

An-Najah National University

Faculty of Graduate Studies

**Insecticide imidacloprid degradation with solar light
catalyzed by Al-doped ZnO and pristine particles
supported on different solids**

By

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the Degree of Master of Chemistry, Faculty of Graduate Studies, at
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Dedication

To my father

To my mother

To my brother

And to my dear sisters

Acknowledgment

I would like to express my warm acknowledgment to my supervisors Prof. Hikmat Hilal and Dr. Ahed Zyoud for their support, help, guidance and encouragement. I would also thank technical staff at An-Najah National University labs especially Mr. Nafith Dweikat for his endless help.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان

Insecticide imidacloprid degradation with solar light catalyzed by Al-doped ZnO and pristine particles supported on different solids

أقر بأن ما شملت عليه الرسالة هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبلي لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة علمية أو بحثية.

Declaration

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

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التاريخ: 27 / 8 / 2020

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List of abbreviations

UV-Vis: Ultraviolet Visible

eV: Electron Volt

POPs: Persistence Organic Pollutants

K_{oc}: Organic Carbon Content to Water Partition Coefficient

K_{ow}: Octanol Water Coefficient

WHO: World Health Organization

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

GO: Graphene Oxide

e⁻ : Negative Electron

h⁺ : Positive Hole

AC: Activated Carbon

MONT: Montmorillonite

AZO: Al doped ZnO

MB: Methylene Blue

MO: Methyl Orange

XRD: X-Ray Diffraction

SEM: Scanning Electron Microscope

EDX: Energy Dispersive X-ray spectroscopy

PL: PhotoLuminescence

P_{ZC}: Point of Zero Charge

Deg. %: Degradation Percentage

QY: Quantum Yield

RQY: Relative Quantum Yield

TN: Turnover Number

TF: Turnover Frequency

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Abstract

ZnO nanoparticles were widely used as semiconductors for treatment of water from organic pollutants. Commercial and prepared ZnO nanoparticles were used in this work. ZnO nanoparticles were modified by doping with Al in different atomic percentages and supported on activated carbon (AC), Montmorillonite (MONT) and Glass. The photocatalytic activities of different systems were studied against *imidacloprid insecticide* which is highly used by agriculture sector in Palestine. The results indicate that Al doping and support have nearly no effect on ZnO band gap (3.2 - 3.3 eV) which has been measured by UV-Vis absorption and luminescence emission spectroscopy. From XRD results all systems show hexagonal wurtzite structure with no additional peaks in case of Al doping. However, in MONT supported system, MONT signals appeared. The particle sizes were increased by increasing Al atomic % and decreased by support. The morphology of pristine and Al-doped ZnO are regular spherical shaped where for ZnO@MONT spherical ZnO particles are distributed at plate-like MONT surface as SEM image show. Point of zero charge (P_{ZC}) for doped and supported systems were higher than pristine ZnO. The photocatalytic activity of commercial ZnO was better than the

prepared one. Factors affecting degradation process like imidacloprid concentration, catalyst loading, time of irradiation, pH and light intensity were determined, as 0.2 g catalyst per 100 ml of 20 ppm imidacloprid at pH 5.6 under light intensity similar to solar light intensity were the optimum parameters. For Al doping effect, the increase in Al content shows depression effect on photocatalytic activity, which reaches zero percentage at 10% of Al. The depression in activity was explained by catalyst surface charge, band gap and surface area. For supported systems no degradation occurred in MONT and glass, while high activity was shown with AC. ZnO stability decreased with increasing Al percent. AC support stabilized the system whereas MONT did not. The catalysts were also studied under visible light radiation and showed lower activity which indicates sensitization effect of some impurities in the solution. The results show that using pristine ZnO nanoparticles is advantageous over the Al-doped in photodegradation of *imidacloprid insecticide* in contaminated water. Using AC as supporting system for ZnO showed highest tendency to remove the contaminant.

Chapter One

Introduction

1.1. Water pollution with pesticides

Agriculture is one of the main economic and food production sectors in Palestine [1]. This sector heavily depends on pesticides, insecticides and herbicides for the crop improvement. Nearly 57% of agriculture in Palestinian lands totally depend on pesticides for crop control as 770 tons of pesticides were consumed in West Bank in 2007 [2, 3]. Researchers claim that less than 1% of consumed pesticides reach the target while the rest end up in the environment and pollute soil, air and mainly water [4]. According to their solubility in water, vapor pressure and adsorption properties these remaining pesticides may adsorb on soil, evaporate into air surrounded applied area, leach to ground water streams or run off with water and pollute surface water [5, 6].

1.1.1. Pesticides

Pesticides are classified according to their stability in water into two main types. Unstable pesticides degrade biologically by microorganisms, chemically by hydrolysis reaction in water or by photolysis reaction under light [7-9]. These pesticides do not accumulate in water and do not directly threaten environment. Other pesticides persist degradation process and are called persistent organic pollutants (POPs). They accumulate in the

environment with continuous use and cause harm to human and animals by infiltration through food chain [6, 8-10].

Pesticides that usually contaminate ground water have different properties such as high water solubility value ($> 30 \text{ mg/L}$), octanol – water coefficient (K_{ow}) less than 1, organic carbon content to water partition coefficient (K_{oc}) less than 300, hydrolysis half-life more than 25 weeks and photolysis half-life more than 1 week. In addition these pesticides usually are negatively charge or partially charged at moderate pH values [11].

1.1.2. Imidacloprid

Imidacloprid insecticide is a widely used insecticides for nearly 70 crops in 100 countries. It has a chemical name 1-[(6-chloro-3-pyridinyl)methyl]-N-nitro-2-imidazolidinimine with $\text{C}_9\text{H}_{10}\text{ClN}_5\text{O}_2$ and chemical structure as shown in Figure (1) [12, 13].

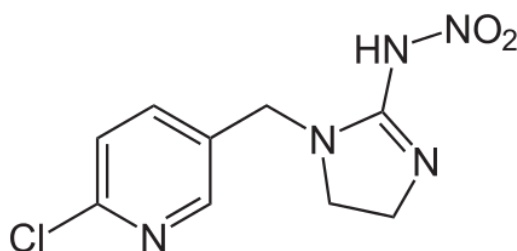


Figure (1): Chemical Structure of imidacloprid [12].

It is a synthetic derivative of nicotine and chemically classified as neonicotinoid, and belongs to chloronicotinyl nitroguanidine family [14]. This chemical affects insect nervous system by blocking nicotinergeric neural pathway that does not exist in warm blooded animals. It is thus not highly

toxic to human and is classified as type III insecticide by WHO [14, 15]. High dependence on this insecticide has harmful effect on honeybees [14].

Its properties [such as solubility in water 610 ppm, $K_{ow} = 0.57$, $K_{oc} = 156$ -960 (temperature dependent), half-life in soil 48-190 days and in water longer than 31 days] indicate that this insecticide is highly persistent to degradation. It favors ground and surface water pollution [14, 16, 17].

1.2. Treatment of contaminated water in imidacloprid

Due to heavily uncontrolled usage of pesticides in crop control locally and globally, pollution and side effects are a de facto. Therefore, it is necessary to treat polluted environment and water from pesticides [18]. Many methods were used for this purpose such as adsorption which is effective and widely used. But in this method pesticides just segregate on the surface of adsorbent without being treated. Other methods like biodegradation, chlorination and ozonation were also used, but in some cases they yield hazardous by-products. So there is a need for using method that ensures complete mineralization of pesticides in water [19]. The best method that achieve this aim is photocatalytic degradation, where contaminants are completely mineralized under solar radiation using safe, cheap, easy and efficient technique.

