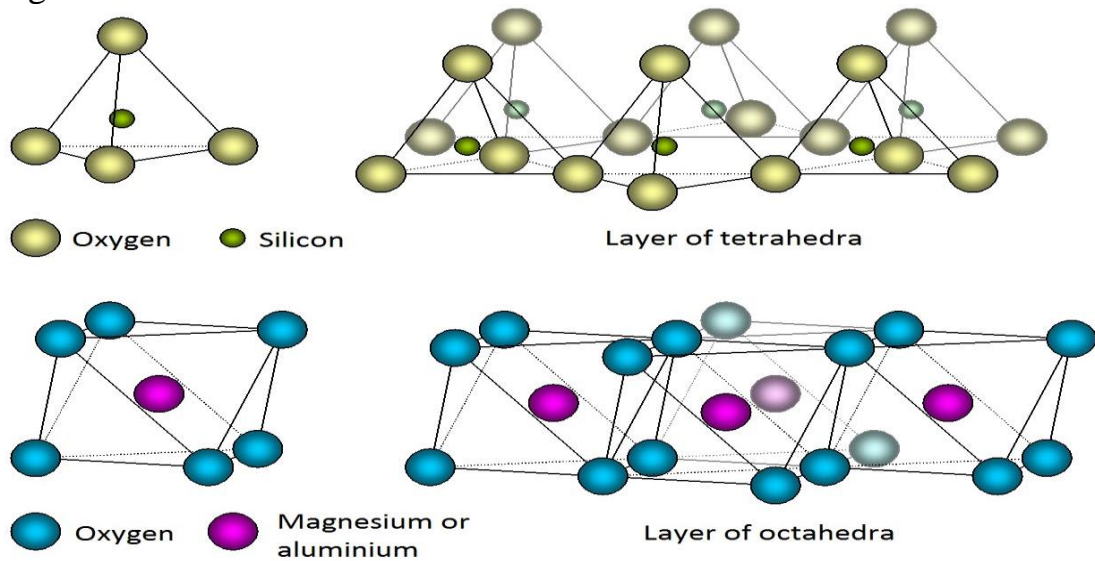
Figure (1.1): The structure of clay mineral

Clays are stacked in polymeric tetrahedral and octahedral layers. The layer types depend on number and arrangement of these sheets and on type of cations between them such as (Mg^{+2}, Fe^{+2}, Na^+ and K^+) [22]. Examples of clays are:

1- Kaolinite 1:1 clay mineral, Figure (1.2). Clay with one tetrahedral sheet and one octahedral sheet per layer.
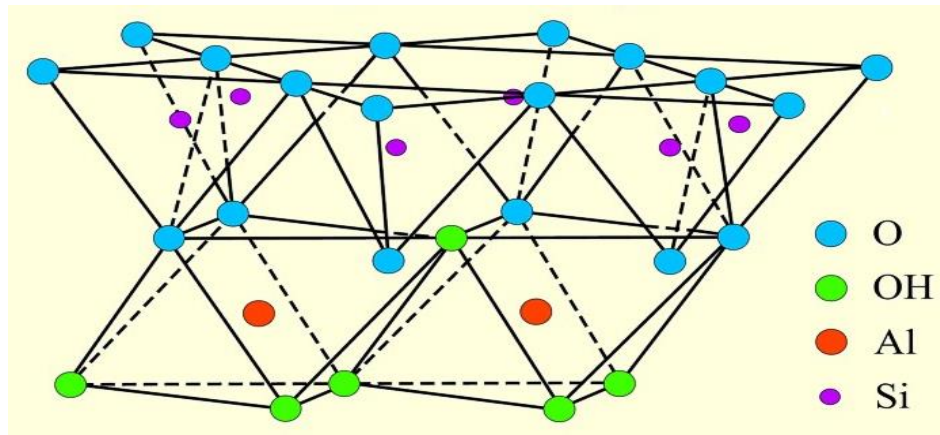
Figure (1.2): Structure of 1:1 clay mineral (kaolinite) showing one tetrahedral sheet and one octahedral sheet [23].

2-   Montmorillonite is a 2: 1 clay mineral, Figure (1.3). The clay has two tetrahedral sheets and one octahedral sheet per layer.
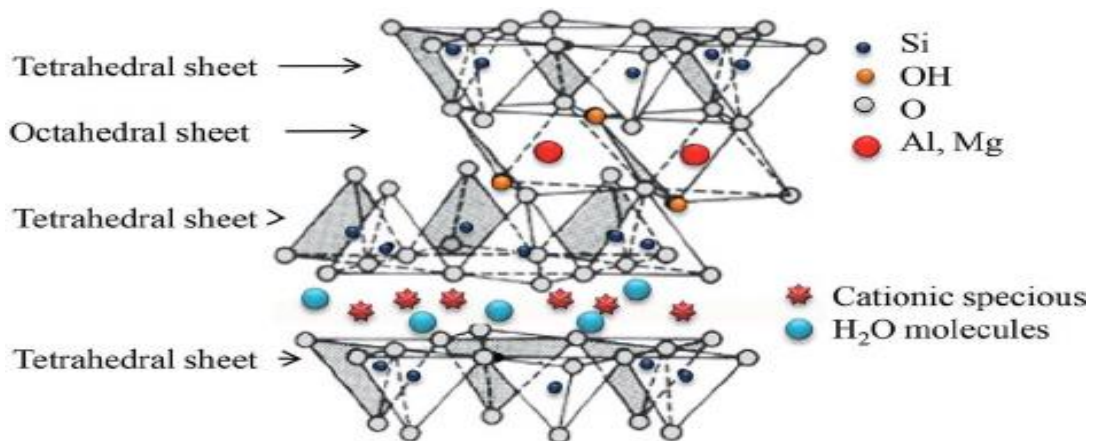
Figure (1.3): Structure of a 2: 1 clay mineral (montmorillonite) showing two tetrahedral sheets [23].

1.3.1 Catalytic Application of clay

In the clay frameworks, there are excessive negative charges, which are equaled by other free positive charges. The charges cause affinity for water and other polar solvents to be trapped inside clay's cavities [24, 25]. These charges facilitate reactions by activating different molecules. Cavities and layers may also increase rate of reactions by forcing the reactant molecules to collide inside cavities. Clays are thus used as heterogeneous catalysts or as supports for catalysts. Clays are also used in waste management facilities [17], health care products and therapeutic products [26].

1.4 Phenols

Phenol is a white crystalline solid. It is an organic compound with the molecular formula (C_6H_5OH), sometimes called carbolic acid. It has moderate solubility in water [6, 7] and may exist in surface and tap water for long time without being biodegraded. Phenol and its derivatives are toxic and known as human cacogens, even at low concentrations [27, 28].

1.4.1 2-Chlorophenol

Also known as 2-hydroxychlorolbenzene, 2-chlorophenol (2CP) is an organic derivative of phenol. It is weakly acidic, colorless, with unpleasant order [29, 30]. 2CP structure is shown in figure (1.4) [31].
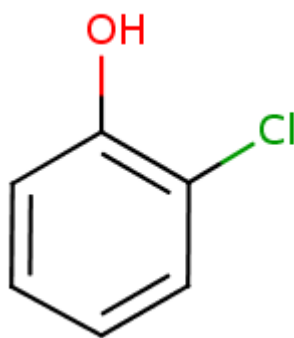
Figure (1.4): Structural formula of 2-Chlorophenol.

2-Chlorophenol has medium solubility (2 g/100 ml) in water compared with phenol (8.5 g/100 ml) due to the bond with Cl. It may enter the environment and water when used in dyes, pesticides and bactericide. It sticks to soil and sediments at the bottom of lakes, rivers and streams [32-35].

Most chlorophenols are highly toxic and cause long term effects to the environment and damage organs such as kidney, liver and immune system [31, 36].

1.5 Adsorptions

Adsorption is a simple, low cost, highly efficient and extremely important process. It has practical applications in technology, environment protection, biological and industrial fields [37].

Adsorption is gaining attention as one of the most useful techniques for treatment of industrial effluents containing toxic materials and removing them from soil, air and water [38]. It is a process which includes the transfer of the solute from the solution to the surface of a solid material [39]. Adsorption is an important step in many catalytic reactions. Different

adsorbents were widely used such as clays [40], montmoronillite [41, 42], kaolinite [41], soil [43, 44], carbon nanotubes [45], aluminum oxide [46], and graphene oxide [47].

1.6 Photo-catalytic degradation

Photo-catalysis is defined as the "speeding up of the photoreaction by the presence of a catalyst" [10]. It is a promising technique for many applications of solar light.

Catalysts are classified based on the phase of the catalyst used, as:

1) Homogenous photo-catalyst: the medium of the reaction and the catalyst had the same phase, such as ozone and photo-Fenton systems (Fe^+ and $Fe^+/H_2O_{2)}$ [48].

2) Heterogeneous photo-catalyst: the catalyst has different phase from that of the reactants, such as most semiconductors (TiO_2, ZnO, and Fe_2O_3).

Photo catalytic degradation is a rapidly expanding method for wastewater treatment [49]. It is an efficient process for the degradation of toxic organic compounds from water into mineral species such as CO_2 and others[50-52].

1.7 Semiconductor

Is normally a solid material [53], with an electrical conductivity between conductor and an insulator [54, 55]. Semiconductors contain two energy bands, one of the highest occupied valance energy band (VB), which is

completely filled with electrons. The lowest unoccupied conduction energy band, is empty of electrons (CB).

Semiconductors are widely used in many applications for example, photo-catalysis of water, purification of soil, water and air, and disinfection from micrograms drugs and other pollutants.

1.7.1 Semiconductor photo catalyst

It is an important technology that rapidly expands for the removal of organic pollutants from water [56-58]. In the presence of a photo-catalyst (ZnO), each band in the semiconductor photo catalyst has a different energy level. The valance band (VB) is the highest filled energy band, and the conduction band (CB) is the lowest empty energy band [59]. The energy band gap separates the VB and the CB.

When absorption of photon with energy greater than the energy of band gap occurs, excitation of electrons occurs from the (VB) to the (CB), leaving a hole (h^+) in VB and an electron in CB. These separated holes and electrons transfer to the semiconductor surface and react with other species. The holes react with a reducible species to produce an oxidized product, and the excited electrons react with oxidants. This series of reactions degrades organic pollutant molecules to give CO_2, H_2O, and other minerals figure (1.5) [60].
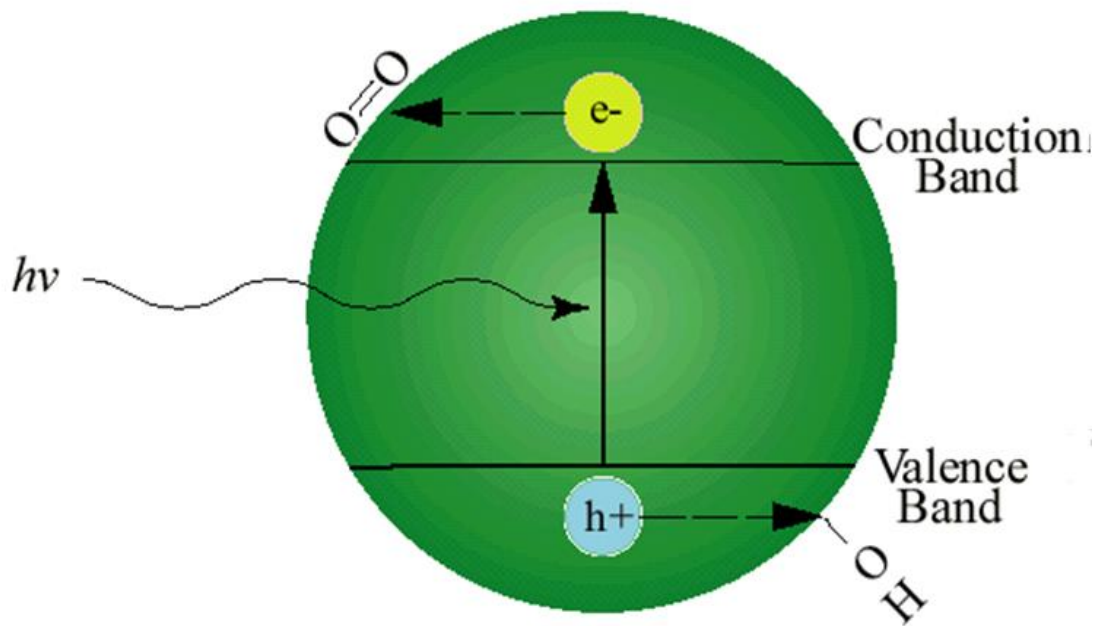
Figure (1.5): How semiconductor photo catalyst reaction occurs [60]

The basic reactions of degradation process are shown below:

$$ZnO + photon \rightarrow \quad h^+ + e^- \tag{1.1}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{1.2}$$

$$h^+ + OH^- \rightarrow OH^\bullet \tag{1.3}$$

$$h^+ + H_2O \rightarrow H^+ + OH^\bullet \tag{1.4}$$

$$e^- + O_2 \rightarrow \quad O_2^{\bullet-} \tag{1.5}$$

$$2\,O_2^{\bullet-} + H^+ \rightarrow 2OH^\bullet + O_2 \tag{1.6}$$

$$H_2O_2 + photon \rightarrow OH^\bullet + OH \tag{1.7}$$

$$Organic + OH^\bullet + O_2 \rightarrow CO_2 + H_2O + other\ possible\ minerals$$

$$[61]. \tag{1.8}$$
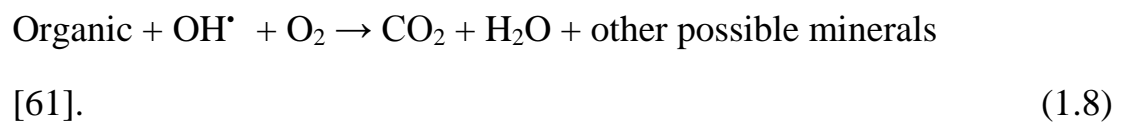
1.7.2 ZnO semiconductor photo-catalyst

Zinc oxide is a white inorganic, fine insoluble powder with the formula ZnO [55, 62], widely used in many applications such as semiconductor devices, additive material (in glass, paints, pigments, food, batteries) and others [63, 64]. ZnO is a promising semiconductor mostly used as a powder photo-catalyst due to its highly photo sensitivity, low cost, strong oxidizing power, stability and nontoxicity [65]. It has wide bandgap (3.2eV) that demands UV light ~380 nm. Therefore, ZnO has been used as a semiconductor photo-catalyst for the degradation of pollutants in water under UV or direct sun light [64].

1.8 Sensitization

In order to improve zinc oxide properties as semiconductor and photo catalyst under solar visible light; studies have been made to sensitize ZnO by adding another element or compound. Using small band gap semiconductor particles (such as CdS) is not an alternative, because they are unstable and degrade into hazardous ions of Cd^{2+} ions [66].

Many synthetic sensitizers are classified as environmentally hazardous (such as Ru based dyes) [14]. Therefore, natural dyes are being proposed as sensitizers in solar cells, due to their safety, low cost and eco-friendliness [13]. Examples of natural dyes are: carotenoids [67],

chlorophyll derivatives and related natural porphyrins [68], and anthocyanins [69].

Anthocyanins occur in all tissues of plants, including leaves, stems, roots, flowers, and fruits. Anthocyanins have been shown to act as a "sunscreen", protecting cells from high-light damage by absorbing blue-green and UV light, thereby protecting the tissues from side effects [70].

Anthocyanin is a safe low cost dye, available, easy to extract and applicable without additional purifications. It has medium band gap of 2.3 eV and absorbs in the visible region. Moreover, it has several carbonyls and hydroxyl groups that make it easy to bond to the semiconductor surface [13] as shown in figure (1.6). Thus it can be used as sensitizer for ZnO photo catalysts.

	R_1	R_2
Pelargonidin	H	H
Cyanidin	OH	H
Peonidin	OCH_3	H
Delphinidin	OH	OH
Petunidin	OCH_3	OH
Malvidin	OCH_3	OCH_3
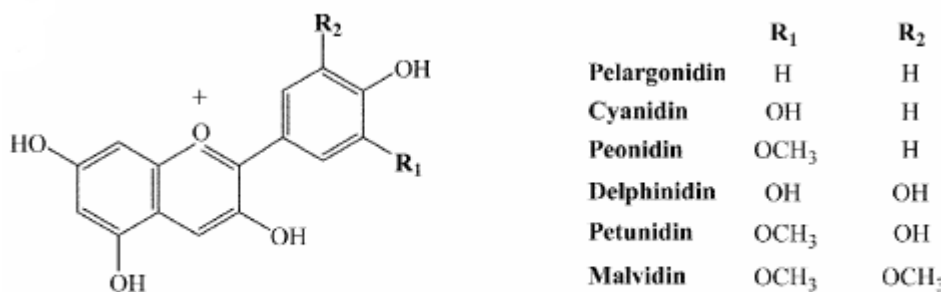
Figure (1.6): Structural formulas for different anthocyanins [13].

1.8.1 Sensitizing ZnO by anthocyanin dyes

ZnO is one of the most used semiconductor materials in dye sensitization of solar cells. It has relatively high stability against photo corrosion [71]. Both ZnO and TiO_2 have similar band gaps of 3.2 eV and similar electron injection efficiency from excited dyes [72]. Moreover, ZnO has higher

performance than TiO$_2$, due to its higher sensitivity to UV fraction of fallen sun light [73].