1.2.1. Photocatalytic degradation method

In photocatalytic degradation semiconductor metal oxides are normally used. When a suspension of semiconductor material in water is irradiated with a photon of energy higher than the semiconductor band gap, an electron (e^-) from valence band (HOMO) is excited to conduction band (LUMO) leaving a positive hole (h^+) in valence band. Electron-hole ($e^- h^+$) pair, have two pathways, the first one is the recombination where e^- returns back to valence band, without affecting photodegradation process. In the other pathway, the e^- acts as reductant that reduces O_2 into $O_2^\cdot$ radical, and the h^+ as oxidant that oxidizes OH^- and H_2O into $OH^\cdot$ radicals. The resulting radicals are very reactive species that are responsible for mineralization of organic pollutants [20]. This mechanism is shown in Figure (2). The resulting $e^- h^+$ pair can directly react with organic pollutants and cause its mineralization [21].

Semiconductors with wide band gaps, UV radiation is needed for electron excitation which is form 5-8% of solar light radiation. Therefore solar radiation can be used as safe, cheap and available driving force for this process [22].

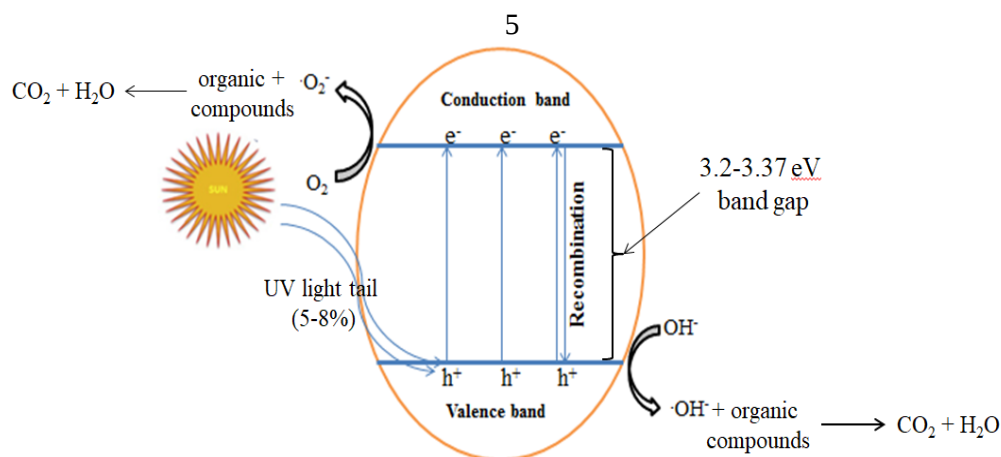


Figure (2): Photocatalytic degradation process using semiconductor.

Different materials were recognized as photocatalysts including CdS [23], ZnS [24], Fe_2O_3 [25], ZnO [24], TiO_2 [26], etc. The most promising materials from these are ZnO and TiO_2 due to their wide band gap (3.0-3.2 eV), good stability, safety and high oxidation power [27]. However, ZnO is preferable over TiO_2 due to its higher absorptivity of UV radiation fraction from sunlight which make it more efficient in photodegradation process under solar light radiation [28].

1.2.2. ZnO catalyst

The ZnO photocatalytic activity is limited to UV tail of solar radiation and can be inhibited by $e^- h^+$ recombination process. Therefore many efforts were attempted to improve ZnO photocatalytic efficiency including its sensitization with dye, doping with other materials, modification of its surface, controlling surface morphology or supporting on other materials [29-33].

1.2.2.1. Al doped ZnO catalyst

Various metals including Co, Ag, Mn, Pd, Ce and Al were used as dopants for ZnO to improve its photocatalytic efficiency [34-39]. High attention was paid to Al doping due to its special properties, availability and low price [40]. Many researchers synthesized Al doped ZnO nanoparticles and thin films for use in solar cells, gas sensors and photocatalysis [40-42]. Al usually enhance the ZnO efficiency as it increase catalyst surface area, enhance light adsorption, inhibit $e^- h^+$ recombination, increase adsorptivity of reactant on catalyst surface and reduction on the band gap resulted from extra electrons provided by Al atoms [38, 39, 43, 44].

Most of prepared Al doped ZnO nanoparticles and thin films show no change in their wurtzite crystal structure which indicates that Al displace Zn atom in the lattice and a decreases in the particle size due to differences in Al^{3+} and Zn^{2+} ionic radius. The blue shift in the band gap in most of cases is associated with Al amount due to decrease in particle size [40-42, 45-50]. However, some authors reported red shift by Al doping [43, 51, 52].

In the present work, different Al doping atomic percentages were used in ZnO to enhance ZnO efficiency in water remediation from imidacloprid insecticide.

1.2.2.2. Supported catalysts

Supporting catalyst on porous materials with large surface areas, is one way to improve efficiency by enhancing adsorption capacity which affects degradation process [53, 54]. It is also advantageous in catalyst recovery after degradation process and in preventing catalyst agglomeration during the degradation process [53, 55]. Many supporting systems were used for this aim like clay, glass and activated carbon.

Activated carbon (AC) is widely used as adsorbent for organic compounds in water treatment due to its high porosity and high surface area. This enhances the attractive process of organic contaminants and so enhances their adsorption capacity [56-59]. In addition it has inert nature that improves its application [59].

Clay and its different types are natural, environmentally friendly and cheap available adsorbents used for organics adsorption [60]. It consists of aluminosilicate layers and holds negative charge which enhances its ability to adsorb positive ions and polar molecules [61]. Its high adsorption capacity of organic compounds is related to hydrogen bonding, ion dipoles and dispersion force [62]. It also has high stability and high surface area [60]. Montmorillonite (MONT) is a clay type that we use in the present study for ZnO supporting in addition to activated carbon and glass surface.

1.3. Literature review

Many researches described photocatalysis degradation using semiconductor particles for imidacloprid treatment in water under UV, Vis or solar light irradiation. The most widely used catalysts are TiO_2 and ZnO in addition to their doped and supported forms.

1.3.1. Degradation of imidacloprid using TiO_2 photocatalysts

Using TiO_2 as catalyst *L. Gomathi Devi et al.* showed that 35% of imidacloprid were degraded under solar light radiation within 2 hours [63]. *S. Malato et al.* showed that complete degradation under solar light needed 122.3 minutes [64]. Under UV-A light *V. kitsion et al.* found that 64% of degradation needed 1 hour [20], whereas under Vis light (wavelength > 400 nm) *H. Heng et al.* showed that only 19% were degraded in 5 hours [65]. *A. Agurea et al.* studied the degradation of imidacloprid in its commercial formula Confidor under solar light, 7.5 hours were needed for complete degradation [66].

Different dopants were used with TiO_2 to enhance its catalytic efficiency in the removal of imidacloprid from water as dopant work as sink for exited electron that retard $e^- h^+$ recombination process [63]. *I. Grover et al.* and *J. Joice et al.* used doping to enhance degradation of imidacloprid under UV light [67, 68]. *I. Grover et al.* used titania nanotubes doped with Ag (0.5%) and achieved 75% of degradation over one hour higher by more than 4 times than TiO_2 [67]. *J. Joice et al.* used CNBF doped in TiO_2 to achieve

complete degradation over 5 hours under both Vis and UV lights [68]. Others used doped TiO_2 under Vis light and solar radiation. *L. Gomathi Devi et al* used different metals with different concentrations as dopant with TiO_2 including Th, Mo and V. The best enhanced efficiency among them was for 0.06% of Th doped TiO_2 which needed 2 hours for complete degradation under solar light radiation [63]. *F. Changgen et al.* used $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{La-TiO}_2$ for imidacloprid degradation under Vis light and achieved 98% degradation over 1 hour [69]. $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2\text{-In}_2\text{O}_3$ was used by *H. Heng et al.* and degraded 83% over 5 hours under visible light which is more than 4 times efficient than TiO_2 [65]. *F. Soltani-nazhed et al.* could nearly completely degrade imidacloprid in a period of 30 minutes using Graphene Oxide (GO)/ $\text{Fe}_3\text{O}_4/\text{TiO}_2\text{-NiO}$ [70].