The dye medium band gap absorbs light wavelengths in the visible region. This leads to electron-hole generation in the dye molecule, by exciting the electrons from dye HOMO to LUMO. Charge transfer from dye LUMO to ZnO conduction band occurs, followed by generation of hydroxyl radicals. Oxidation of pollutants by excited ZnO/dye then occurs. The dye with medium band gap may not itself oxidize some organic pollutants, depending on their needed Oxidation potentials.
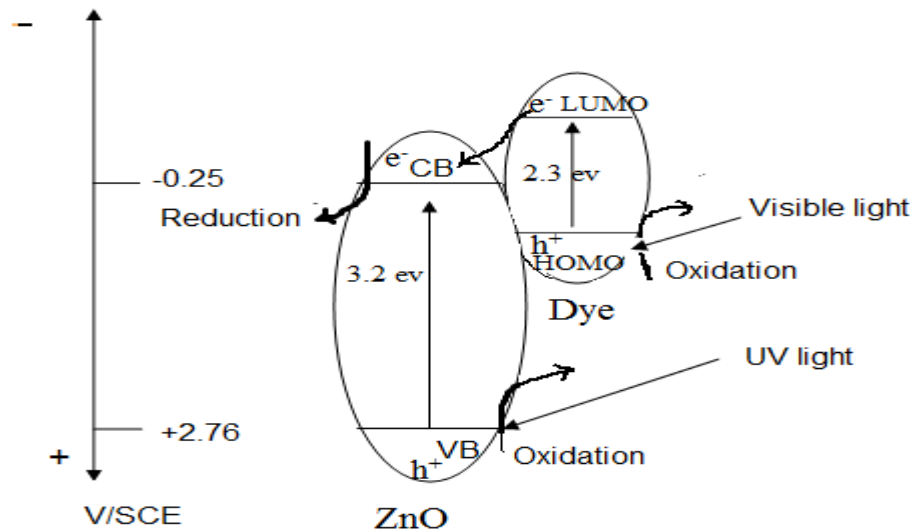
Figure (1.7): Sensitized ZnO semiconductor photo-degradation reaction [13].

1.9 Objectives

The main purpose of this work is to purify water from organic contaminant (2-chlorophenol) by two ways: adsorption and photocatalytic degradation under direct solar light, using an inexpensive and non-toxic semiconductor material (ZnO). The prepared nano-sized ZnO particles are supported on

solid natural clay. Safe, natural and low cost Anthocyanin dye is used to sensitize the supported ZnO catalyst. This work is expected to lower the pollutant concentration in water using a simple and cheap method without any expensive or dangerous chemicals.

Technical objectives:

- Preparation of nano-ZnO powder.

- Characterization of the prepared ZnO nano- particles using photoluminescence, UV-Visible spectroscopy, FT-IR spectroscopy, XRD and SEM.

- Preparation of new nano-sized composite material **ZnO/Clay** and characterizing them using photoluminescence, UV-Visible spectroscopy, FT-IR spectroscopy, XRD and SEM.

- Using the supported catalyst in the photo degradation of aqueous organic contaminants (2-chlorophenol) in water.

- Sensitization of the composite catalyst (**ZnO/Clay**) with anthocyanin natural dye.

- Using the sensitized-supported catalyst in the photo degradation of 2-chlorophenol in water under direct sunlight.

- Study effects of different parameters (pH, contaminant concentration, sensitization, catalyst concentration) on catalyst activity in degradation process.

- Recover the catalyst after the photo degradation process of 2CP and study the possibility of reusing it in another fresh degradation process.

1.10 Novelty of this work

During recent years the photo catalysis process has been widely investigated for the purification of water from many toxic and organic pollutants. It is a new promising environmental protection technology. Naked TiO_2 and ZnO have been used as photo catalysts for degradation of widespread pharmaceutical wastes [55]. Other studies used pristine and kaolinite supported ZnO catalyst in the degradation of 2CP in water under direct sun light [74]. Another study used ZnO/montmorillonite nanoparticles as catalyst for the adsorption and photo-degradation of tetracycline in water [54]. Earlier studies did not combine supporting ZnO photocatalysts and sensitizing them together. In this work, sensitized and non-sensitized natural clay supported nano ZnO particles are used for the degradation of 2-chlorophenol under direct sun light. To our knowledge, natural dye sensitized ZnO particles have not been supported onto natural clays for photo degradation purposes. The newly prepared composite clay/ZnO/dye is used for photo catalytic degradation of 2-chlorophenol, by direct sun light, for the first time.

On one hand, supporting the ZnO nano particle onto natural clay would provide high efficiency due to clay distinctive physical properties, such as large specific area, layered structure and high adsorption. On the other hand, supporting facilitates the catalyst separation and removal after the degradation experiment. This allows the catalyst recycling and reuse in additional degradation process [18, 24, 25].

On other hand, as only ~4% of the solar radiations are in the UV region, the ZnO semiconductor can be sensitized by dye molecules to work in abundant the visible range. The natural dye-sensitized ZnO can then be used in the visible light, as the dye has smaller band gap and absorbs in the visible region.

Chapter 2
Materials and methods

Chapter Two

Materials and methods

2.1 Materials

Zinc acetate dihydrate [$Zn(OOCCH_3)_2 \cdot 2H_2O$] was purchased from Sigma Aldrich and NaOH from Frutarom Co. Natural clay was purchased in its solid state from local pottery workshop at Jaba-Jenin-Palestine. All these materials were used for the preparation and synthetic the ZnO and composite **ZnO/Clay** nanoparticles. The contaminant model 2-chlorophenol was purchased from Sigma Aldrich. Anthocyanin dye was extracted from dried karkade flowers which were purchased from local markets.

2.2 Equipment

Stirred thermostated reactor with water bath model 80 from Fisher was used for reaction. A Lux-meter (Lux-102 light meter) was used to determine the intensity of sunlight that reaches the water sample under study. A Scientific Ltd model 1020 D.E centrifuge was used to separate contaminant solution from solid material and prepare the aliquots for analysis.-

Water 1525 Binary High performance liquid chromatography, equipped with water 2998 photodiode array detector and detection wavelength of 280 nm, was used to study the absorbance of remaining 2-chlorophenol in

solutions during adsorption and photo degradation processes. The sunlight was used as source of light.

Crystal structure ZnO and other composite catalysts were investigated by X-Ray diffractometer (XRD) with Cu kα ($\lambda_{1.5418 \ A^\circ}$) as source. The measurements of XRD and SEM were kindly conducted in the laboratories of the UAEU at United Arab Emirate.

Loss-Angloss Abrasion machine was used for aggregation of used Crockery to form fractions of clay, which were separated according to their sizes.

A Shimadzu UV-1601 spectrophotometer, equipped with a thermal printer Model DPU-411-040, type 20BE, was used for the determination of anthocyanin dye concentration, and for characterization of prepared catalysts (sensitized and non-sensitized ones).

A Perkin-Elmer LS50 Luminescence Spectrophotometer was used for photoluminescence measurements of each catalyst.

Fourier-Transform Infrared Spectroscopy (FT-IR), Nicolet iS5 connected with iD3 ATR Thermo Scientific, was used for each composite catalyst characterization.

 A Jenway 3510 pH meter was used to adjust the reaction mixture pH as desired. A mercury thermometer was used to measure temperature. The accurate masses were measured by using a fourdigit balance (AR-3130 from OHAUS Crap).

2.3 Preparation of solutions

- Stock solution preparation:

2-chlorophenol stock solution (1000 ppm) was prepared by dissolving 0.1 g 2-chlorophenol in distilled water and then diluting it to 100 ml. The stock solution was kept in the dark for further uses.

- Dilute solutions of both NaOH and HCl were prepared for the purpose of controlling the pH in the catalytic experiments.

- Sodium Hydroxide NaOH (0.9 M) solution was prepared by dissolving 9 g in 250 ml aqueous solution.

- Zinc acetate (0.68 M) was prepared by dissolving 15 g of zinc acetate dihydrate in 250 ml aqueous solution.

2.4 Catalyst preparation

2.4.1 ZnO particle preparation:

ZnO particles have been prepared using the precipitation method. A 250 mL of sodium hydroxide solution (0.9 M) was heated to 55 C. then 250 ml of zinc acetate solution (0.68) was added drop wise to the heated solution under high speed magnetic stirring. The resulting powder was decanted and washed with distilled water until the solution became neutral. Finally ZnO powder was then separated using a centrifuge (speed 6000 round per min, for 6 min).

2.4.2 Preparation of clay particles

Pre-heated solid pottery clay (from local producers) was crushed using Loss Anglos Abrasion machine for 30 min. The resulting clay fractions were then separated by sieving. The Clay powder with diameter < 75 μm was used to prepare supported catalyst for further study.

2.4.3 Supporting ZnO powder onto clay particles

Clay powder (10 g) were placed in 250 mL of 0.9 sodium hydroxide solution. The mixture was heated to 55°C with magnetic stirring, and Zinc acetate solution (250ml, 0.68 M) was added dropwise. Adding excess NaOH was intentionally made to push the reaction of Zn^{-2} ions to completion. The resulting powder was decanted and washed with distilled water until neutral. The **ZnO/Clay** dispersed powder was calcinated and dried at 450°C under air for 60 min using heating mantel with mechanical stirring to allow enough time for ZnO particles to be entrapped on clay particles. The powder was then collected, and stored in dark for characterization and further use.

2.4.4 Extraction of anthocyanin dye

Karkade (Hibiscus tea) dried flowers (40 g) was placed in 100 mL ethanol and soaked inside a container with magnetic stirring for 60 min. The mixture was then left to settle down, and the extracted anthocyanin dye was then filtered and kept in dark for further analysis and uses. The deep

red color was achieved at pH< 1 by adding drops of concentrated HCl. Under acidic conditions, anthocyanin solution becomes more stable [75].

2.4.5 Sensitization of composite catalyst

ZnO/Clay catalyst (4 g) was mixed with suitable amount (30 mL) of extracted anthocyanin dye (1.4×10^{-6} M) solution and magnetically stirred for 60 min in 100 mL beaker at room temperature. The mixture was then stored and left overnight in dark. The resulting sensitized **ZnO/Clay** solid was then filtered and air dried away from light. A filtrate sample (10 mL) was taken in each trial and stored for determination of anthocyanin concentration, and to calculate the amount of adsorbed anthocyanin.

2.4.6 Determination of Anthocyanin dye concentration

Anthocyanin dye concentration before and after sensitization was measured in acidic form (pH = ~1). The absorption wavelength is 533 nm. Based on anthocyanin molar absorptivity ($\epsilon = 30{,}000$ $M^{-1}cm^{-1}$) [76], Beer's law was used to calculate the anthocyanin concentration.

2.5 Photo-catalytic experiments:

2.5.1 2-Chlorophenol contaminant removal:

The adsorption experiment was performed by stirring a known concentration of 2-chlorophenol contaminant with the composite catalyst

in a 250 mL Erlenmeyer flask. The experiment was carried out under shaking for 60 min at 150 rpm in dark at room temperature.

The photo-degradation experiment was carried out under direct sun light in a magnetically stirred thermostated 100 mL beaker for 120 min. The beaker was thermostated by using water-bath to keep the temperature constant as desired (25°C).

Direct sunlight (with about 4% UV) was applied to reaction mixture surface, the average measured sun light intensity during May – July months in Nablus city-Palestine, was 100000 lux (0.0146 w/cm^2). At different reaction times, small aliquots of solution were syringed and double centrifuged (6000 round/minute for 6 minutes). HPLC was used to measure the change of 2CP concentration with time during the photo catalytic degradation reaction. The photo catalytic reaction was studied under different conditions. Effects of pH, catalyst loading, concentration of 2-Chlorophenl, and effect of sensitization, on reaction progress were all investigated.

2.5.2 Effect of 2CP contaminant concentration on the photo-degradation:

Different solutions of 2CP (10, 20, 40, 60 ppm) were prepared and mixed with 0.1 g ZnO (0.2g **ZnO/Clay**) for the adsorption-photo degradation process (for 1 hour of shaking in dark to reach equilibrium then under direct sunlight for 120 min).

2.5.3 Effect of composite catalyst loading on the photo-degradation:

Different amounts of **ZnO/Clay** (0.1, 0.2, 0.4 g) were mixed with 100 ml of 20 ppm aqueous 2CP contaminant solution to study the effect of catalyst amount on the degradation process.

2.5.4 Effect of pH

The pH medium was changed by adding a few drops of sodium hydroxide (NaOH) or hydrochloric acid (HCl). The reaction was carried out by mixing 0.2 g of **ZnO/Clay** catalyst with 100 ml of 20 ppm 2CP aqueous solution, the mixture was shaken in dark until equilibrium and then under direct sun light for 120 min. Acidic medium (pH= 3.5, neutral medium (pH 7.0) and basic medium (pH=10.5) were all examined.

2.6 Control experiments

A number of control experiments were preformed, as follows:

1- In the absence of catalyst, the solution of 2CP 20 ppm was shaken in dark for 60 min and then placed under direct sun light for 120 min. Concentration of pollutant, measured with time, did not change, which indicates that the pollutant did not photo-degrade with no catalysts.

2- In the dark, 100 ml of 2CP were shaken with 0.2 g composite catalyst (containing 0.1g ZnO) for 60 min until equilibrium. The contaminant concentration was measured with time. About 11% of 2CP was absorbed by the composite catalyst in the dark.

3- 20 ppm 2CP solution was shaken in dark with 0.2 g of **ZnO/Clay** catalyst one time and another with sensitized **ZnO/Clay** catalyst for 60 min, and then exposed to direct sun light for 4 hrs. Both composite catalysts show ~ 95% loss of 2CP contaminant.

4- Anthocyanin dye solution, with no ZnO, was studied alone as catalyst, in dark and under sun light. The dye did not affect the 2CP contaminant concentration.

5- Sensitized composite catalyst was used under cutting off UV light (eliminating 400 nm and shorter wavelengths) for 120 min. The absorbance spectra of 2CP contaminant amount loss was measured with time. Shows ~10% degradation loss of 2CP contaminant. Thus sensitized catalyst was almost not affected by UV light from the sun light. This indicates the role of the dye in sensitizing **ZnO/Clay** to the visible light.

2.7 Calibration curve of 2-chlorophenol.

High performance liquid chromatography analysis was conducted for the 2-chlorophenole analysis. The used detector was photodiode array and the detection wavelength was 280 nm, the eluent solution was [55% methanol, 55% (0.3 M) H_3PO_4] in flow rate 1 mL/min, the injection volume was 10μl. Figure (2.1) shows a well formed peak of 2-chlorophenole at t_R ~ 6 min. A calibration curve was built for 2-chlorophenol analysis, Figure (2.2).
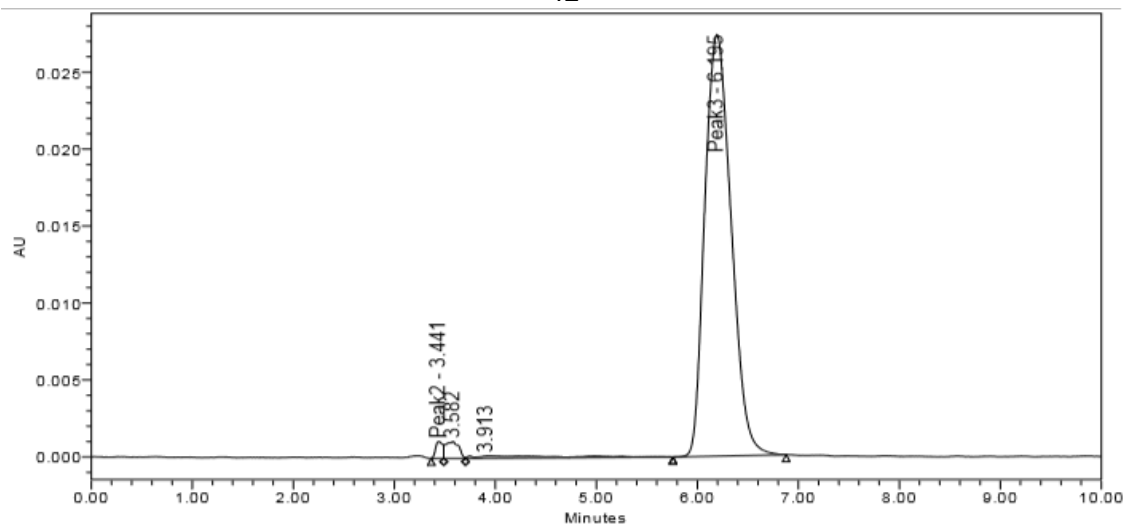
Figure 2.1: HPLC chromatogram for freshly prepared 2CP solution (20 ppm).
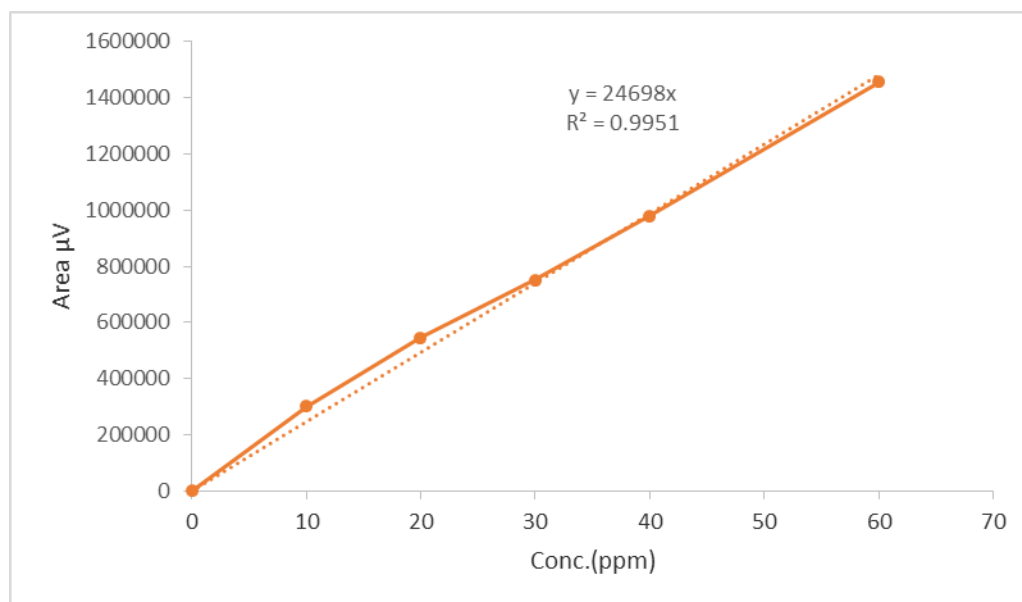
Figure (2.2): Calibration curve for 2-Chlorophenol in Distilled water by HPLC method.