To enhance TiO_2 efficiency two researchers supported TiO_2 on solid materials. *R. Zabar et al.* supported TiO_2 on glass sheets, 2 hours were needed for approximately complete degradation to happen under UV radiation [71]. *J. Tang et al.* supported TiO_2 on zeolite H-ZSM-5, 96.4% of imidacloprid were degraded over 40 minutes under UV radiation [72]. Literature findings are summarized in Table (1).

Table (1): Pristine, doped and supported TiO₂ catalysts used for imidacloprid degradation.

Catalyst used	Deg. %	Time Period (hours)	Light Source	Reference
TiO ₂ (P-25)	35	2	Solar	[63]
	64	1	UV-A	[20]
	100	2.03	Solar	[64]
TiO ₂ (In presence of formulating agent)	100	7.5	Natural sun	[66]
Th(0.06%)-TiO ₂	100	2	Solar	[63]
H ₃ PW ₁₂ O ₄₀ /La-TiO ₂	98.17	1	Vis	[69]
HPW/TiO ₂ -In ₂ O ₃	83	5	Vis	[65]
CNBF-TiO ₂	100	5	Vis or UV	[68]
GO/Fe ₃ O ₄ /TiO ₂ -NiO	97.47	0.5	Vis	[70]
TiO ₂ @glass sheets	98.8	2	UV	[71]
TiO@zeolite H-ZSM-5	94.4	0.67	UV	[72]

1.3.2. Degradation of imidacloprid using ZnO photocatalysts

ZnO and its doped form were used as catalysts for photodegradation of imidacloprid. *Z. Papp* used ZnO under natural sunlight and 37.9% were degraded over 1 hour [73]. *M. Kanwal et al.* used UV radiation for degradation and 62.3% were degraded over 1 hour [74]. *Z. Papp* and *M. Kanwal et al.* used Ag as dopant to enhance ZnO efficiency in imidacloprid degradation and achieve 66% of degradation over 1 hour under solar light radiation [73]. *M. Kanwal et al.* use different Ag concentrations, the highest efficiency was 3% Ag-ZnO which reached 92.75% under UV light in a period of 1 hour [74]. Literature results for ZnO catalyst systems are summarized in Table (2).

Table (2): ZnO and doped ZnO catalysts used for imidacloprid degradation.

Catalyst used	Degradation%	Time Period (hours)	Light Source	Reference
ZnO	37.4	1	Natural sun	[73]
	42		UV	[74]
Ag-ZnO	66.3		Natural sun	[73]
Ag(3%)-ZnO	92.75		UV	[74]
Ag(5%)-ZnO	84.1			
Ag(7%)-ZnO	82.6			

1.3.3. Al doped ZnO as photocatalyst

Hsiao et al. used Al doped ZnO (AZO) nanoparticles for photodegradation of methylene blue (MB) under UV light. A slightly enhanced in ZnO catalytic efficiency was observed due to increase in surface area in AZO nanoparticles [75]. *Lee et al.* applied AZO nanoparticles with different Al% doping concentrations for degradation of methylene blue (MB) and methyl orange (MO) under UV light. The best efficiency was for 3% of Al, were higher surface area enhanced adsorption process as a prerequisite for photodegradation process. The presence of Al retarded $e^- h^+$ recombination process which enhanced photodegradation efficiency [40]. *Zhang et al.* also used AZO nanoparticles with different Al% for degradation of MO under UV radiation and 10% of Al showed best efficiency with 30% degradation percentage in 30 minutes due to higher surface area corresponding to increase decrease in particle size and retarding $e^- h^+$ recombination process [49]. *Mahdavi et al.* showed the same efficiency over 1 hour using 5% Al AZO nanoparticles [52]. *Saber et al.* used AZO nanoparticles for naphthol green B degradation under solar radiation. The best efficiency was for 10%

of Al doping as complete mineralization happened within 6 hours which is 2.5 time better than undoped one [43].

1.4. Novelty of this work

Imidacloprid is highly used by agriculture sector in Palestine and causes contamination to water, where nearly 99% of applied pesticide migrates to environment and causes its pollution. Using photodegradation for water treatment is one of promising methods for water treatment. To our knowledge, Al doping of ZnO and using it at the same time as supported catalyst have not been studied before. This work is the first attempt to dope ZnO with Al and to support it onto Activated carbon, Montmorillonite and glass surface. The different systems will be assessed as photocatalysts for imidacloprid degradation in water for the first time.

1.5. Objectives

The aim of this work was to make new, safe, cheap and easy photocatalyst system for the degradation of aqueous imidacloprid, which is expected to be a widely spread water contaminant in Palestine. To achieve this objective, ZnO was doped with Al to enhance its activity in visible region. The ZnO systems were supported on different supporting substance and the resulting system were used for photoderadation of imidacloprid in water.

The following technical objectives will be achieved in this work:

1. Preparation and characterization of ZnO, Al-doped ZnO and ZnO@MONT, ZnO@Glass and ZnO@AC.
2. Studying and comparing the photocatalyst efficiency of pristine, Al-doped and supported systems in the degradation of imidacloprid.
3. Studying the effects of reaction parameters such as pH, contaminant concentration, catalyst loading amount, light intensity and time of irradiation on the photodegradation efficiency.

Chapter Two

Materials and Methods

2.1. Chemicals

ZnO (CAS No. 1314-13-2), $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (CAS No. 5970-45-6), Monmorillonite (CAS No. 1318-93-0), NaCl, acetic acid, HPLC grade water, HPLC grade methanol and HPLC grade acetonitrile were purchased from Sigma Aldrich. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was purchased from Riedel DeHaen. NaOH was purchased from Frutarom. Activated carbon from Merck. Confidor (Imidacloprid 250 g/l) was purchased from local market.

2.2. Catalysts preparation

ZnO nanopowder was prepared by the addition of $\text{Zn}(\text{OOCCH}_3)_2$ (250 ml, 1.0 M) solution to NaOH (250 ml, 2.5 M) solution at 55 °C temperature drop wise with continuous stirring. The resulting precipitate was decanted and washed with distilled water until liquid phase became neutral. The re-suspended solid was centrifuged, washed and dried. Resulting powder were annealed at 450 °C using an oven (Lindberg Hevi-Duty and mrc) to produce ZnO nanoparticles.

Al-doped ZnO nanopowder was prepared with the same procedure by using $\text{Zn}(\text{OOCCH}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ solution. Different $\text{Al}(\text{NO}_3)_3$ concentrations were used to have different doping densities.

ZnO@MONT was prepared by the addition of $\text{Zn}(\text{OOCCH}_3)_2$ solution (250 ml, 1.0 M) to a suspension of 10 g Monmorillonit in NaOH solution (250 ml, 2.5 M) with continuous stirring. The resulting composite solid was decanted and washed with distilled water until neutralization. Resulting solid was annealed at 450 °C. Al-doped ZnO@MONT was prepared using the same procedure by using $\text{Zn}(\text{OOCCH}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ solution. ZnO@AC was prepared using the same procedure by using AC. Annealing at 450°C was under N_2 .