Chapter 3
Results and discussion

Chapter Three

Results and discussion

3.1 Catalysts Characterization

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

3.1.1-UV-Visible absorption spectrophotometry characterization

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

1- ZnO catalyst:

Figure (3.1) represent the absorption spectrum of the prepared ZnO powder, the absorption spectrum shows absorption maximum ($\lambda_{max} \approx 380$ nm) similar to that of literature [77].
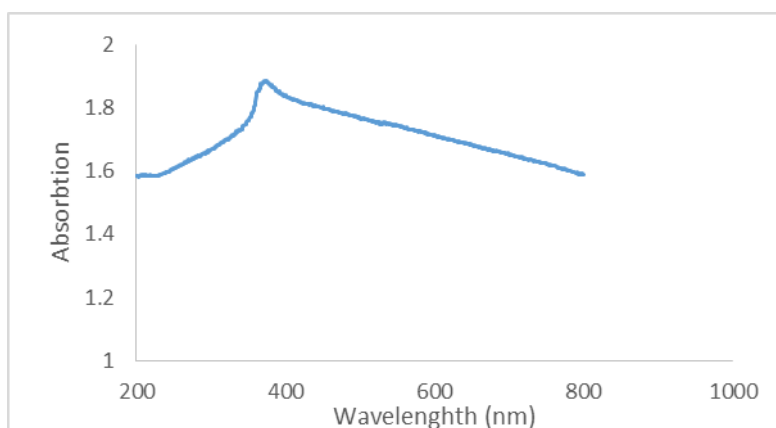
Figure (3.1): The Electronic absorption spectra of prepared Zno powder.

2- ZnO/Clay composite catalyst

Figure (3.2) shows the electronic absorption spectrum for **ZnO/Clay** and clay catalyst. Naked clay shows no absorption maxima in the range 200-800 nm, while the other system of **ZnO/Clay** show absorption maxima at $\lambda_{max} \approx$ 375 nm with shorter wavelength than the naked ZnO powder. The slightly blue shift compared with the prepared ZnO is attributed to smaller particle size of ZnO supported onto clay [78].
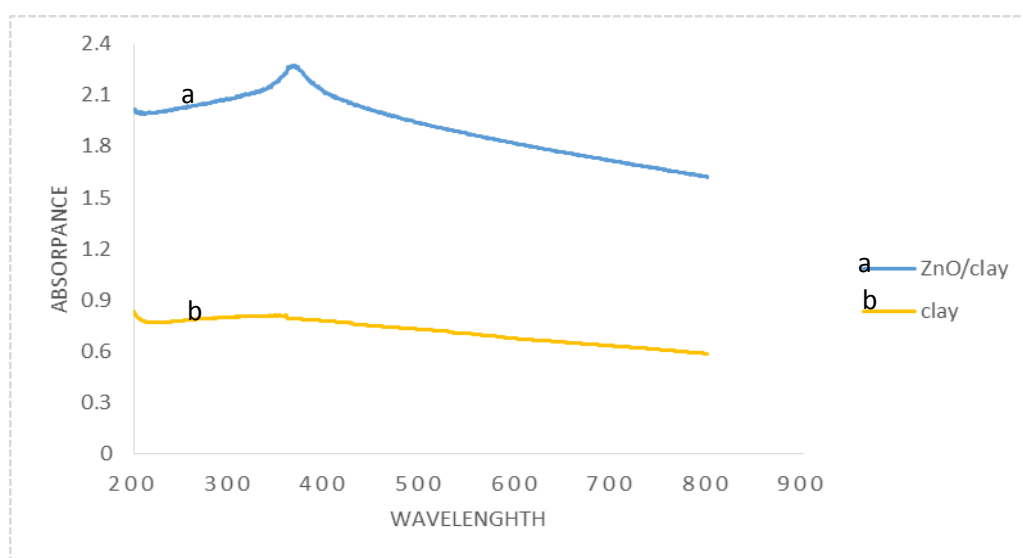
Figure (3.2): Electronic absorption spectra of a) ZnO/Clay catalyst, and b) Naked Clay.

3- Extracted Anthocyanin dye determinations:

Figure (3.3) shows the molecular absorption spectrum for extracted Anthocyanin. The absorption spectrum is similar to the anthocyanin spectrum reported in literature before [79].
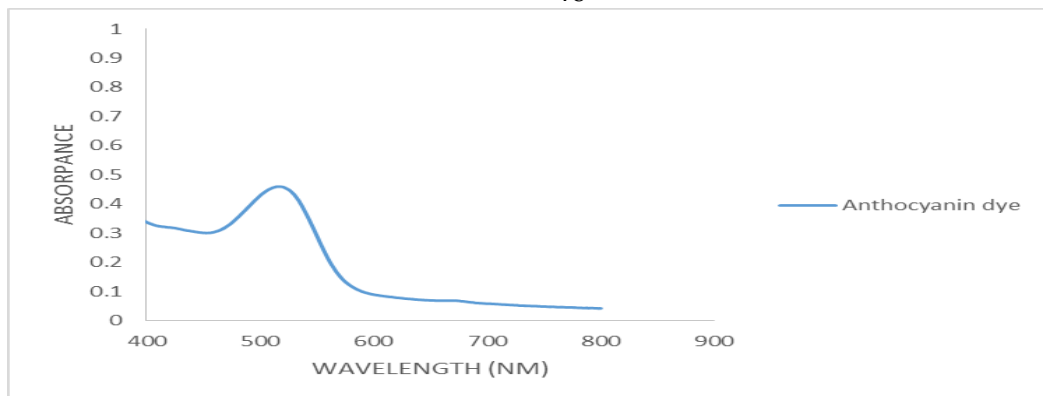
Figure (3.3): Molecular absorption spectrum for extracted Anthocyanin.

Dye-sensitized ZnO/Clay catalyst

Figure (3.4) shows the UV-Visible absorption spectra for **Anthocyanin/ ZnO/Clay** catalyst. Sensitized system show two absorption maxima, one at $\sim$ 600 nm (attributed to the anthocyanin absorption), and the other at $\sim$ 380 nm (attributed to ZnO absorption).
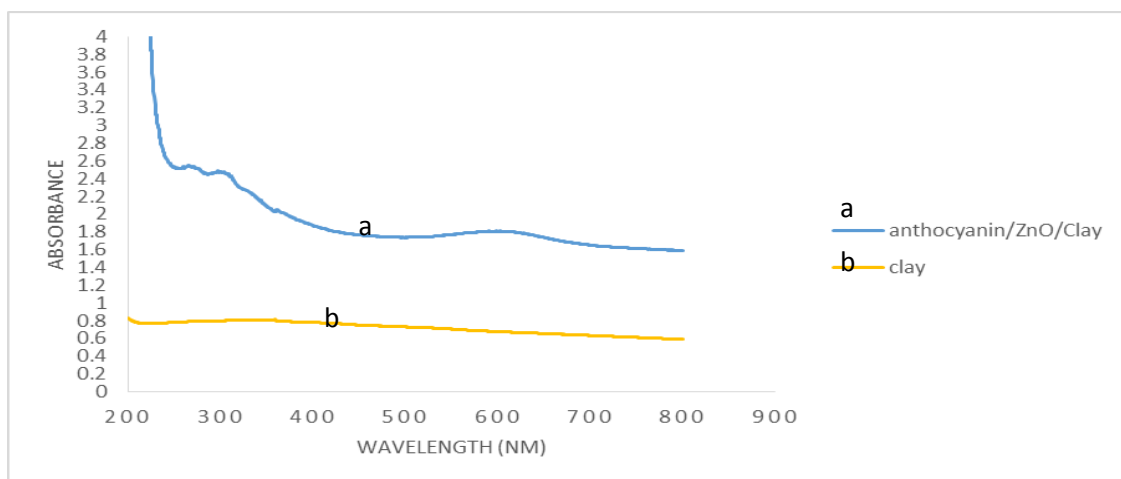
Figure (3.4): UV-Visible Absorption spectra of anthocyanin dye-sensitized solids a) ZnO/Clay catalyst, b) naked clay.

- Effect of Solution pH on Anthocyanin absorption.

Anthocyanins may exhibit different colors, depending on their pH, structure, and the presence of co-pigments. The absorbance is responsible for the red-purple color of anthocyanin (complementary to green chlorophyll in photo synthetically-active tissues) [80]. Anthocyanin dye may degrade at higher pH mediums. Thus the absorbance of anthocyanin dye in visible region is higher at pH<8. Figure (3.5a) shows the absorption spectrum of anthocyanin in basic form (pH = 8.5), while Figure (3.5b) is the absorption spectrum of anthocyanin in its acidic form (pH = 3.5). As shown in Figure (3.5) bellow, the acidic anthocyanin shows higher molar absorptivity with shifting to lower wavelength.
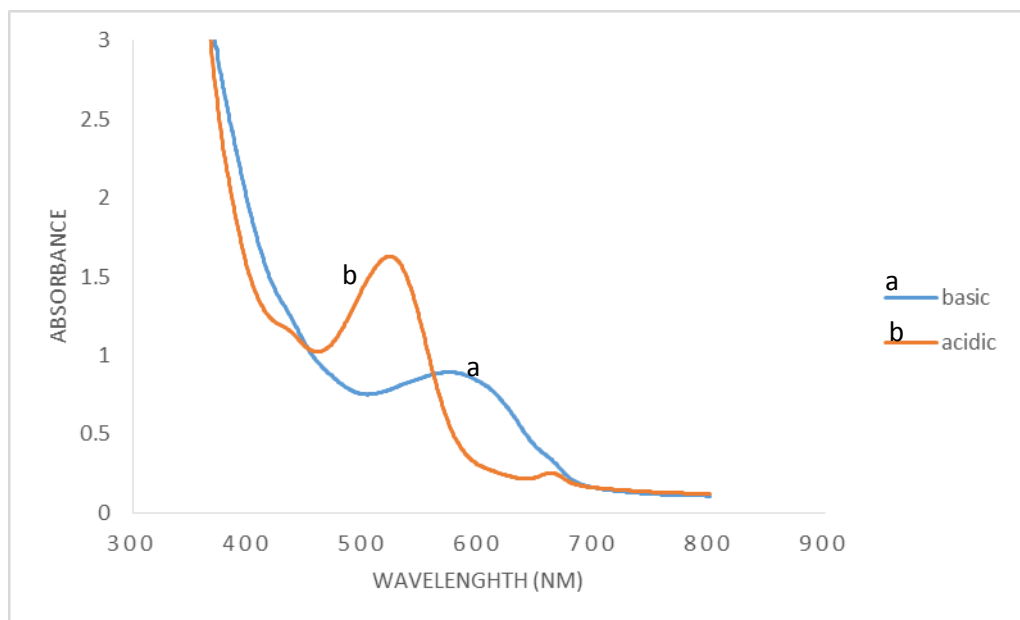
Figure (3.5): Anthocyanin dye UV-Visible spectra under different pH mediums a) pH =8.5 and b) pH =3.5. Spectra were measured using same dye concentration solution in each case.

- Spectrophotometric determination of Anthocyanin dye concentration:

Figure (3.6) shows the absorbance of anthocyanin dye before and after sensitization. The concentration of anthocyanin in the extracted solution was calculated and found to be ($1.4*10^{-6}$ M). The concentration of the solution after catalyst filtration and separation was ($0.91*10^{-6}$ M). The calculated loading of dye onto ZnO is thus $0.71*10^{-6}$ molecule dye/molecule ZnO.
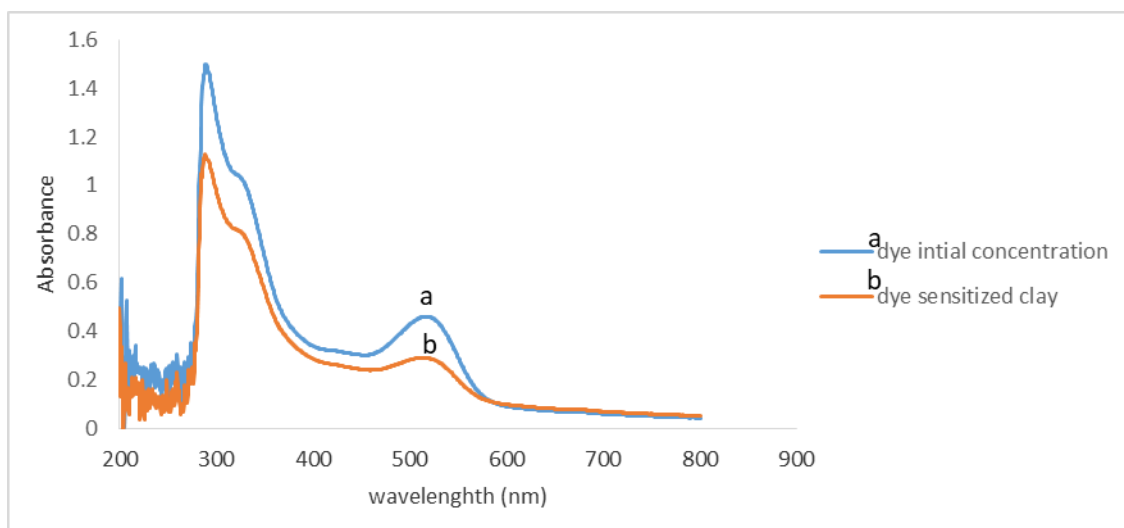
Figure (3.6): Anthocyanin dye absorption spectra a) Anthocyanin in the extracted solution, and b) the filtrate after sensitization of ZnO/Clay catalyst.

3.1.2 Photoluminance spectrometry characterization

A Perkin-Elmer LS50 Luminescence Fluorometer was used for photoluminescence measurements. Emission spectra were used to determine catalyst band gap. Small amount (0.1 g) of each composite catalyst systems were suspended in distilled water (10 mL) and placed in

quartz cell. The suspensions were excited at λ_{EX}=420 nm. As shown in figure (3.7), the sensitized **ZnO/Clay** composite show increases in the emission intensity at λ_{EM} = 420 nm comparing with **ZnO/Clay** and ZnO, this is an indication of increasing the number of photons being absorbed.
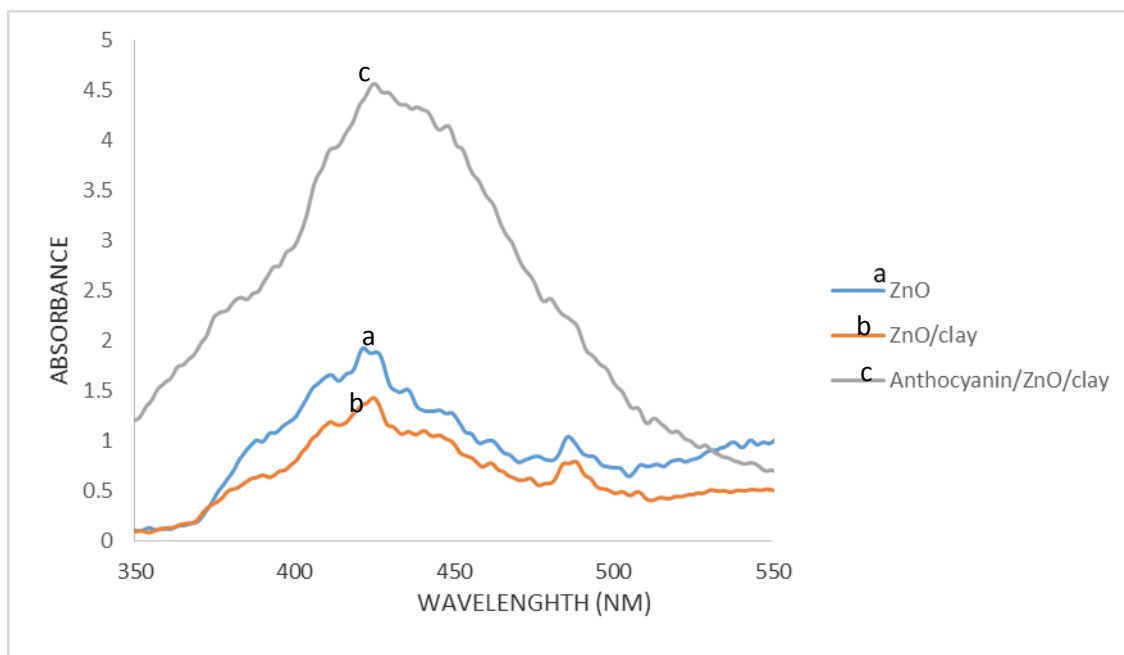
Figure (3.7): Photoluminance emission spectra of a) ZnO, b) ZnO/Clay, and c) Anthocyanin/ZnO/Clay catalysts. Excitation wavelength was 4-20 nm.

3.1.3 Fourier-transform infrared spectroscopy (FT-IR) characterization

Fourier-Transform Infrared Spectroscopy (FT-IR), Nicolet iS5 connected with iD3 ATR Thermo Scientific was used for the composite catalysts characterization. Figures (3.8), Shows the FTIR spectra of the synthesized ZnO. The spectrum is clearly shows the ZnO absorption band near IR (wavenumber ~ < 500 cm^{-1}) [81, 82]. The 3450cm^{-1}, and 2350 cm^{-1} absorption indicate the presence of atmospheric moisture, CO_2, or adsorbed acetic acid on the ZnO surface [83].
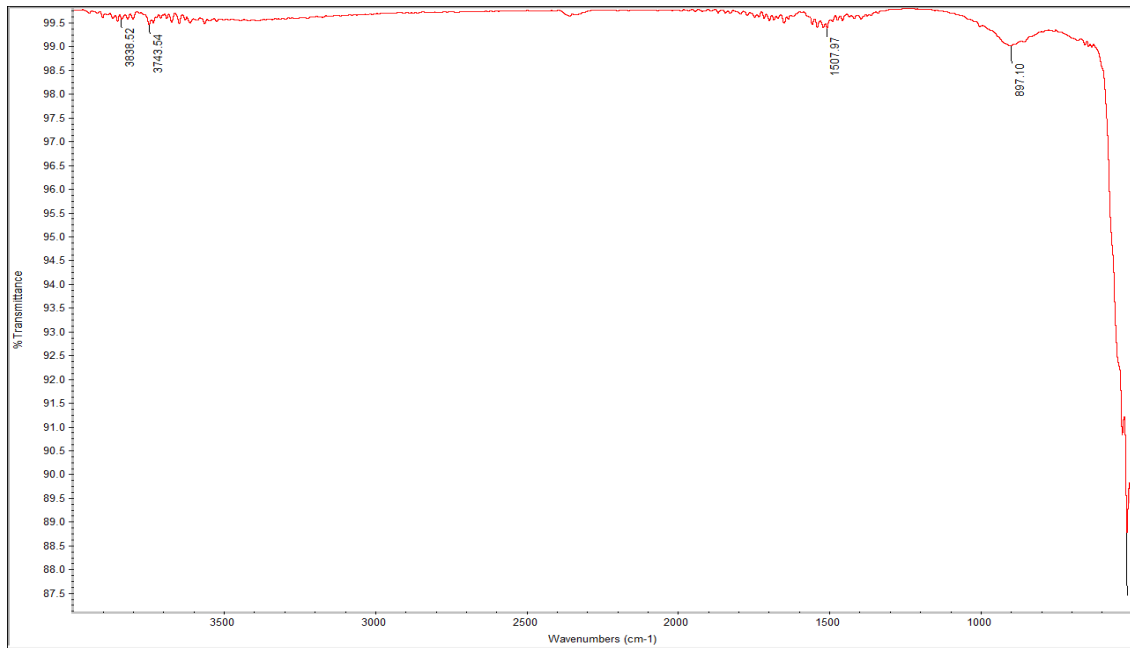
Figure (3.8): IR-Spectram of prepared ZnO nano-particles**.**

Figure (3.9) shows the FT-IR spectrum of extracted Anthocyanin, the spectrum proofing the presence of anthocyanin by comparing with literature anthocyanin spectrum, Figure (3.10).
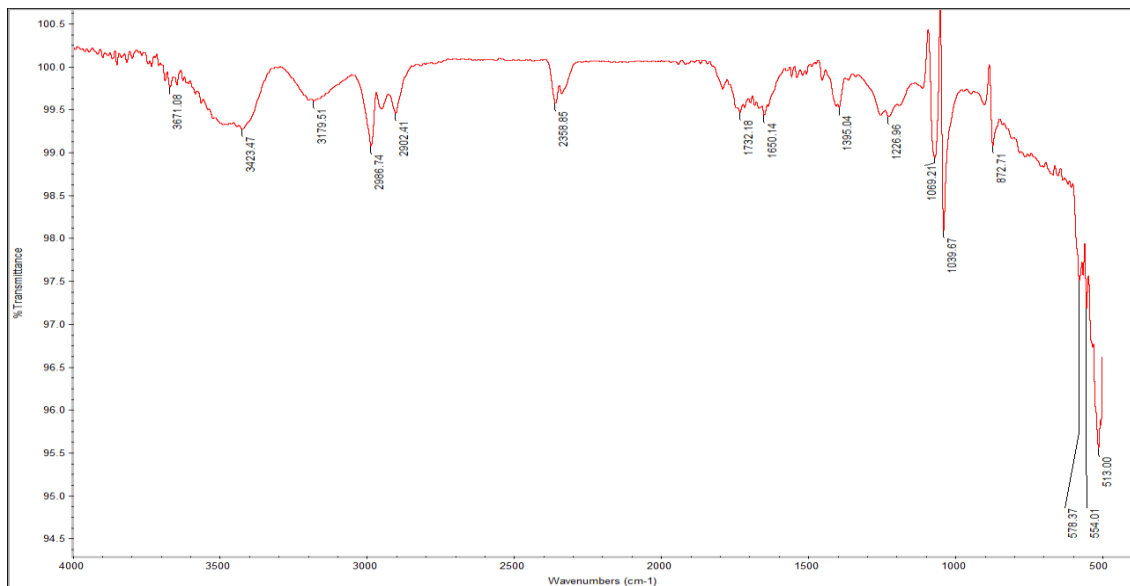
Figure (3.9): IR-Spectrum of ethanol-extracted anthocyanin from karkade.
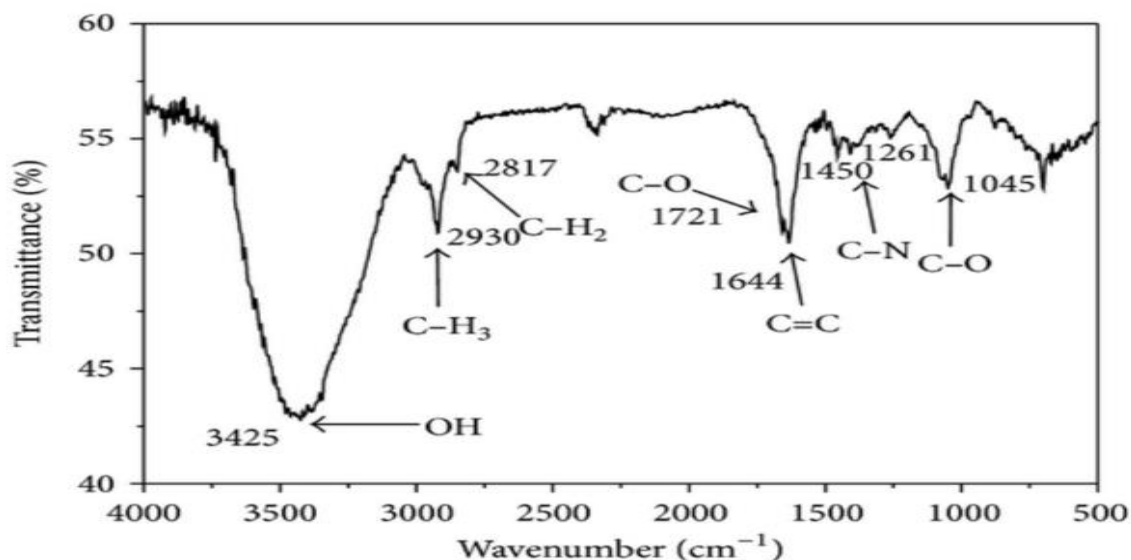
Figure (3.10): literature IR-Spectra of pure anthocyanin dye [84].

The FT-IR of **Anthocyanin/ZnO/Clay** system is shown in Figure (3.11). Distinguished peaks of Anthocyanin (3000, 1043, 1070, 1233, and 1398 cm^{-1}) are shown in the spectrum. The shift of peaks is attributed to the chemisorption of anthocyanin onto catalyst surface. This is an evidence of presence of adsorbed anthocyanin on the catalyst surface which chemical bond formation.
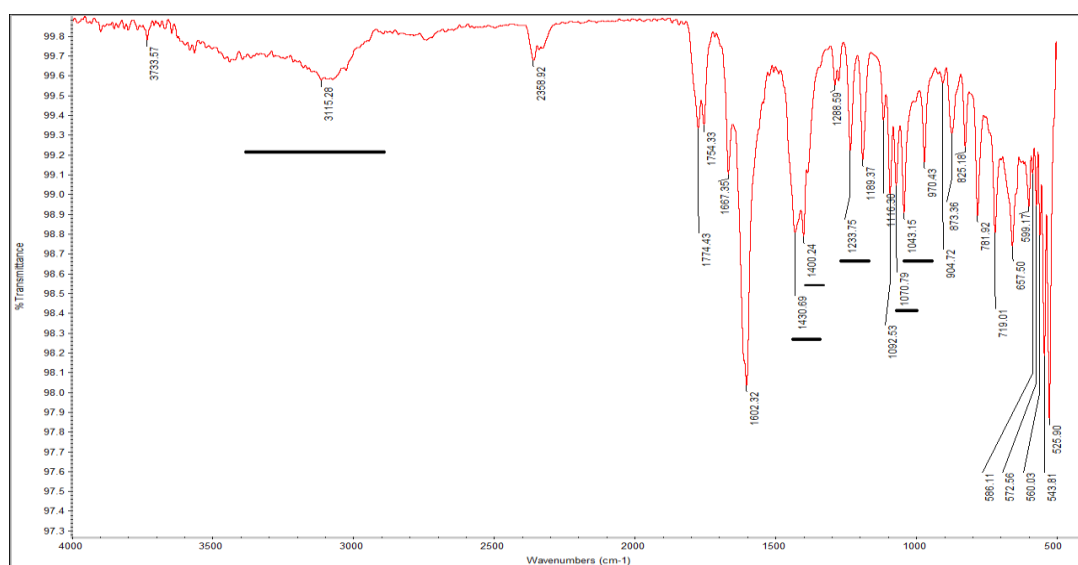
Figure (3.11): IR-Spectra of sensitized Anthocyanin/ZnO/Clay catalyst.

3.1.4 X-Ray diffraction characterization

X-ray diffraction (XRD) patterns were measured with Cu Kα radiation (λ = 1.5418 Å) as a source. Scherrer equation was used to calculate the particle size.

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

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

X-Ray diffraction analysis of ZnO:

X-ray pattern was measured for prepared ZnO nano-powder, Figure (3.12). The figure shows distinguished peaks at 2Ө = (31.6°), (34.1°), (36°), (47.4°), (56.5°), (62.7°) and (68.4°). The comparison of XRD pattern of the prepared ZnO with a pattern of ZnO in literature, Figure (3.13), confirms the hexagonal Wurtzite type.

Prepared nano-ZnO particle size was calculated using Scherrer equation and found to be ~20 nm [85].
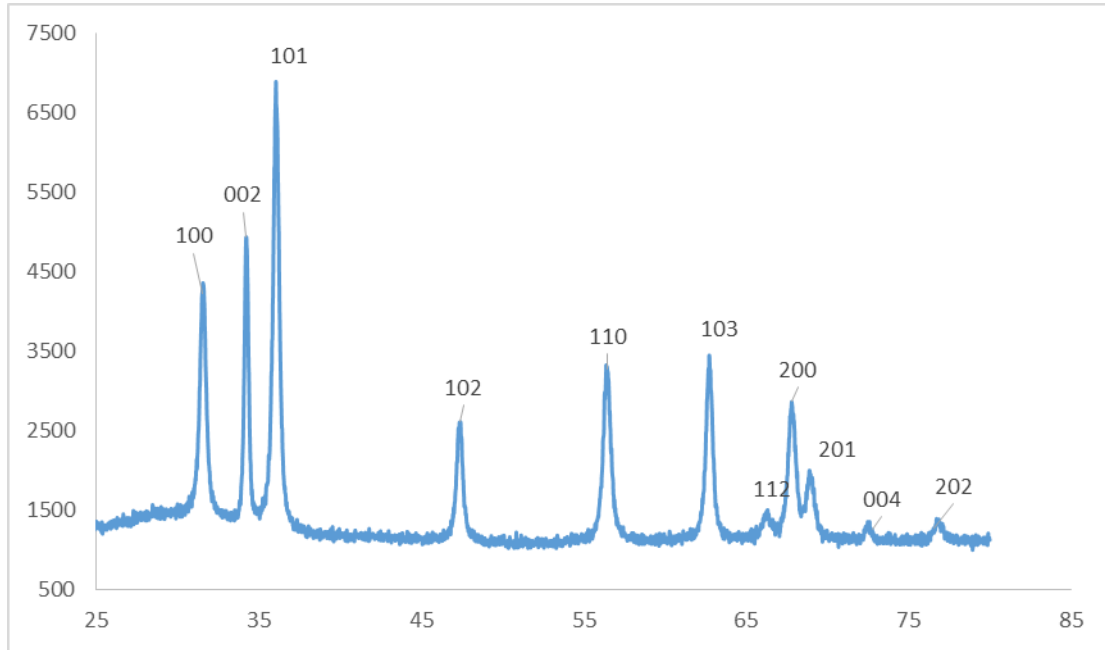
Figure (3.12): Measured XRD-pattern of prepared ZnO nano-particles.
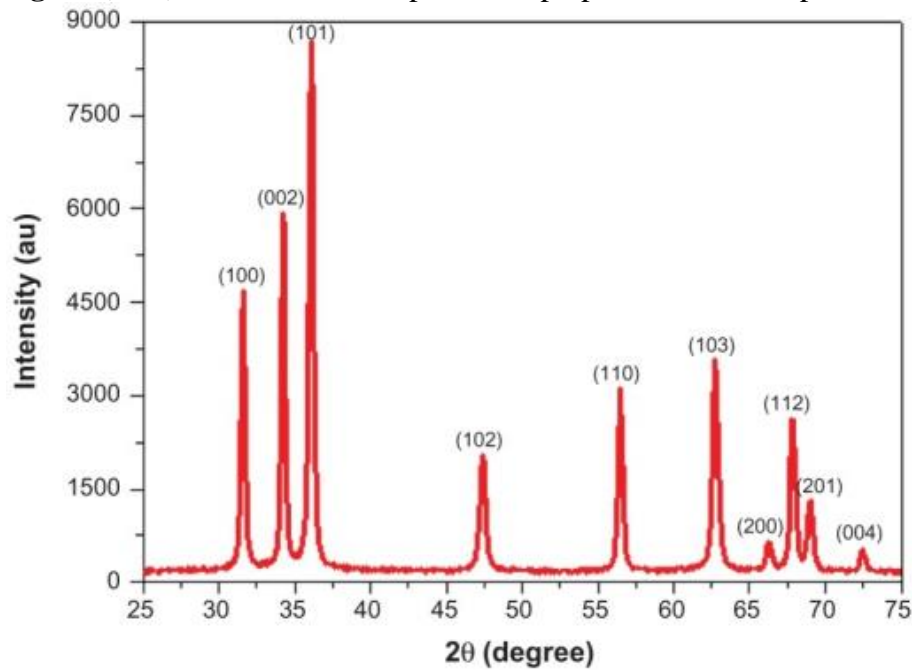
Figure (3.13): Literature XRD-pattern of Wurtizite Crystal ZnO nano-material [86].

X-Ray analysis of ZnO/Clay:

X-Ray pattern was measured for prepared **ZnO/Clay** composite Figure (3.14).The XRD pattern in Figure (3.14) shows distinguished peaks for ZnO hexagonal wurtzite type of ZnO powder. The calculation of Sherrer

equation based on peaks shows a decrease in the particle size of ZnO on clay surface, the calculated ZnO particle size is ~15.2 nm.

The inter layer distance of the clay was 0.3 nm, as calculated by Bragg's law [87], d = $n\lambda/2sin\Theta$ (Where d is the inter planer distance in the crystal, Θ is the Bragg angle, and n is an integer = 1 at λ = 1.5418 °A).

A comparison of XRD pattern of prepared **ZnO/Clay** catalyst with the XRD pattern of clay sample from literature, Figure (3.15) [88, 89] was done. The comparison proves the presence of the following composition in the Clay.

1- Kaolinite: the kaolinite peaks are at 2Θ = (13.3°), (23°), (39.5°) and (43°). The interlayered distance of kaolinite clay exists in prepared clay was = 0.3 nm. Compared with that of literature sample interlayer distance = 0.29. Kaolinite is non expandable clays, and has a small interlayer distance. So that ZnO nanoparticles can't penetrate between Kaolinite layers.

2- Quartz: the quartz peaks are at 2Θ = (20.8°), (26.6°) and (50.2°). Quartz is non layered structure, and the ZnO particles also can't penetrate inside. [90]

3- Montmorillonite: the montmorillonite is at 2Θ = (29.5°) with interlayer distance ~0.31 nm.

The results thus improves that ZnO particles presence only on the clay surface (do not penetrated between clay layers).
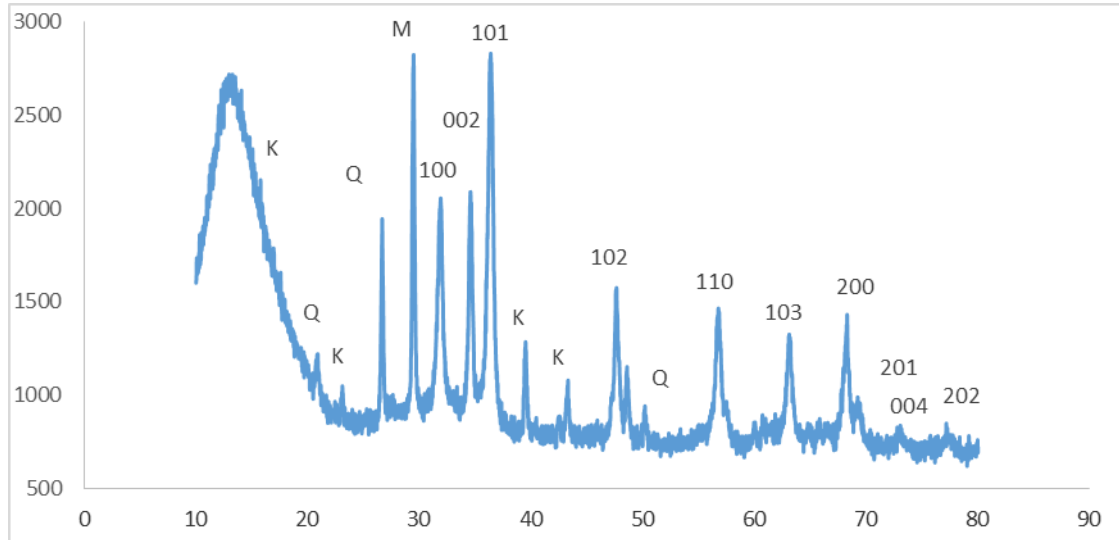
Figure (3.14): Measured XRD-pattern of ZnO/Clay composite catalyst.
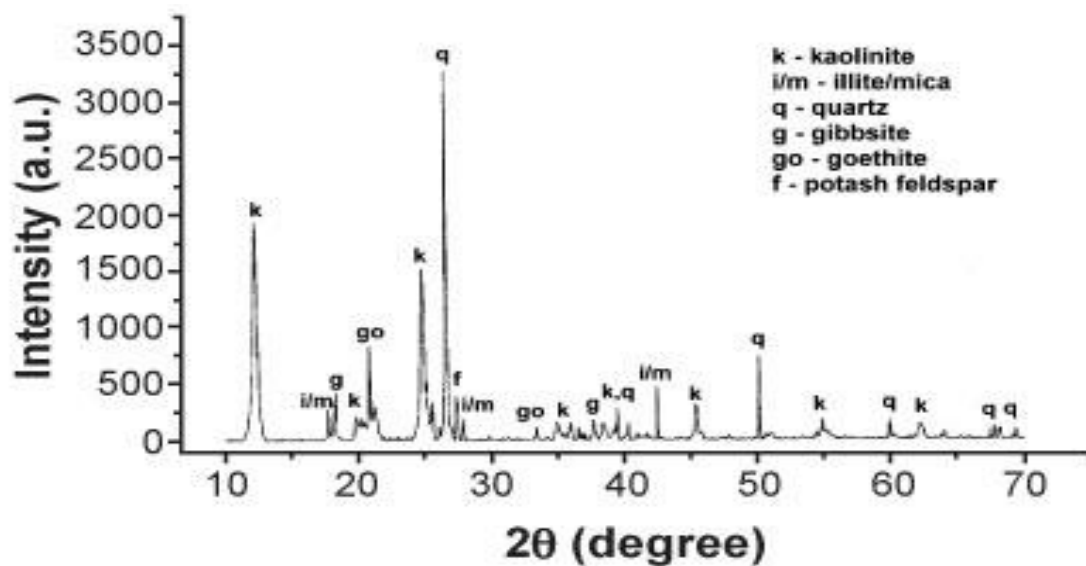
Figure (3.15): Literature XRD-pattern of clay sample [88, 89].