Thin film of ZnO@Glass was prepared by preparing a suspension of prepared ZnO and spreading it on the bottom of beaker. The resulting system was dried and then annealed at 450 °C.

2.3. Catalysts characterization

2.3.1. XRD

XRD patterns were collected using a Philips XRD XPERT PRO diffractometer with $\text{Cu}\alpha$ to determine the crystal structure and particle size of the prepared catalysts systems. The measurements were made at UAE University, Al Ain, UAE.

2.3.2. SEM

SEM images were taken by a Joel Model JSM-6700F to determine the morphology of the prepared systems. This measurements were performed at UAE University, Al Ain, UAE.

2.3.3. UV-Vis and PL spectroscopy

UV-Vis spectra were measured for a suspensions of 0.1 g of different prepared catalysts in 50 ml distilled water on a Shimadzu UV-1800.

To measure band gap, emission fluorescence spectra were also measured for catalyst suspensions. The spectra were measured using a Perkin Elmer LS50 Luminescence spectrometer. Catalyst samples were excited at 294 nm.

2.3.4. Point of zero charge (P_{ZC})

The pH where catalyst surface has no charge P_{ZC} was determined by pH drift method [76]. A solution of 0.01 M NaCl was prepared and boiled to get rid of dissolved CO_2 . The pH_i of 6 samples of 50 ml of solution was adjusted to different pH values between 2 – 10 using 0.1 M NaOH and 0.1 M HCl solutions under N_2 gas. The catalyst (0.1 g) was added to each sample in capped glass vial and shaken for 6 h to reach equilibrium. The pH_f of the equilibrated solution was measured. The value of ΔpH ($pH_f - pH_i$) was plotted against pH_i and the x-intercept represents P_{ZC} value for each catalyst.

2.3.5. Catalyst composition

Energy-dispersive X-ray spectroscopy (EDX) elemental analysis was used to determine the elements and their relative proportion (atom % and

mass %) in each catalyst. This analysis was measured at UAE University, Al Ain, UAE.

Atomic absorption spectroscopy (AAS) was also used to determine ZnO% in each catalyst system. A sample of 0.1 g of each catalyst were digested with 5 ml of concentrated HCl (32%) and then diluted in 500 ml volumetric flask with water. 20 ml of this solution was diluted with water in 100 ml volumetric flask. Absorption value for each solution was measured using AAS Thermo scientific iCE 3000 series using Zn lamp. This value was used to calculate Zn concentration in each sample.

2.4. Photocatalytic degradation experiment

Catalyst sample was added to 100 ml of imidacloprid sample with known concentration at 5-6 pH value (similar to natural water), sonicated and stirred in water bath under simulated solar light (Philips, low voltage halogen lamp, 36V and 400 W) with light intensity 100000 lux (similar to natural sun light intensity) over 1 hour. Aliquots were taken at different times, centrifuged to separate catalyst and analyzed using UV-Vis spectrophotometer at wavelength 269.5 nm (maximum absorption wavelength of imidacloprid). The degradation efficiency was calculated from these data.

2.4.1. Control experiments

A sample of imidacloprid solution without catalyst was irradiated under simulated solar radiation to determine imidacloprid photolysis. Other

control experiments were made using imidacloprid solution with catalyst but without irradiation to determine adsorbed amount of imidacloprid at catalyst surface.

2.4.2. Commercial and prepared ZnO

To compare efficiency of prepared ZnO with commercial one, experiments were done using 100 ml of 20 ppm imidacloprid solution with 0.2 g of commercial or prepared ZnO nanoparticles under simulated solar light irradiation (100000 lux light intensity) for 1 hour.

2.4.3. Effect of reaction parameters

Different parameters affect photodegradation of imidacloprid using prepared ZnO nanoparticles include imidacloprid concentration, catalyst loading amount, time of irradiation, pH, light intensity, Al doping and supporting were studied.

2.4.3.1. Effect of imidacloprid concentration

Degradation experiments were done using 100 ml of different imidacloprid concentrations (10, 20 and 30 ppm) with 0.2 g of ZnO nanoparticles under simulated solar light irradiation (100000 lux light intensity) for 1 hour.

2.4.3.2. Effect of catalyst loading

Degradation experiments were made using 100 ml of 20 ppm imidacloprid solution with different ZnO amounts (0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g) under simulated solar light irradiation for 1 hour.

2.4.3.3. Effect of time of irradiation

Degradation experiments were made using 100 ml of 20 ppm imidacloprid solution with 0.2 g of ZnO nanoparticles under simulated solar light for different period of time (30, 60, 120, 180, 240 and 300 minutes).

2.4.3.4. Effect of pH

Degradation experiments were done using 100 ml of 20 ppm imidacloprid solution with 0.2 g of ZnO nanoparticles under simulated solar light irradiation for 1 hour. Initial pH of imidacloprid solution were adjusted to different values 2-10 using 0.1 M HCl and 0.1 M NaOH solutions.

2.4.3.5. Effect of light intensity

Degradation experiments were made using 100 ml of 20 ppm imidacloprid solution with 0.2 g of ZnO nanoparticles under light with intensity 50000 and 100000 lux for 1 hour. Light intensity was adjusted using Lux 102 light meter.

2.4.3.6. Effect of Al doping

To study effect of Al doping amount, Al-ZnO with different Al atomic% (0, 2, 4, 6, 8 and 10%) were used for degradation of 100 ml of 20 ppm imidacloprid under simulated solar light irradiation for 1 hour using 0.2 g of catalyst.

2.4.3.7. Effect of support type

To study effect of support type on degradation efficiency of supported ZnO, ZnO supported on different materials (glass, AC and MONT) were used for degradation of 100 ml of 20 ppm imidacloprid solution under simulated solar light irradiation for 1 hour using catalyst amount equivalent to 0.2 g ZnO. Samples of blank supporting materials were also used by carrying degradation process using naked materials of glass, AC and MONT under the same conditions.

2.4.4. HPLC analysis

To determine the presence of intermediates through degradation experiment and to confirm imidacloprid mineralization, samples of different time intervals (0, 30, 60, 120, 180, 240 and 300 minutes) of degradation, were analyzed using HPLC-DAD Water1525. The separation was achieved by C18 column (5 μ m, 4.6 $\times$ 250 mm cartridge). The mobile phase involved acetonitrile: 0.1% acetic acid (1:1) at flow rate 1.6 ml/min. The detection for imidacloprid was at 270 nm and injection volume is 20 μ l.

2.4.5. Zn²⁺ residues

To determine amount of Zn²⁺ dissolved during degradation experiments, a sample was taken after 1 hour, decanted, and the liquid was then analyzed by AAS using Zn lamp.

2.4.6. Catalyst reuse

For degradation sample, after 1 hour of radiation ZnO nanoparticles were settling in the bottom of the beaker, supernatant solution was decanted (no significant losses of ZnO was observed) and a fresh 100 ml of 20 ppm imidacloprid solution was added. The degradation process was repeated using the recovered catalyst.

2.4.7. Degradation under visible light radiation

Degradation experiments were made using 100 ml of 20 ppm imidacloprid with 0.2 g of ZnO nanoparticles and using cut-off filter to prevent UV fraction for simulated solar light to reach the degradation solution. The cut-off filter blocks radiations with wavelength shorter than 410 nm, leaving only visible light.

Chapter Three

Results

In this work different catalyst systems were used for photodegradation of imidacloprid insecticide in pre-contaminated water. These catalysts are commercial ZnO, prepared ZnO and ZnO doped with Al in different atomic% 0-10%. In addition different supported ZnO systems including Monmorillonite, activated carbon and glass supports were used.

3.1. Catalyst characterization

Different techniques were used for characterization of the used catalysts including structure, shape, band gap, charge and composition.

3.1.1. XRD patterns

Figure (3) shows XRD patterns for commercial and prepared ZnO nanoparticles. Sharp signals for both systems indicate crystallinity structure for ZnO nanoparticles. Diffraction signals of (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes in both catalysts match hexagonal wurtzite ZnO structure (JCPDS 36-1451). No other signals appear in both which indicate high purity of prepared nanoparticles. Prepared ZnO signals show some broadening compared to commercial one which indicate smaller particle size of prepared ZnO. Particle size for both catalysts were determined using Debye-Scherrer's equation:

$$d = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where, d : particle size ($\text{\AA}$)

λ : X-ray wavelength ($\text{\AA}$)

β : full width at half maximum for signal (radians)

θ : diffraction angle (degree).

Average particle size of commercial ZnO was 57.4 nm and for prepared one was 23.7 nm.

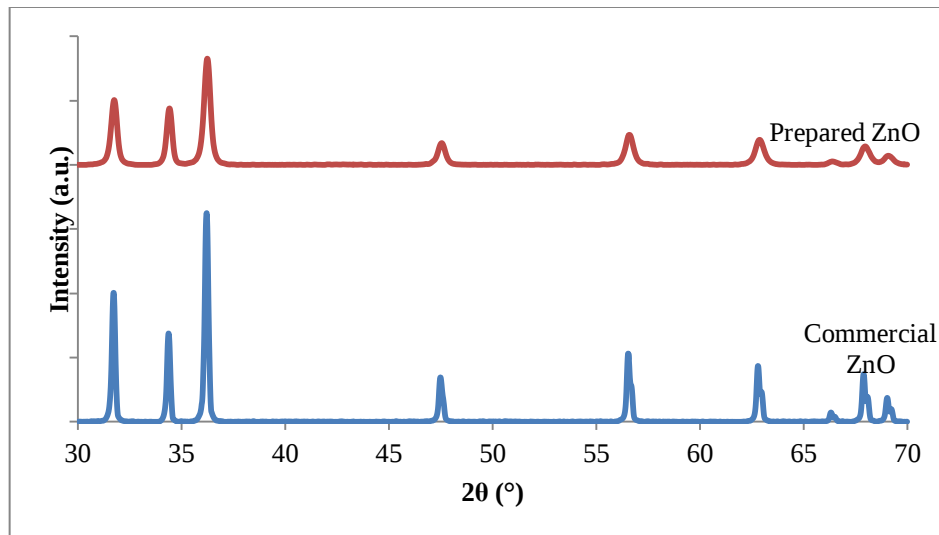


Figure (3): XRD patterns for commercial and prepared ZnO powders.

Figure (4) show XRD patterns for Al doped ZnO with different Al atomic%. All Al-ZnO nanoparticles with different Al atomic% show hexagonal wurtzite polycrystalline structure, where Al presence has no effect on the ZnO crystal structure. In all patterns no separate diffraction signal for Al_2O_3 appears which was expected to appear due to Al doping. The presence of Al cause an increase in ZnO particle size which is highly marked with higher Al% ($>6\%$) as shown in Table (3).

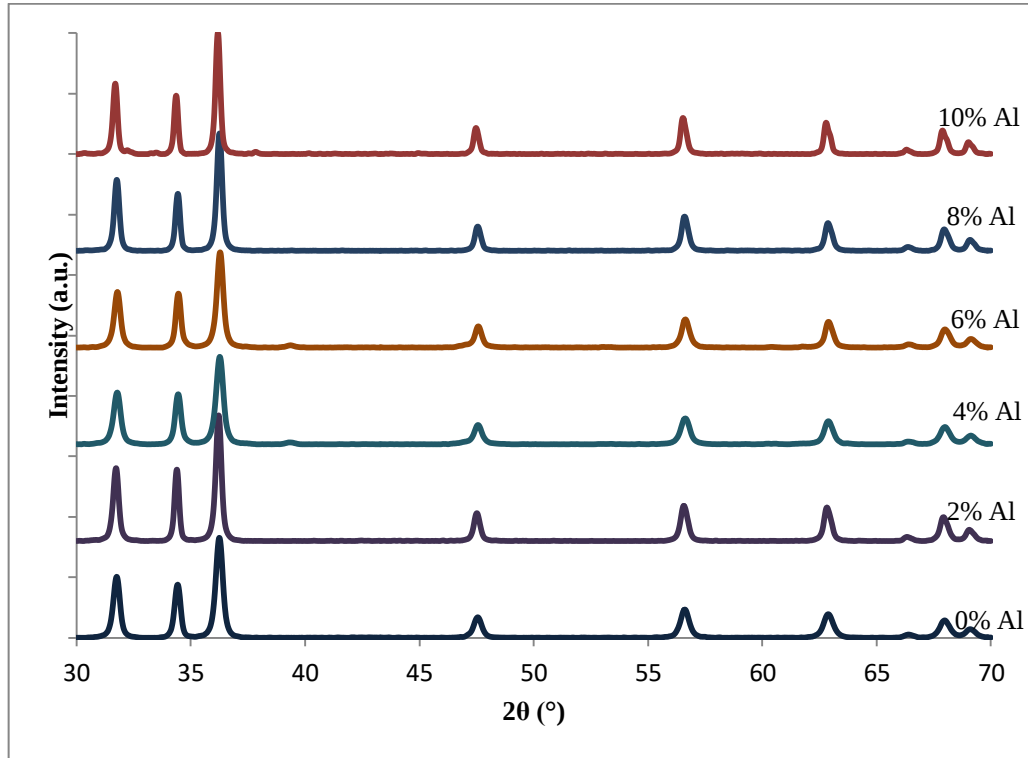


Figure (4): XRD patterns for Al doped ZnO with Al atomic% (0-10%).

Table (3): Particle size for Al-ZnO with Al atomic% (0-10%).

Al atomic%	0	2	4	6	8	10
Particle size (nm)	23.73	33.20	23.93	28.29	33.89	41.87

XRD patterns for MONT supported systems are shown in Figure (5). From MONT XRD pattern marked signal at 17.86, 26.66 and 33.49° are observed. For ZnO@MONT and Al-ZnO@MONT systems XRD diffraction angles match those of pristine-ZnO and MONT except 26.66° signal which is missing in the supported systems. No signals in both systems match Al₂O₃ XRD reference, while all signals match those of ZnO with same hexagonal wurtzite polycrystalline structure. By comparing ZnO signal intensities, the supported one show lower intensity and some broadening. This indicates decrease in particle size of ZnO in

ZnO@MONT and Al-ZnO@MONT, 11.9 and 18 nm respectively compared to 23.7 nm for pristine ZnO, as shown in Table (4).