3.1.5 Scanning electron microscopy (SEM) characterization

Surface morphology and estimated size were measured for **ZnO/Clay** composite catalyst with field emission scanning electron microscopy using the energy dispersive spectroscopic FE-SEM/EDS technique.

Figure (3.16a) shows the SEM of prepared **ZnO** catalyst. Figure (3.16b) shows the SEM of prepared **ZnO/Clay** catalyst. Both figures show ZnO particles living in agglomerates on the clay surface. The ZnO powder involves larger agglomerates (~ 400 nm) than supported ZnO (~ 200 nm).
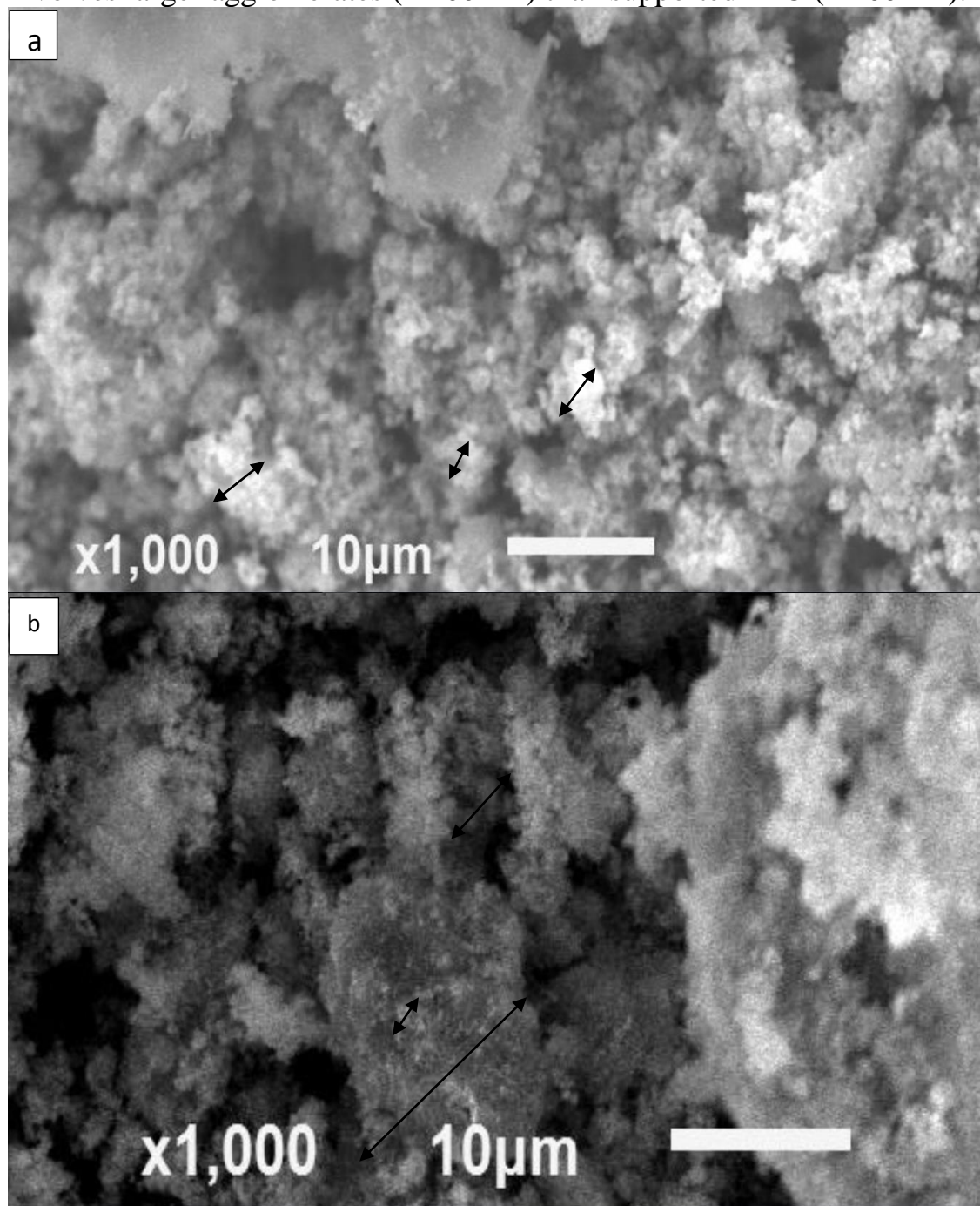
Figure (3.16): SEM micrographs a) for prepared naked ZnO particles. b) Supported ZnO/Clay catalyst.

3.2 2-Chlorophenol adsorption

adsorption reaction of 100 ml 2CP aqueous solution mixed with **ZnO/Clay** catalyst in dark for 60 min with continues shaking before exposed to sun light was studied, different parameters where also investigated.

3.2.1 Effect of 2CP contaminant concentration on adsorption reaction

Table (3.1) shows a decrease in the parentage of adsorption as 2CP concentration increase. When changing the initial concentration of 2CP solution from 10 ppm to 60 ppm, the amount absorbed increased from ~1 ppm (14% removal) to 4 ppm (7% removal).

Table (3.1): Values of 2CP removal percentage by adsorption using different contaminant concentrations in dark for 60 min.

2CP concentration	10 ppm	20 ppm	40 ppm	60 ppm
% 2CP removal	14 %	12 %	11 %	7 %

3.2.2 Effect of catalyst loading

Table (3.2) shows the results of changing catalyst amounts (0.1g - 0.4 g), an increase of percentage of adsorption was observed as catalyst amount increase.

Table (3.2): Values of 20 ppm 2CP solution removal percentage by adsorption using different catalyst amounts in dark for 60 min.

ZnO/Clay amount	0.1 g	0.2 g	0.4 g
% 2CP removal	11 %	12 %	12 %

3.2.3 Effect of pH

Table (3.3) shows the results of adsorption of 20 ppm 2CP solution mixed with 0.2 g ZnO/Clay catalyst in different pH media. The highest adsorption percentage was observed in acidic medium, due to the interactions between negatively charged surface of clay and cations of 2CP contaminate, thus encourage adsorption onto the surface [54]. Low adsorption was observed with more basic conditions due to repulsion between negatively charged surface area and 2CP anionic form [91, 54].

Table (3.3): Values of 2CP removal by adsorption under different pH media (acidic = 3.5, neutral = 7, basic = 10.5).

pH	Acidic	Neutral	Basic
% 2CP removal	16 %	12 %	4 %

3.2.4 Effect of Anthocyanin-sensitization

Sensitized prepared catalyst shows low adsorption efficiency by ~ 6 % in neutral conditions, due to the competition between molecules of dye and 2CP contaminate to the sites and pores on **ZnO/Clay** catalyst surface area.

3.3 2-Chlorophenol photo catalytic degradation

ZnO/Clay in photo-degradation of 100 ml 2CP contaminant solution was investigated under direct sun light with 0.0146 w/cm^2 intensity for 120 min. different condition of concentration of 2CP contaminant, amount of used catalyst, pH and sensitization of catalysts on photo degradation reactions, were all studied

The percentage of photo- degradation, values of overall rate, turnover number (T.N), turnover frequency (T.F) and quantum yield (O.Y) were all measured for each experiment [74].

$$The\ turnover\ number\ (T.N) = \frac{Number\ of\ moles\ of\ 2-CP\ reacted\ contaminant}{Number\ of\ moles\ of\ ZnO\ catalyst}$$

$$The\ turnover\ frequency\ (T.F) = \frac{turnover\ number}{Time\ (min)}$$

$$Quantum\ yield\ (Q.Y) = \frac{number\ of\ 2-CP\ contaminant\ reacted\ molecules}{Total\ number\ of\ photons.}$$

At 555 nm (assumed average wavelength of light), the total number of photons after 120 min = 4.98 $X10^{19}$ according to Plank's equation.

$$E(J) = nh\nu$$

Where, E(J) = (incident power per unite area) X (total area) X (exposure time in second).

And, $\nu = c/\lambda$

Incident power = 0.0146 w.

Time in seconds = 120 min X 60 second.

c = 3 X 10^8.

h (Plank constant)= 6.62 $X10^{-34}$ m^2 kg/s.

3.3.1 Effect of 2-chlorophenol contaminant concentration on degradation reaction

Figure (3.17) shows the degradation experiment using different initial concentrations of contaminant solutions ranging from 10 ppm – 60 ppm. Table (3.4) shows that the contaminant degradation percentage decreased with increased concentration, but this does not indicate lowering in catalyst activity, as other parameters (rate, T.N, and Q.Y) show higher efficiency with higher contaminant concentrations. Increasing of T.N due to light scattering [92]
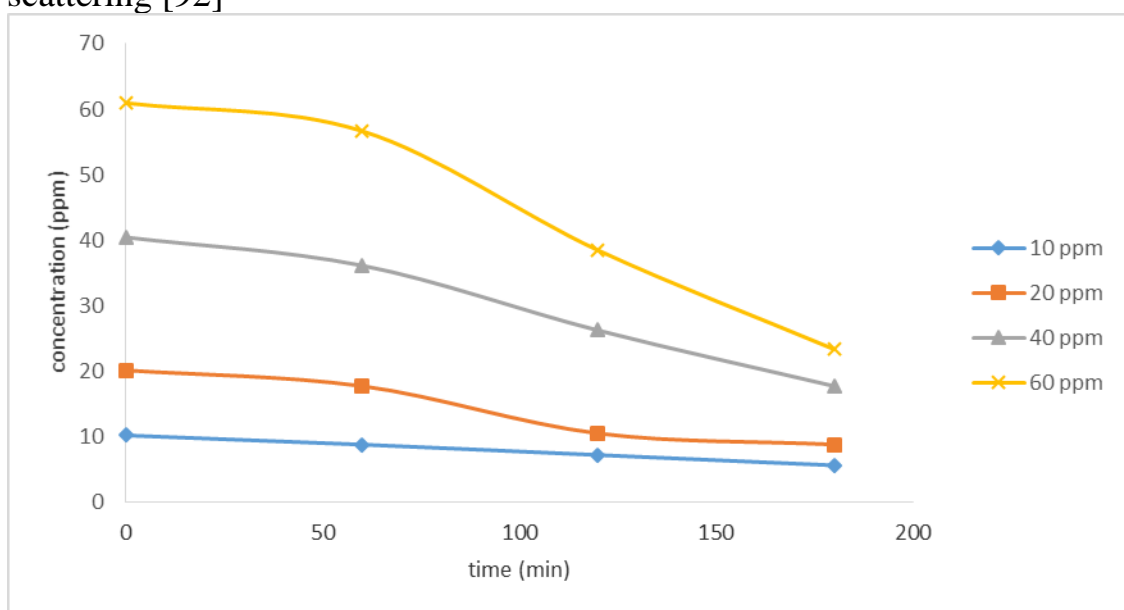
Figure (3.17): Effect of 2CP concentration on its degradation reaction: a) 10 ppm b) 20 ppm c) 40 ppm d) 60 ppm. All reactions were conducted using 0.2 g of ZnO/Clay composite catalyst at room temperature under direct sun light for 120 min.

Table (3.4): Values of percentage of Photo-degradation, rate of reaction, turnover number, turnover frequency, and quantum yield using 0.2g of ZnO/Clay catalysts mixed with 100ml of different concentrations of 2CP contaminant solution.

Initial 2CP concentration (ppm)	% photo-degradation	rate	T.N (10^{-3})	T.F (10^{-3})	Q.Y (10^{-25})
10	45	0.15	0.725	0.004	3.6
20	56	0.38	1.8	0.01	8.87
40	44	0.59	2.833	0.016	13.9
60	35	0.72	3.392	0.02	16.7

3.3.2 Effect of ZnO/Clay catalyst loading

Figure (3.18) shows photo catalytic degradation experiments of 20 ppm 2CP solutions using different amounts of prepared **ZnO/Clay** catalyst (0.05-0.2 g ZnO).The results indicate that the degradation of 2CP increased with increasing catalyst amount as the number of active sites available increased. However, degradation at higher concentrations decreased, as ZnO molecules being screening the light and prevent it from reaching the of catalyst surface, which lowers the catalyst efficiency as shown in Table (3.5).

Figure (3.18): Effect of different amounts of ZnO/Clay prepared catalyst: a) 0.1g b) 0.2 g c) 0.3 g d) 0.4 g. on to degradation reaction of 2CP under direct sun light at room temperature and natural pH.

Table (3.5): Values of percentage of Photo-degradation, rate, turnover number, turnover frequency, and quantum yield using variable amounts of ZnO/Clay catalysts mixed with 100ml of 20 ppm 2CP contaminant solution.

Amount of **ZnO/Clay** (g)	% photo-degradation	rate	T.N (10^{-3})	T.F (10^{-3})	Q.Y (10^{-25})
0.1	43	0.071	2.703	0.015	6.66
0.2	56	0.094	1.8	0.01	8.87
0.4	49	0.082	0.775	0.0043	7.65

3.3.3 Effect of pH on photo-degradation of 2-chlorophenol contaminant

Figure (3.19) shows the photo-degradation experiment of 2CP contaminant at different pH values (acidic =3.5, neutral =7, basic= 10.5) of reaction medium. Table (3.6) shows that the highest percentage of degradation, T.N

and Q.Y was in the basic medium followed by the neutral one, due to adsorption of high concentrations of hydroxide anion in basic medium which will encourage the formation of hydroxide radicals, and enhance the oxidation of contaminant molecules [93]. In acidic medium, ZnO catalyst undergo photo-corrosion and dissociation yielding Zn^{+2} ions [14, 93].

$$ZnO + 2h+ \rightarrow Zn^{2+} + 1/2\ O_2 \tag{3.1}$$

$$ZnO + 2H+ \rightarrow Zn^{2+} + H_2O \tag{3.2}$$

At pH < 9, ZnO assumes the form ($ZnOH^{2}+$) [74], while 2CP exists in the protonated form and acquire a positive charge, thus the protonated 2CP will be retarded from ZnO catalyst surface (repulsion) and the active species •OH. The photo degradation efficiency will thus be inhibited at low pH.

Figure (3.19): Effect of pH on 2CP removal by 0.2 g of ZnO/Clay composite catalyst with time: a) basic at pH= 10.5 b) neural at pH= 7 c) acidic at pH= 3.5.

Table (3.6): Values of percentage of Photo-degradation, rate, turnover number, turnover frequency, and quantum yield using 0.2 g of ZnO/Clay catalysts mixed with 100ml of 20 ppm 2CP contaminant solution under different pH media (acidic = 3.5, neutral = 7, and basic = 10.5) for 120 min under direct sun light.

Sample	% photo-degradation	rate	T.N (10^{-3})	T.F (10^{-3})	Q.Y (10^{-25})
Acidic	28	0.0475	0.895	0.005	4.41
Neutral	56	0.094	1.8	0.01	8.87
Basic	66	0.112	2.125	0.012	10.5

3.4 Anthocyanin dye sensitization of ZnO/Clay prepared catalyst

Anthocyanin-sensitized **ZnO/Clay** catalyst used for the degradation of 100 ml 2CP contaminant solution in water under direct sun light with 0.0146 w/cm^2 intensity for 120 min. Different conditions were studied. Values of photo degradation percentage, overall rate, T.N, T.F and Q.Y were all calculated.