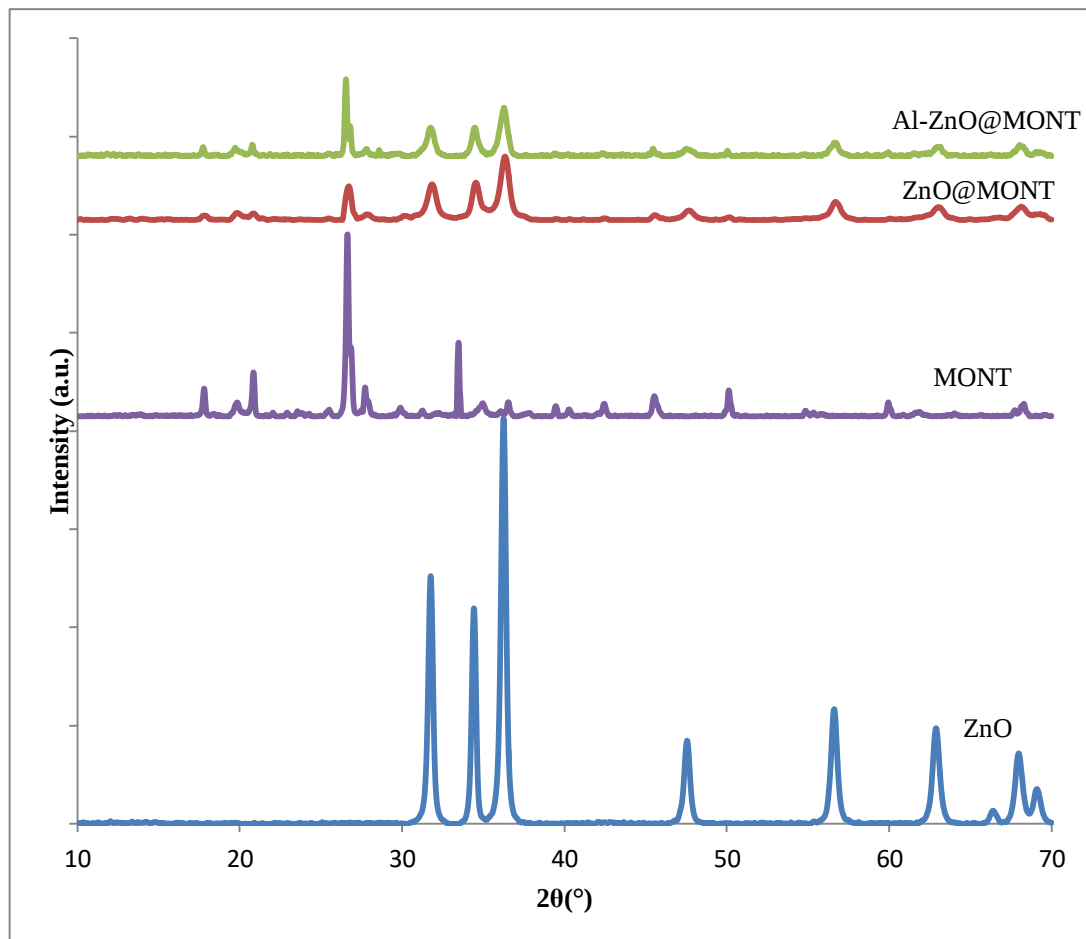


Figure (5): XRD patterns for ZnO, MONT, ZnO@MONT and Al-ZnO@MONT.

Table (4): Particle sizes for ZnO, MONT, ZnO@MONT and Al-ZnO@MONT.

Catalyst	ZnO particle size (nm)	MONT particle size (nm)
ZnO	23.7	-
MONT	-	47.6
ZnO@MONT	11.9	17.8
Al-ZnO@MONT	18.0	63.0

3.1.2. SEM images

Scanning electron microscope (SEM) images were used for catalyst morphology study. Figure (6) shows SEM images for commercial and prepared ZnO nanoparticles. Commercial ZnO particles have a uniform spherical structure and form agglomerates with homogenous distribution of 327.9 nm diameter. Prepared ZnO particles have uniform spherical structure with larger agglomerates homogenously distributed and have 483.3 nm diameter.

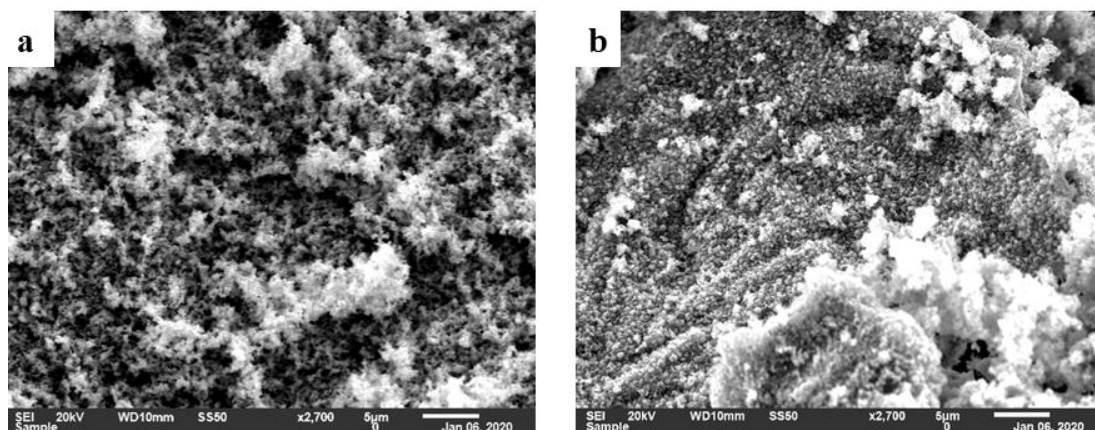


Figure (6): SEM images for (a) Commercial ZnO and (b) Prepared ZnO.

For Al doping effect on morphology, Figure (7) shows SEM images for different Al% doped system. For all Al atomic% of different systems, different agglomerate distributions appear with sizes of 200 – 700 nm, where larger agglomerate diameters appear for Al atomic% > 6%.

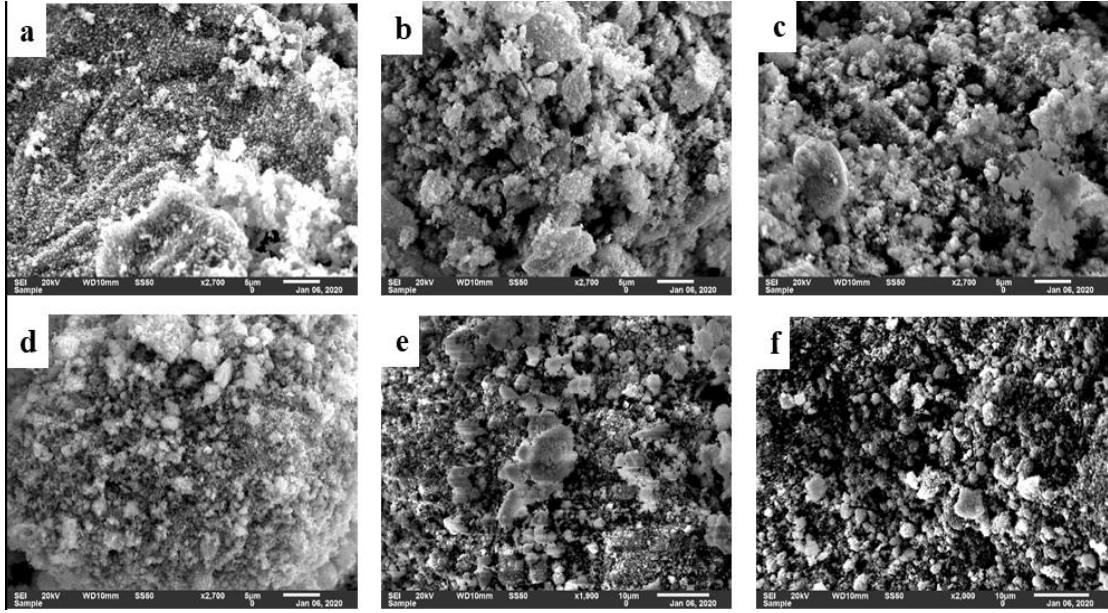


Figure (7): SEM images for (a) ZnO, (b) Al(2%)-ZnO, (c) Al(4%)-ZnO, (d) Al(6%)-ZnO, (e) Al(8%)-ZnO and (f) Al(10%)-ZnO.

For supported system, SEM images of ZnO, Al-ZnO, MONT, ZnO@MONT and Al-ZnO@MONT are shown in Figure (8). MONT has smooth flat plate structure where ZnO@MONT and Al-ZnO@MONT have rough surface structure. The diameter for MONT plates is $6.667\mu\text{m}$. For MONT supported ZnO and Al-ZnO the diameters are 5.44 and $3.91\mu\text{m}$, respectively. The diameter of ZnO agglomerates at MONT surface is around 350 nm .

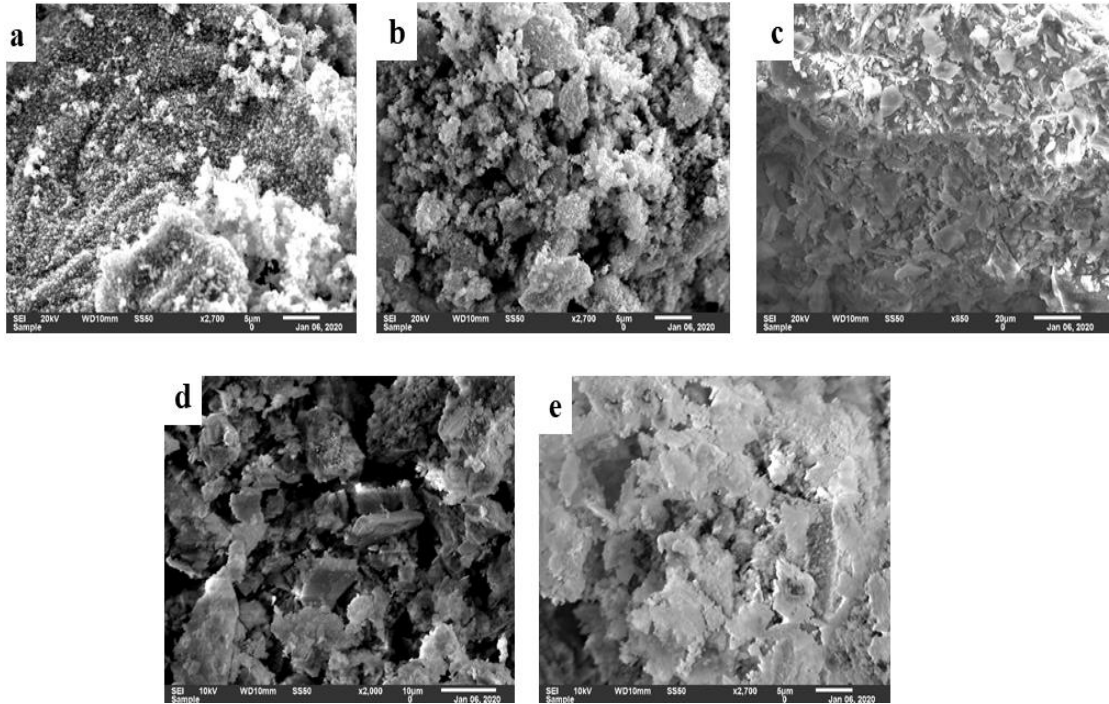


Figure (8): SEM images for (a) ZnO, (b) Al-ZnO, (c) MONT, (d) ZnO@MONT and (e) Al-ZnO@MONT.

3.1.3. UV-Vis and PL spectra

To determine band gap of different nanoparticles, absorption and emission spectra for nanoparticles were collected. From UV-Vis spectrum and PL spectrum band gap energy (E_g) was found using the following relation:

$$E_g = 1240 / \text{maximum wavelength (nm)}$$

Figure (9) shows UV-Vis spectra for commercial and prepared ZnO nanoparticles where both have same maximum wavelength with band gap 3.3 eV, as shown in Table (5). Figure (10) for Al-ZnO spectra shows that different Al atomic% have no significant differ in the band gap of ZnO which is 3.3 eV. Supporting ZnO@MONT causes a slight blue shift on

ZnO band gap to 3.35 eV, as shown in Figure (11), whereas ZnO@AC has no shift in ZnO band gap as shown in Figure (12).

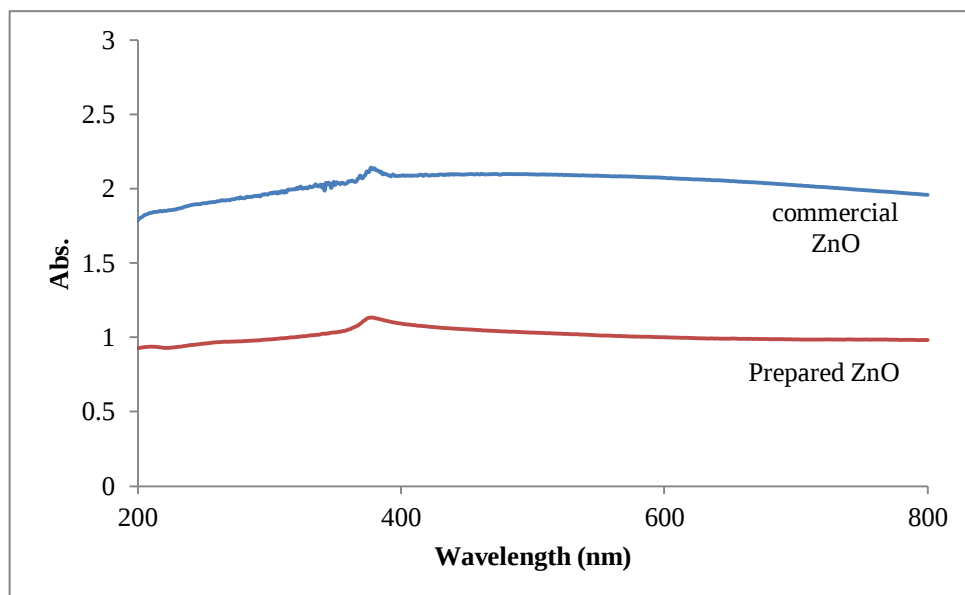


Figure (9): UV-Vis spectra for commercial and prepared ZnO nanoparticles.

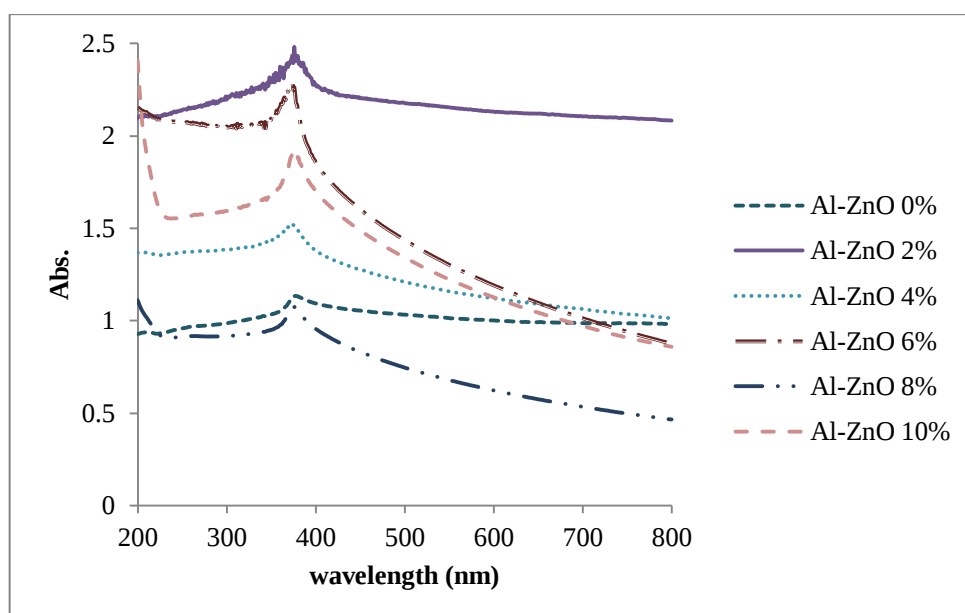


Figure (10): UV-Vis spectra for Al-ZnO nanoparticles with Al atomic% (0-10%).