3.4.1 Effect of 2-Chlorophenol Concentration

Figures (3.20) shows the degradation experiment using different initial concentrations of 2CP solutions ranging from 10 ppm – 60 ppm, using 0.2 g dye-sensitized **ZnO/Clay** catalyst. Table (3.7) shows the contaminant degradation percentage decreases with increased concentration, however, the rate, T.F and Q.Y of 2CP degradation increased with increased initial

65

concentration. Indicates the catalyst efficiency and activity did not affected by concentration.
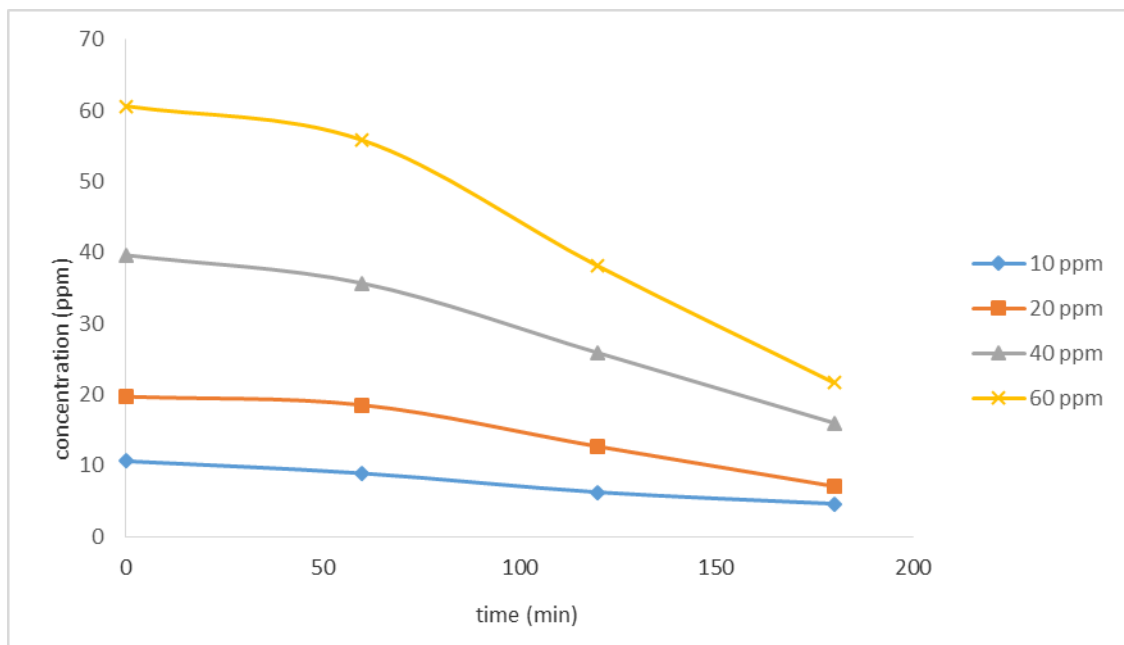
Figure (3.20): Effect of 2CP concentration on degradation reaction: a) 10 ppm b) 20 ppm c) 40 ppm d) 60 ppm. All reaction were conducted using 0.2 g of anthocyanin/ZnO/Clay composite catalyst at room temperature under direct sun light for 120 min.

Table (3.7): Values of percentage of Photo-degradation, rate of reaction, turnover number, turnover frequency, and quantum yield using 0.2g of anthocyanin/ZnO/Clay catalysts mixed with 100ml of different concentrations of 2CP contaminant solution.

Initial 2CP concentration (ppm)	% photo-degradation	rate	T.N (10^{-3})	T.F (10^{-3})	Q.Y (10^{-25})
10	56	0.18	0.95	0.0053	4.7
20	64	0.431	2	0.011	9.86
40	50	0.68	3.2	0.018	15.7
60	44	0.873	4.25	0.024	21.0

3.4.2 Effect of dye sensitized ZnO/Clay catalyst loading

Figure (3.21) shows the photo catalytic degradation experiments using different amounts of prepared **Anthocyanin/ZnO/Clay** catalyst (0.05-0.2g ZnO). Similar to the previous results of **ZnO/Clay** catalyst, the degradation of 2CP increased with increasing catalyst amount. However, at higher amounts ZnO molecules screening the light, which reduce light penetration and lowering the catalyst efficiency.
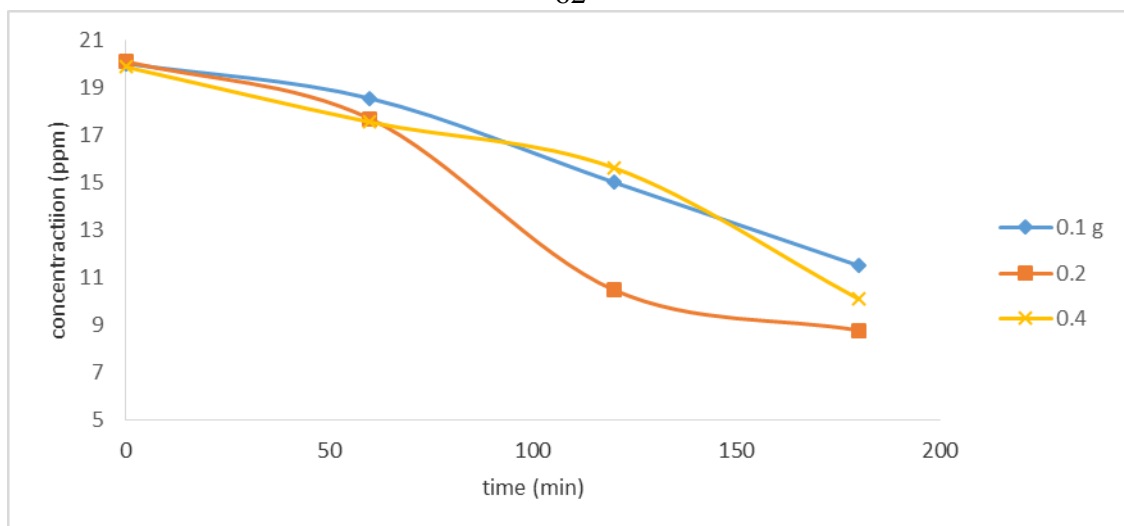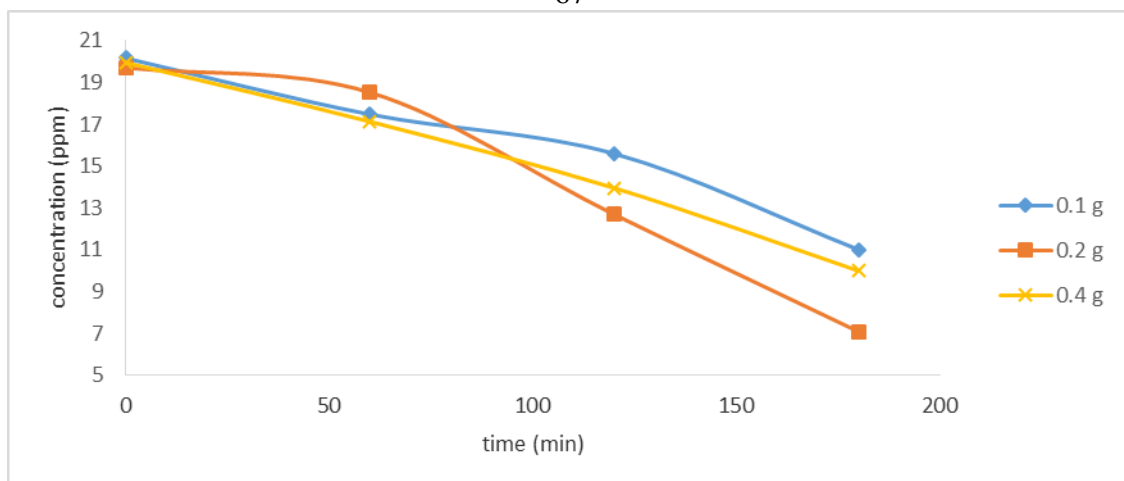
Figure (3.21): Effect of different amounts of anthocyanin/ZnO/Clay prepared catalyst: a) 0.1g b) 0.2 g c) 0.3 g d) 0.4 g. on to degradation reaction of 2CP under direct sun light at room temperature and natural pH.

Table (3.8): Values of percentage of Photo-degradation, rate, turnover number, turnover frequency, and quantum yield using variable amounts of ZnO/Clay catalysts mixed with 100ml of 20 ppm 2CP contaminant solution.

Amount of ZnO/Clay (g)	% photo-degradation	rate	T.N (10^{-3})	T.F (10^{-3})	Q.Y (10^{-25})
0.1	46	0.076	3	0.016	7.15
0.2	64	0.105	2	0.011	9.86
0.4	50	0.082	0.8	0.0044	7.8

3.4.3 Effect of pH on photo catalytic degradation of 2CP by sensitized ZnO/Clay catalyst

Figure (3.22) shows the degradation results for 2CP contaminant at different pH values (acidic =3.5, neutral =7, basic= 10.5) of solution mixture. Similar to **ZnO/Clay**, the basic medium showed the highest percentage of degradation followed by the neutral one, while the acidic medium showed lower photo degradation efficiency. T.N and Q.Y values confirm these results, as shown in Table (3.9). At acidic pH, ZnO catalyst undergo photo-corrosions and assumes the form ($ZnOH_2^+$) [74], while 2CP exists in the protonated form and acquire a positive charge, thus The photo degradation efficiency will be inhibited due to repulsion between protonated 2CP and ZnO catalyst surface at low pH.

At high pH values the dye itself may degrade, which require adding new portions of anthocyanin dye to recover catalyst efficiency. The dye also may degrade under photo degradation conditions.
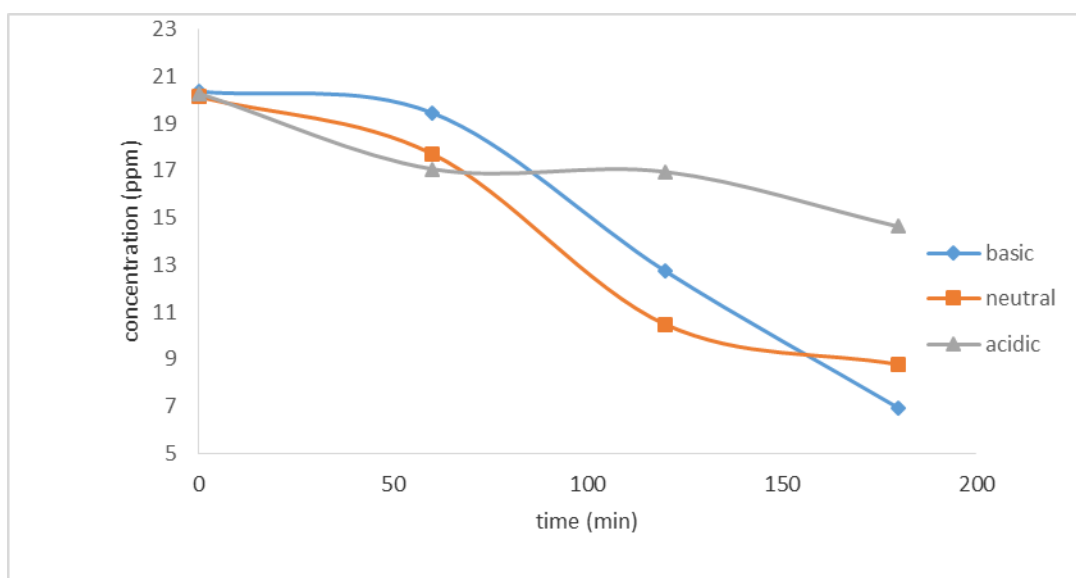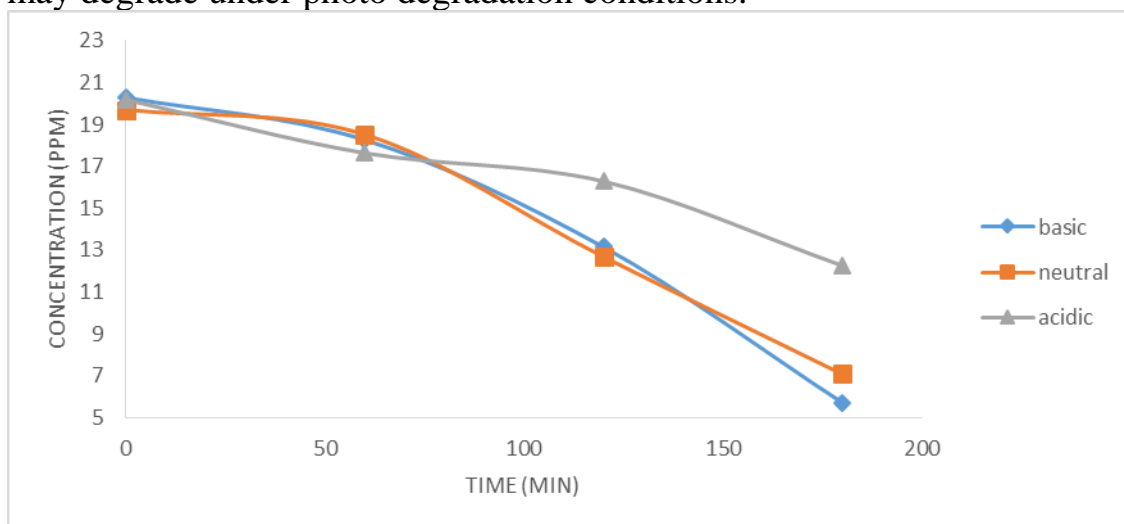

 Figure (3.22): Effect of pH on 2CP removal by 0.2 g of Anthocyanin/ZnO/Clay composite catalyst with time: a) basic at pH= 10.5 b) neural at pH= 7 c) acidic at pH= 3.5.

Table (3.9): Values of percentage of Photo-degradation, rate, turnover number, turnover frequency, and quantum yield using 0.2 g of anthocyanin/ZnO/Clay catalysts mixed with 100ml of 20 ppm 2CP contaminant solution under different pH media (acidic = 3.5, neutral = 7, and basic = 10.5) for 120 min under direct sun light.

Sample	% photo-degradation	rate	T.N (10^{-3})	T.F (10^{-3})	Q.Y (10^{-25})
Acidic	39	0.066	1.26	0.013	6.22
Neutral	64	0.105	2	0.011	9.86
basic	72	0.122	2.31	0.007	11.4

3.5 Comparison between Sensitized ZnO/Clay catalyst and non-sensitized ZnO/Clay photo catalysts

ZnO semiconductor has wide band gap (3.2 eV).Therefore, it can oxidize organic pollutants to simple non-toxic molecules. However, ZnO demands UV regions of solar light, which limits its degradation activity to only 4% of fallen sunlight [94]. Using alternative smaller band gap semiconductor is unfavorable due to its instability [66].

In this work, Anthocyanin dye was used to improve ZnO catalyst properties. Anthocyanin has a medium band gap of 2.3eV and absorbs visible regions of fallen sun light. This leads to electron-hole generation in the dye molecule. The electrons move from dye LUMO to ZnO conduction band, lead to generation of oxygen radical which reacts with hydrogen to produce hydroxyl radicals that oxidize the pollutant, as shown in figure

(3.23). Thus dye-sensitized composite **ZnO/Clay** catalyst uses both UV (by ZnO) and visible (by dye) regions together. This increases its photo catalytic degradation activity.
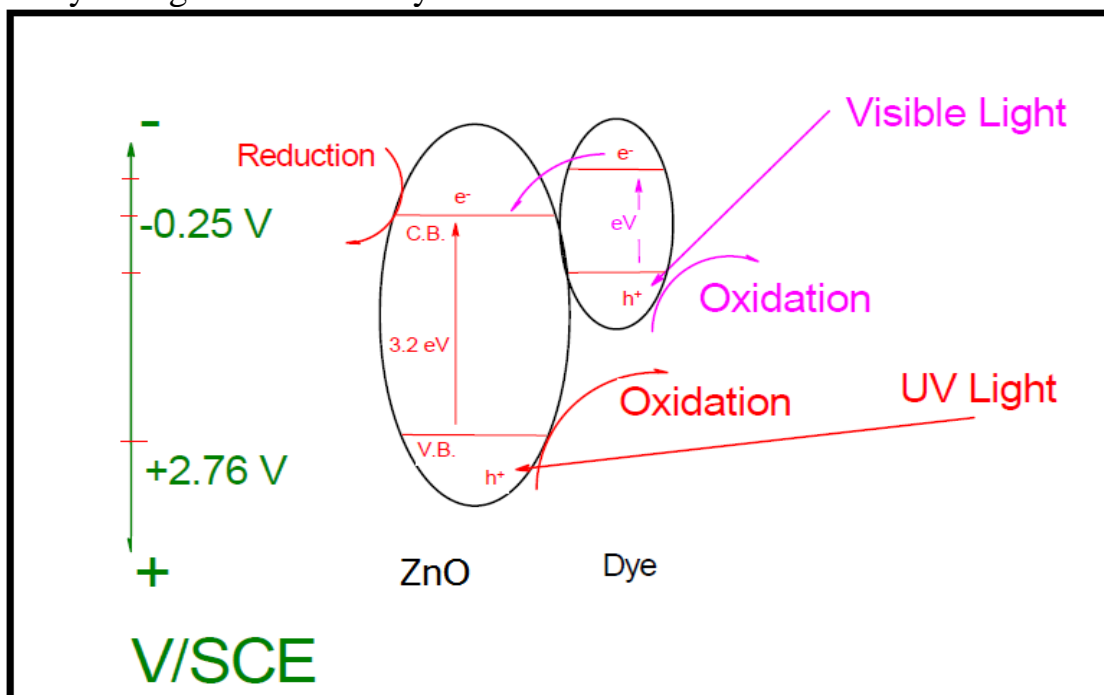
Figure (3.23): anthocyanin dye sensitized ZnO semiconductor excitation reaction.

This explain the increase in photo-degradation of 2CP pollutant when **Anthocyanin/ZnO/Clay** catalyst was used, as shown in Figure (3.24) and Table (3.10), indicates that anthocyanin-sensitization improved activity of the supported catalyst by ~ 10%.
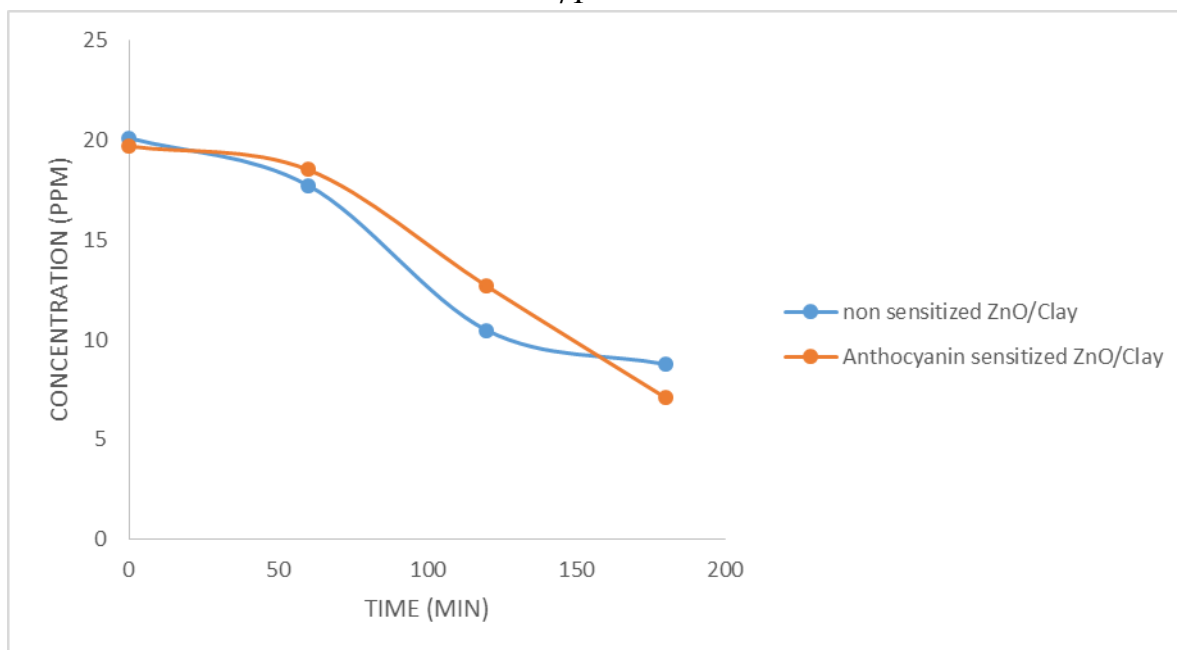
Figure (3.24): Photodegradation of 100 ml 20ppm 2CP solution using 0.2 g of a) non-sensitized ZnO/Clay b) sensitized ZnO/Clay catalysts under direct sun light for 120 min.

Table (3.10): Values of percentage of photo-degradation, rate, turnover number, turnover frequency, and quantum yield of 2-Chloropenol degradation reaction using anthocyanin sensitized and non-sensitized ZnO/Clay composite catalyst under direct sun light for 120 min.

Type of catalyst	% photo-degradation	rate	T.N (10^{-3})	T.F (10^{-3})	Q.Y (10^{-25})
Anthocyanin/ZnO/Clay	64	0.105	2	0.011	9.86
ZnO/Clay	56	0.094	1.8	0.01	8.87

3.6 Recovery of the ZnO/Clay catalyst and sensitized ZnO/Clay catalyst

The ability of catalyst recovery and reuse in photo-catalytic reactions is an important characteristic. This can contribute significantly to lowering the cost of water treatment processes, and prevents further water contamination.

 After the end of the photo-degradation reaction, the treated mixture was filtered, and catalysts were collected and reused for fresh reactions, following the same procedures. In another experiment the filtered sensitized composite catalyst was re-dyed in attempt to restore its efficiency as photo-catalyst under direct sun light.

The recovered composite catalyst used showed good but decreased efficiency (~41%) loss of 2CP. Re-dying the used catalyst was found to restore its efficiency to (~50%) loss of 2CP in each run. The lowering in contaminant removal by recovered catalyst is due to loss of catalyst while recovery.

Asper catalyst efficiency, in terms of T.N and T.F, the catalyst did not lose its efficiency on recovery and reuse, as shown in table (3.11).

Table (3.11): Efficiency of recovered anthocyanin-sensitized ZnO/Clay catalyst in photo-degradation reaction of 2-Chlorophenol.

Catalyst sample	% removal of 2-Chlorphenol	T.N (10^{-3})	T.F (10^{-3})
Fresh catalyst	64	2	0.01
Recovered catalyst	41	1.5	0.0125
Re-dying recover catalyst	50	1.87	0.015

3.7 Complete contaminant mineralization:

Figure (2.1) shows the HPLC chromatogram for fresh 100 ml of 20 ppm 2CP contaminant solution, with retention time ~ 6 min.
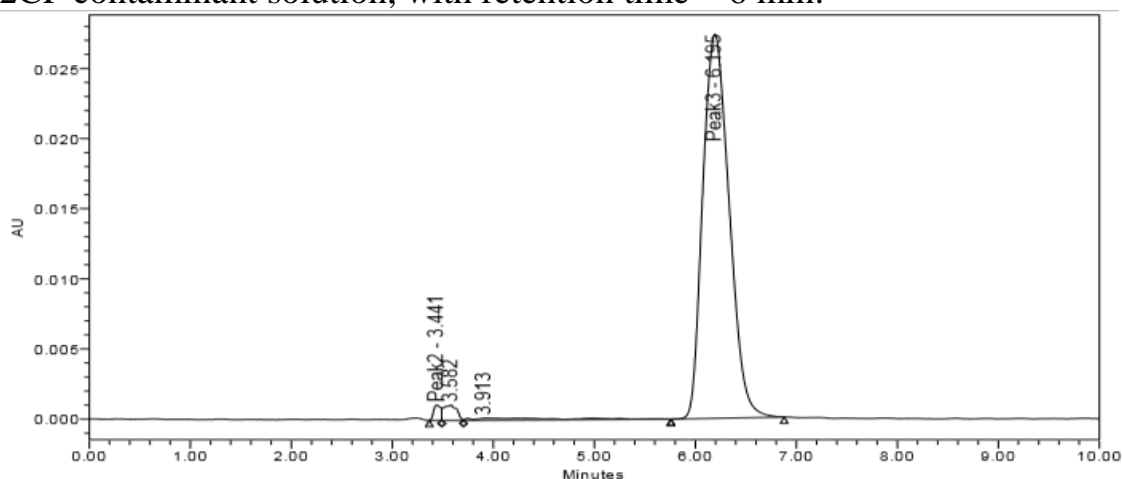
Figure (2.1): HPLC absorbance chromatogram of fresh prepared 20 ppm 2CP solution.

Figure (3.25) shows the HPLC chromatography of chloride ion (Cl⁻) solution (prepared by dissolving 0.1 g of KCl in 100 ml distilled water). The retention time for Cl⁻ ions is ~ 3.9 min.
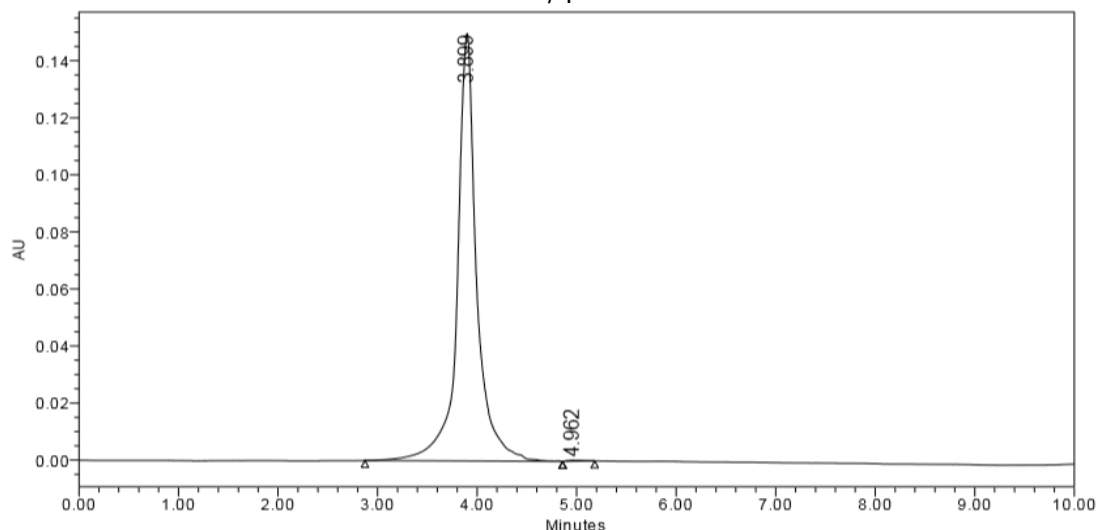
Figure (3.25): HPLC absorbance chromatogram of Cl⁻ ions in KCl aqueous solution.
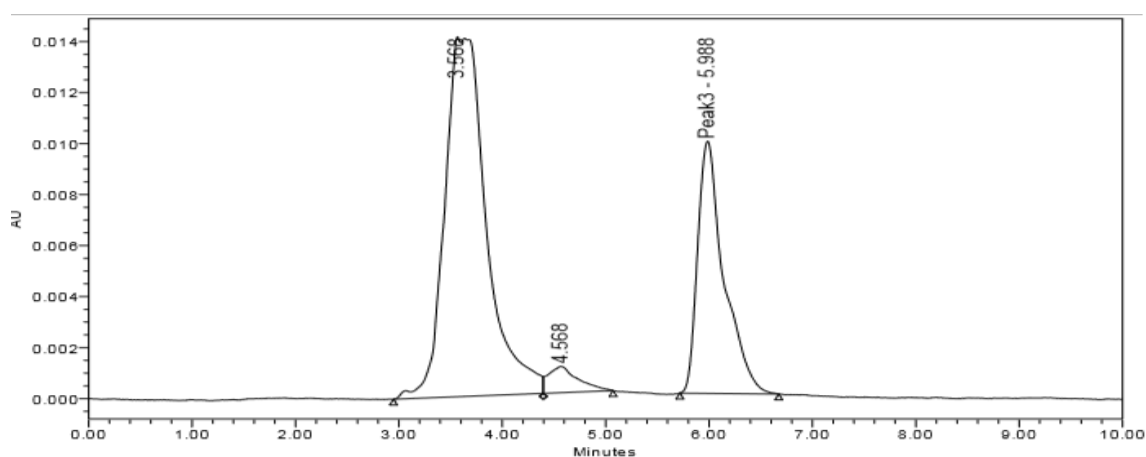
Figure (3.26): HPLC absorbance chromatogram of 7 ppm 2CP after treatment 120 min under direct sun light.

Figure (3. 26) show two major absorption peaks. At ~6 min (for 2CP contaminant), and at ~ 4 min peak (for Cl⁻ ion in solution mixture) [95, 96] as proofed in figure (3.25). The figures show decrease in 2CP peak area and increase in Cl⁻ ion peak area with time under photo degradation conditions. The HPLC results confirm the production of Cl⁻ ions at the expense of reacting 2CP. Moreover, no appearance for small organic

molecules is noticed in the chromatograms with time. Therefore, reacted 2CP molecules are being mineralized under photo degradation experimental conditions.

Chapter 4
Conclusion and Recommendations

Chapter 4

Conclusions and Recommendations

4.1 Conclusions

1. Photo degradation of 2-Chlorophenol contaminant was successfully studied under direct sun light using prepared **ZnO/Clay** composite catalyst.

2. Photo degradation of 2-Chlorophenol contaminant was successfully studied under direct sun light using anthocyanin sensitization **ZnO/Clay** composite catalyst.

3. Anthocyanin sensitized **ZnO/Clay** catalyst showed higher photo-degradation activity of 2-Chlorophenol contaminant than that of non-sensitized **ZnO/Clay** composite catalyst.

4. Adsorption and photo-degradation process of 2-Chlorophenol with both catalyst systems was affected by the pH.

5. Anthocyanin-sensitized composite catalyst functioned efficiently in presence and absence of UV light under sun light, this due to sensitizing effect of the anthocyanin dye.

6. XRD-characterization results of prepared **ZnO/Clay** catalyst showed no intercalation of ZnO nano-particles, only present onto the surface of clay molecules.

7. The catalysts (**ZnO/Clay**, and **Anthocyanin/ZnO/Clay**) were recovered and reused without losing their efficiency.

8. The results confirm the future value of using clay supported ZnO photo catalysts (with and without anthocyanin) in water purification process.

4.2 Recommendations for future work

1. Study the effect of **ZnO/Clay** composite catalyst in there sensitized and non-sensitized form on other contaminants.

2. Do more mechanistic study on photo degradation of 2CP by **ZnO/Clay** systems (trapping intermediates for example)

3. Using anthocyanin dye from sources other than Karkade with different colors, as sensitizers for **ZnO/Clay** catalyst.

4. Study the effect of changing temperature on photo-degradation of 2CP contaminant.

5. Determine the occurrence levels of 2-Chlorophenol pollution in Palestine waste and drinking water.

References

1. *Bastianoni, S.* **"A definition of pollution based on thermodynamic goal functions"** Ecological Modeling 113.1, 1998, 163-166.

2. *Wang, H and Ame, O.S.* **"Heavy Metal pollution in Air-Water-Soil-Plant system of Zhuzhou City, Hunan Province, China"** Water, Air, and soil Pollution 147, 2003, 79-107.

3. *Helmer, R, and Hespanohol, I.* **"Water Pollution Control: A Guide to the Use of Water Quality Management Principles"** London, E & FN Spon, 1997.

4. en.wikipedia.org/wiki/pollutant. (Accessed Feb.2018).

5. *Aksu, Z.* **"Application of biosorption for the removal of organic pollutants, a review"** Process Biochemistry 40.3, 2005, 997-1026.

6. en.wikipedia.org/wiki/Phenol. (Accessed Feb.2018).

7. *Stoughton, R. W.* **"A method for the quantitative determination of phenols"** Journal of Biological Chemistry 115.1, 1936, 293-298.

8. *Elsami, S., Nasseri, S., Yadollahi, S., Mesdaghinia, A., Vaezi, F., Nabizadeh, R., and Nazmara, S.* **"Photocatalytic degradation of Methyl TertButyl Ether (Mtbe) in conraminated water by ZnO Nano-particles"** Journal of Chemical Technology and Biotechnology 83, 2008, 1447-1453.

9. *Morrision, T.R., and Boyd, N. R.* **"Organic Chemistry"** 3rd ed, Boston, 1973, 55.

10. *Ohama. Y., and Van Gemert. D.* **"Application of Titanium Dioxide Photocatalysis to Construction Materials"** RILEM State-of-the-Art Reports 5, DOI 10.1007/978-94-007-1297-3_2, 2011, 5-10.

11. *Wiswanathan, B., Kannan, S., and Deka, R.C.* **"Catalysts and Surfaces characterization and techniques"** Narosa Publishing House, 2010, 3-8.

12. *Burce, C. Gates* **"Catalytic Chemistry"** Jon Wiley & Sons, Toronto, 1992, 1-3,265-392.

13. *Zyoud, A., Dwikat. M., Al-Shakhshir. S., Ateeq. S., Shteiwi. J., Zu'bi. A., and Hilal, S.H.* **"Natural dye-sensitized ZnO nano-particles as photo-catalysts in complete degradation of E. coli bacteria and their organic content"** Journal of Photochemistry and Photobiology, Volume 328, 2016, 207-216.

14. *Hilal, S.H., Al-Nour, M.Y.G., Zyoud, A., Helal, H.M., and Saadeddin, I.* **"Pristine and Supported ZnO based catalysts for Phenazopyridine degradation with Direct Solar light"** Solid State Sciences 12, 2010, 586-578.

15. *Knozinger, H., and Kochloefl, K.* **"Heterogeneous Catalysis and Solid Catalysts"** Ullmann's Encyclopedia of Industrial Chemistry, 2002.

16. *Goldman, J.L., Greenfield, S.A., Damle, Kingsbury, L.G., Northeim, M.C., and Truesdale, S.R.* **"Clay Liners for Waste Management Faciliti ES, Design, construction and Evaluation"** Gothard House Publications, New Jersey (U.S.A), 1990.

17. *Terry, R., Baker, and Murrell, L.L.* **"Novel Materials in Heterogeneous Catalysis"** ACS Symposium Series 437, 1990.

18. *Bedioui, F.* **"Zeolite Encapsulated and Clay Intercalated Metal Porphyrin Phthalocyanine and Schiff-Base Complexes as Models for Biomimetic Oxidation Catalysts, review"** Coordination Chemistry Reviews 144, 1995, 39-68.

19. *Madejova, J.* **"Review FTIR Techniques in Clay Mineral Studies"** Vibrational Spectroscopy 31, 2003, 1-10.

20. *Murray, H.H.* **"Developments in Clay Science: Applied Clay Mineralogy Occurrences, Processing and Application of kaolins, Bentonites, PalygorskiteSepiolite and Common Clays"** Elsevier 1st ed, 2007, 7-9.

21. *Uddin, F.* **"Clays, Nanoclays, and Montmorillonite Minerals"** Metallurgical and Material Transactions 39A, 2008, 2804-2814.

22. *Tsipursky, I.S., and Drits, A.V.* **"The Distribution of Octahedral Cations in the 2:1 Layers of Octahedral Symmetric Studied by Oblique Texture Electron Diffraction"** Clay minerals 19, 1984, 177-193.

23. https://pubs.usgs.gov/of/2001/of01-041/htmldocs/clays/kaogr.htm (Accessed Feb 2018).

24. *Tong, Z., Shichi, T., Guozhrnzhang, and Takag, K.* **"The Intercalation of metalloporphyrin Complex Anions into Layered Double Hydroxides"** Chemical Intermediate 29, 2003, 335-341.

25. *Constantino, V., Barbosa, C., Bizeto, M., and Dias, M.P.* **"Intercalation Compounds Involving Inorganic Layers Structures"** Anais da Academia Brasileira de Ciencias 72, 2000.

26. http://www.The freedictionary.com/clay. (Accessed Feb.2018).

27. *Al-Khalid, T., and El-Naas, M.H.* **"Aerobic Biodegradation of phenols, A Comprehensive review"** Environmental Science and Technology 42.16, 2012, 1631-1690.

28. *Michalowicz, J., and Duda, W.* **"Phenols Sources and Toxicity"** Journal on Environmental Studies 16.3, 2007, 347-362.

29. http://nj.gov/health/eoh/rtkweb/documents/fs/1659.pdf. (Accessed Feb.2018).

30. www.Chemblink.com/MSDS/MSDSFiles/95-97-8_Acros%20Organics.pdf. (Accessed Feb.2018).

31. www.sigmaaldrich.com/catalog/product/aldrich/536261?lang=en&region=IL. (Accessed Feb.2018)

32. *Turves, I., Rodriguez, I., Garcia, M., and Cela, R.* **"Determination of Chlorophenols in Drinking Water with High Resolution Gas Chromatography-Tandem Mass Spectrometry"** Journal of Chromatography A743.2, 1996, 282-292.

33. *Ahmed, S., Rasul, G., Marten, N., Brown, j., and Hashib, A.* **"Heterogeneous Photocatalytic Degradation of Phenols in wastewater, a review on Current Status and Developments"** Desalination 261.1, 2010, 3-18.

34. *Oswald, I.D., Allan, D.R., Motherwell, W.S., and Parsons, S.* **"Structures of The Monfluoro and Monochlorophenols at Low Temperature and High Pressure"** ActaCrystallogrphica Section B, Structural science 61.1, 2005, 69-79.

35. *Luukkonen, V.* **"Determination of Chlorophenols from Water by Solid Phase Micro-Extraction Ion Mobility Spectrometry"** Master Thesis, Lappeenranta University of Technology, 2013.

36. *Liao, C.H., Huang, C.W., and Wu, J.* **"Hydrogen Production from Semiconductor Based Photocatalysis via Water Splitting"** Catalysts 2.4, 2012, 490-516.

37. *Dabrowski, A.* **"Adsorption from Theory to Practice"** Advances in a Colloid and Interface Science 93, 2001, 135-224.

38. *Mittal, A.* **"Adsorption Kinetics of Removal of a Toxic Dye, Malachite Green, from Wastewater by Using Hen Feathers"** Journal of Hazardous Materials 133, 2006, 196-202.

39. *Rashed, N.M.* **"Adsorption Technique for The Removal of Organic Pollutants from Water and Wastewater, Organic Pollutants Monitoring, Risk, and Treatment"**, 2013.

40. *Figueroa, A.R, Leonard, A., and Mackay, A.A.* **"Modeling Tetracycline Antibiotic Sorption to Clays"** Environmental Science and Technology 38, 2004, 476-483.

41. *Essington, M., Lee, Y., and Seo.* **"Adsorption of Antibiotics by Montmorillonite and Kaolinite"** Soil Society of America Journal 74, 2010, 1577-1588.

42. *Avisar, D., Primor, O., Gozlan I., and Maman, H.* **"Sorption of Sulfonamides and Tetracycline to Montmorillonite Clay"** Water, Air and Soil Pollution 209, 2010, 439-450.

43. *Jia, D., Zhou, D., Wang, Y., Zhu, H., and Chen J.* **"Adsorption and Cosorption of Cu and Tetracycline on Two Soils with Different Characteristics"** Geoderma Journal 146, 2008, 224-230.

44. *Sassman, A.S., and Lee, S.L.* **"Sorption of Three Tetracycline by Several Soil: Assessing the Role of pH and Cation Exchange"** Environmental Science and Technology 39, 2005, 7452-7459.

45. *Ji, L., Chen, W., Duan, L., and Zhu, D.* **"Mechanisms for Strong Adsorption of Tetracycline to Carbon Nanotubes, A Comparative Study Using Activated Carbon and Graphite as Adsorbents"** Environmental Science and Technology 43, 2009, 2322-2327.

46. *Chen, W., and Huang, C.* **"Adsorption and Transformation of Tetracycline Antibiotics with Aluminum Oxide"** Chemosphere 79, 2010, 779-785.

47. *Geo, Y., Li, Y., Zhang, L., Huang, H., Hu, J., Shah, M.S., and Su, X.* **"Adsorption and Removal of Tetracycline Antibiotics from Aqueous Solution by Graphene Oxide"** Journal of Colloid and Interface Science 368, 2012, 540-546.

48. *Castleman, W.A., Toennies, P.J., Yamanouchi, K., and Zinth, W.* **"Homogenous Catalysis with Metal Complexes: Fundamentals and Applications"** Gheorghe Duca, Academy Sciences of Moldova, Chisinan Moldova 2.4, 2012, 54-61.

49. *Bhatkhande, S.D., Pangarkar, G.V., and Beenackers, A.A.* **"Photocatalytic degradation for Environmental Applications, a review"** Journal of Chemical Technology and Biotechnology 77.1, 2002, 102-116.

50. *Lindner, M., Theurich, J., and Bahnemann, D.* **"Photocatalytic Degradation of Organic Compounds: Accelerating the Process Efficiency"** Water Science and Technology 35.4, 1997, 79-86.

51. *Parida, M.K., and Parija, S.* **"Photocatalytic Degradation of Phenol Under Solar Radiation Using Microwave Irradiation Zinc Oxide"** Solar Energy 80.8, 2006, 1048-1054.

52. *Ibhadon, O.A., and Fitzpatrick, B.* **"Heterogeneous Catalysis: Recent Advances and Applications"** Catalysts 3.1, 2013, 189-218.

53. *Nath, K.R., Zain, F.M., and Kadhum, A.H.* **"Photocatalysis, A Novel Approach for Solving Various Environmental and Disinfection Problems: a brief review"** Journal of Applied Sciences Research 8.8, 2012, 4147-4155.

54. *Al-Daqqa, N.* **"ZnO/Montmorillonite Nanoparticles as a Photo Degradation Catalyst and Adsorbent for Tetracycline in water"** Master Thesis, An-Najah National University, 2014.

55. *Hejjawi, S.* **"TiO$_2$ and ZnO Photocatalysts for Degradation of Widespread Pharmaceutical Wastes"** Master Thesis, An-Najah national University, 2013.

56. *Oliveira, A., Saggioro, M.E., Moreria, C.J., Ferreria, V., and Pavesi, T.* **"Solar Photochemistry for Environmental Remediation,**

Advanced Oxidation Process for Industrial Wastewater Treatment" INTECH Open Access Publisher, 2012.

57. www.greenearthnanoscience.com/what-is-phtopcatalsyt. (Accessed Feb.2018).

58. *Radich, G.J., and Kamat, V.P.* **"Making Graphene Holey. Gold Nanoparticle Mediated Hydroxyl Radical Attack on Reduced Graphene Oxide"** American Chemical Society 7.6, 2013, 5546-5557.

59. *Kim, Y.J., Kim, H.S., Lee, H.H., Lee, K., Ma, W., Gong, X., and Heeger, J.A.* **"New Architecture for High Efficiency Polymer Photovoltaic Cells Using Solution Based Titanium Oxide as an Optical Spacer"** Advanced materials 18.5, 2006, 572-576.

60. http://www.chem.purdue.edu/raftery/research/photocat.pdf. (Accessed Feb.2018).

61. *Meng. Z., and Juan. Z.* **"Wastewater treatment by photocatalytic oxidation of Nano-ZnO"** Global Environmental Policy in Japan, No.12, 2008, 1-9.

62. *Battez, H.A., Gonzalez, R., Viesca, L.J., Fernandez, E.J., Fernandez, D.J., Machado, A., and Riba, J.* **"CuO, ZnO_2 and ZnO Nanoparticles as Antiwear Additive in Oil Lubricants"** Wear 265, 2008, 422-428.

63. *Brown, H.E.* **"Zinc Oxide Properties and Applications, International Lead Zinc"** Research Organization, New York, 1976.

64. *Janotti, A., and Van De Walle, G.C.* **"Fundamentals of Zinc Oxide as A Semiconductor"** Repots on Progress in Physics 72, 2009, 126-501.

65. *Wiberg, E., and Holleman, F.A.* **"Inorganic Chemistry"** Elsevier Chapter 23, 2001, 1291-1300.

66. *Portier, J., Hilal, H.S., Saadeddin, I., Hwang, S. J., Subramanian, M.A., and Campet, G.* **"Thermodynamic Correlations and Band gap Calculations in Metal Oxides"** Solid State Chemistry 32, 2004, 207–217.

67. *Yamazaki, E., Murayama, M., Nishikawa, N., Hashimoto, N., Shoyama, M., and Kurita, O.* **"Utilization of Natural Carotenoids as Photosensitizers for Dye-Sensitized Solar Cells"** Solar Energy *81,* 2007, 512-516.

68. *Kay, A., and Graetzel, M.* **"Research ArticleArtificial Photosynthesis, Photosensitization of Titania Solar Cells with Chlorophyll Derivatives and Related Natural Porphyrins"** Journal of Physical Chemistry 23**,** 1993, 6272–6277.

69. *Benjamin, S., Vaya, D., Punjabi, P.B., and Ameta, S. C.* **"Enhancing Photocatalytic Activity of Zinc Oxide By Coating with Some Natural Pigments"** Arabian Journal of Chemistry 4, 2011, 205-209.

70. *Sullivan, J.* **"Anthocyanin"** Carnivorous Plant Newsletter 27, 1998, 86-88.

71. *Chen, Z., Tang, Y., Zhang, L., and Luo, L.* **"Electrodeposited Nanoporous ZnO Films Exhibiting Enhanced Performance in Dye-Sensitized Solar Cells"** Electrochemistry Academy 51, 2006, 5870–5875.

72. *Ke, L., Bin Dolmanan, S., Shen, L., Pallathadk, P. K, Zhang, Z., Lai, D. M. Y., and Liu, H.* **"Degradation Mechanism of ZnO-Based Dye-Sensitized Solar Cells"** Solar Energy Material and Solar Cells 94, 2010, 323–326.

73. *Al-Nour, G.* **"Photocatalytic Degradation of Organic Contaminants in the Presence of Graphite Supported and Unsupported ZnO Modified with CdS Particles"** Master Thesis, An-Najah National University, 2009.

74. *Zorba, T.* **"Photocataytic Degradation of 2-Chlorophenol in Water with Direct Sun lightUsing Pristine and Kaolinite Supported ZnO"** Master Thesis, An-Najah National University, 2015.

75. http://www.nshtvn.org/ebook/molbio/Current%20Protocols/CPFAC/faf 0101.pdf. (Accessed Feb.2018)

76. *Ahmadiani. N., Robbins. R., Collins. T., and Giusti. M.* **"Molar absorptivity (ε) and spectral characteristics of cyanidin-based anthocyanins from red cabbage"** Food Chemistry Volume 197, Part A, 2016, 900-906.

77. *Zyoud, A., Zu'bi, A., Helal, M., Park, D., Campet, G., and Hilal, S.H* **"Optimizing Photo-Mineralization of Aqueous Methyl Orange by Nano-ZnO Catalyst Under Simulated Natural Conditions"** Iranian Journal of Environmental Health Science and Engineering, 2015, 2-5.

78. *Shan, F.K., Liu,G.X. Lee, W.J., and shin, B.C.* **"Stokes shift, blue shift and red shift of ZnO-based thin films deposited by pulsed-laser deposition"** Journal of Crystal Growth 291, 2006, 328-333.

79. *Eli. D., Owolabi. J., Olowomofe. G., and Jonathan. G.* **"Plasmon Enhanced Efficiency in Dye Sensitized Solar Cells Decorated with Size-Controlled Silver Nanoparticles Based on Anthocyanins as Light Harvesting Pigment"** Journal of Photonic Materials and Technology Volume 2, 2016, 6-13

80. *Karageorgou, P., and Manetas, Y.* **"The Importance of Being Red When Young: Anthocyanins and The Protection of Young Leaves of Quercus Coccifera from Insect Herbivory and Excess Light"** Tree Physiology 26, 2006, 613–621.

81. *Radzimaska, k.A., Markiewicz, E., and Jesionowaski, T.* **"Structural Characterization of ZnO Particles Obtained by the Emulsion Precipitation Method"** Journal of Nanomaterials 656353, 2012, 5-6.

82. *Handore, K., Bhavsar, S., Horne, A., Chhattise, P., and Pande, N.* **"Novel Green Route of Synthesis of ZnO Nanoparticles by Using Natural Biodegradable Polymer and Its Application as a Catalyst for Oxidation of Aldehydes"** Journal of Macromolecular Science Part A Pure and Applied Chemistry 967078, 2014, 942-944.

83. **"Synthesis and characterization of zinc oxide nanoparticles: Application to textiles as UV-absorbers".** Available from: https://www.researchgate.net/publication/226802367_Synthesis_and_c haracterization_of_zinc_oxide_nanoparticles_Application_to_textiles_a s_UV-absorbers. (Accessed Mar.2018).

84. *Chang, H., kao, J.M., Chen, H.C., Cho, C.K., and Lai, R.X.* **"Characterization of Natural Dye Extracted from Wormwood and**

Purple Cabbage for Dye-Sensitized Solar Cells" International Journal of Photoenergy 6346, 2013.

85. Shape factor (X-ray diffraction), U.S. Department of Energy, Office of Scientific and Technical Information, available from: http://www.osti.gov/engage/rrpedia/Shape_factor_%28Xray_diffraction%29#cite_note-0. (Accessed Mar.2018).

86. *Akhtar, M.J., Ahamed, M., Kumar, S., Khan, M.M., Ahmad, J., and Alrokayan, S.A.* **"Zinc oxide Nanoparticles Selectively Induce Apoptosis in Human Cancer Cells Through Reactive Oxygen Species"**, International Jourdnal of Nanomedicine, 2012.

87. https://en.wikipedia.org/wiki/Bragg%27s_law. (Accessed Mar.2018).

88. *Saleiro, T.G., and Holanda, F.N.J.* **"Processing of Red Ceramic Using a Fast Firing Cycle"** Ceramica 58, 2012.

89. *Mansour, W.* **"Hydrosilyation Reactions Catalyzed by Novel Metalloporphyrin Catalysts Intercalated Inside Clay Nano and Micro Particles"** Master Thesis, An-Najah National University, Palestine, 2013, 55-65.

90. www.tulane.edu/~sanelson/eens211/weathering&clayminerals. (Accessed Mar.2018).

91. *Porubcan, L.S., Serna, J.C., White, J., and Hem, S.L.* **"Mechanism of Adsorption of Clindamycin and Tetracycline by Montmorillonite"** Journal of Pharmaceutical Sciences 67, 1978, 1081-1087.

92. *Hermann, M.J.* **"Heterogeneous Photocatalysis: An Emerging Discipline Involving Multiphase Systems"** Catalysis today 24, 1995, 157-164.

93. *Palominos, A.R., Mondaca, A.M., Giraldo, A., Penuela, G., Perezmoya, M., and Mansilla, D.H.* **"Photocatalytic Oxidation of Antibiotic Tetracycline on TiO₂ and ZnO Suspension"** Catalysis Today 144, 2009, 100-105.

94. *Hamza, A., Fatuase, J., Waziri, S., and Ajayi, O.* **"Solar Photocatalytic Degradation of Phenol Using Nanosized ZnO and A-Fe₂O₃"** Journal of Chemical Engineering and Materials Science 4, 2013, 87-92.

95. https://chem.libretexts.org/Textbook_Maps/Analytical_Chemistry_Textbook_Maps/Map%3A_Analytical_Chemistry_2.0_(Harvey)/12_Chromatographic_and_Electrophoretic_Methods/12.6%3A_Other_Forms_of_Liquid_Chromatography. (Accessed Mar.2018).

96. http://www.sielc.com/Compound-Chloride.html. (Accessed Mar.2018).

جامعة النجاح الوطنية

كلية الدراسات العليا

إستخدام دقائق اكسيد الزنك النانونية المثبتة على الفخار الطبيعي لتنقية المياه من الهالوفينولات تحت أشعة الشمس المباشرة

إعداد

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ب

استخدام دقائق اكسيد الزنك الناونية المثبتة على الفخار الطبيعي لتنقية المياه من الهالوفينولات
تحت اشعة الشمس االمباشرة
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الخلاصة

تعتبر عملية التحطيم الضوئي والامتزاز من اكثر الطرق الحديثة فعالية في تنقية المياه من الملوثات الحيوية و الكيميائية. تعتمد عملية التحطيم الضوئي على وجود حفاز (أكسيد الزنك) الذي يعمل على امتصاص الاشعة الفوق بنفسجية لتحطيم المادة الملوثة (2-كلورفينول). طور الباحثون العديد من الانظمة التي تساعد و تزيد من حساسية هذا الحفاز تجاه الاشعة المرئية و بالتالي تمكنوا من استخدام اشعه الشمس المباشرة في عملة التحطيم الضوئي.

في هذا البحث تم دراسة التحطيم الضوئي لمركب 2-كلورفينول في الماء باستخدام دقائق أكسيد الزنك النانونية المثبتة على الفخار الطبيعي تحت اشعة الشمس المباشرة. كما تم دراسة تحسين حساسية أكسيد الزنك للضوء المرئي باستخدام صبغة الأنثوسيانين الطبيعية. تم تحقيق التحطيم الضوئي بواسطة كلا الحفازين في ظروف مختلفة (تأثير تركيز الملوثات⬚ كمية الحفاز⬚ و درجة الحموضة). و قد اظهر تحليل الحفاز (الغير مثبت والمثبت على جزيئات الفخار) بواسطة XRD و SEM تفرقاً و توزعاً جيداً لحبيبات اكسد الزنك بقطر يساوي 20 nm للحفاز الغير مدعم و 15.2 nm للحفاز المدعم. كما وتم اثبات وجود صبغة الانثوسيانين على سطح الحفاز و ارتباطها مع سطح الحفاز بشكل كيميائي. و اظهرت نتائج دراسة التحطيم الضوئي لمادة ال 2-كلورفينول ان نسبة التحطيم الاعلى كانت عند استخدام الحفاز المثبت و المحسن وتساوي 64%±0.01 على درجة حموضة ~ 7 و درجة حرارة 25 °C, بينما كانت تساوي ~ 56%±0.01 عند استخدام الحفاز المثبت غير المحسن عند نفس درجة الحموضة و الحرارة.

ج

اما فيما يخص دراسة امكانية اعادة استرجاع الحفاز و استخدامه مره اخرى في تحطيم عينات جديدة من 2-كلورفينول□ فقد اظهر الحفاز فعالية نسبية جيدة بعد فصله واعادة استخدامه. هذا و تبين من الدراسة انه يمكن اعادة تنشيط الحفاز باضافة محلول من الصبغة اليه ثانية بعد استخدامه.