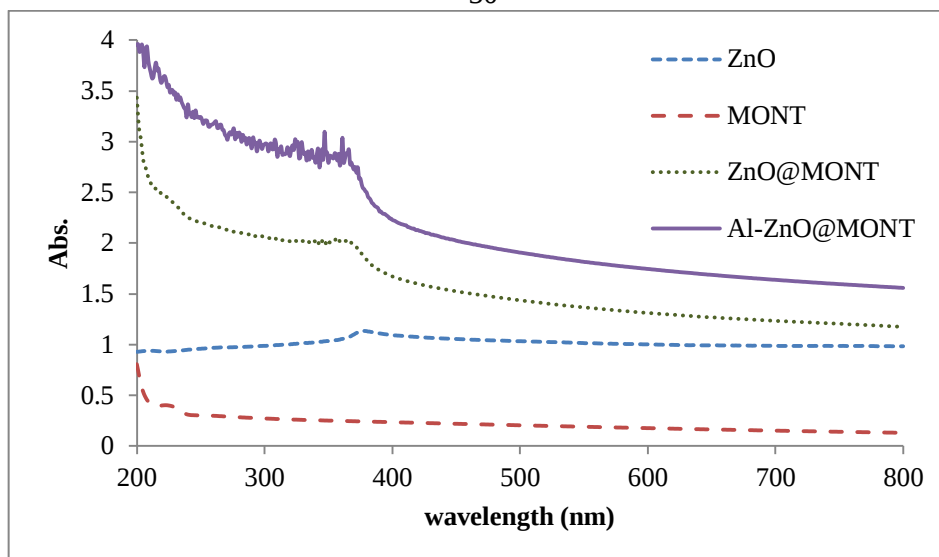


Figure (11): UV-Vis spectra for MONT, ZnO, ZnO@MONT and Al-ZnO@MONT.

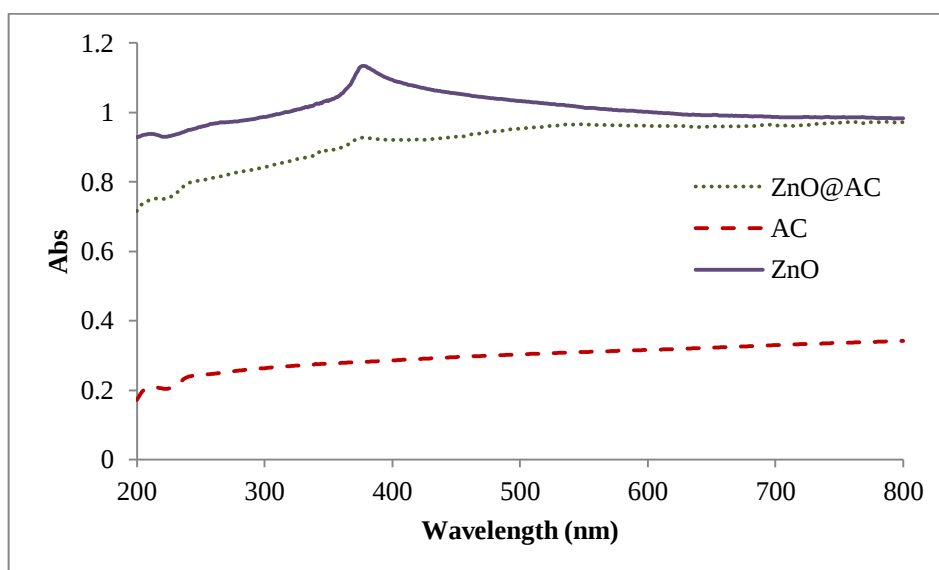


Figure (12): UV-Vis spectra for AC, ZnO and ZnO@AC.

Table (5): Values of UV-Vis spectral maximum wavelengths and band gap energies for catalysts.

Catalyst	Maximum wavelength (nm)	Band gap (eV)
commercial ZnO	377	3.29
prepared ZnO	377	3.29
Al:ZnO (2:98)	376	3.30
Al:ZnO (4:96)	374	3.32
Al:ZnO (6:94)	372	3.33
Al:ZnO (8:92)	376	3.30
Al:ZnO (10:90)	376	3.30
ZnO@MONT	370	3.35
Al-ZnO@MONT	371	3.34
ZnO@AC	377	3.29

UV-Vis spectral data were confirmed by photo luminescence (PL) spectra of different catalysts. PL emission spectra were collected for different catalysts at 294 nm excitation wavelength. The bands in spectra in range 350-400 nm represent catalyst emission wavelengths where other peaks and bands are related to oxygen vacancies which result from oxygen deficiencies.

As shown in Figure (13) for commercial and prepared ZnO nanoparticles nearly no significant differ in the band gap appears as shown in Table (6). For Al doping effect and supporting at MONT and AC there is nearly no effect on band gap, as shown in Figures (14), (15) and (16).

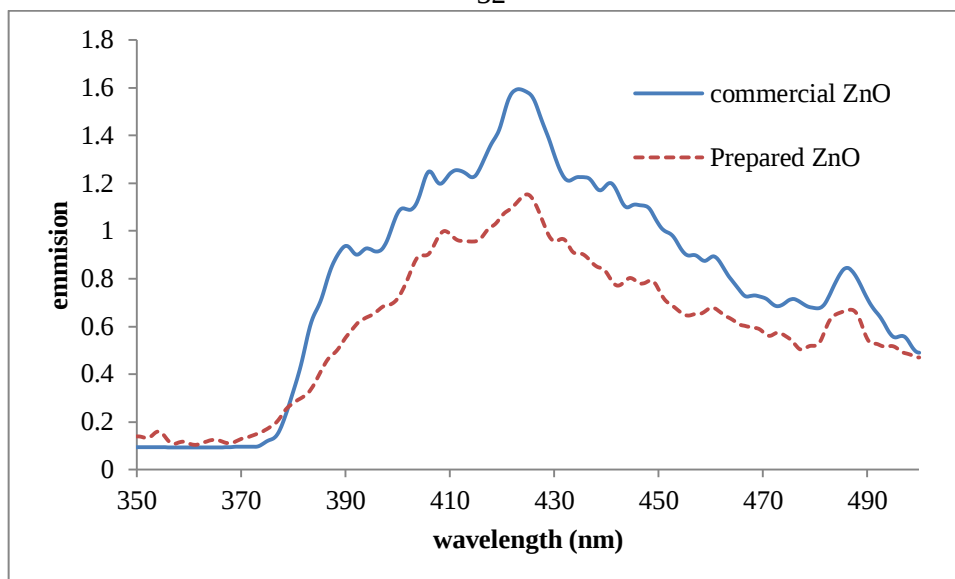


Figure (13): PL spectra for commercial and prepared ZnO nanoparticles.

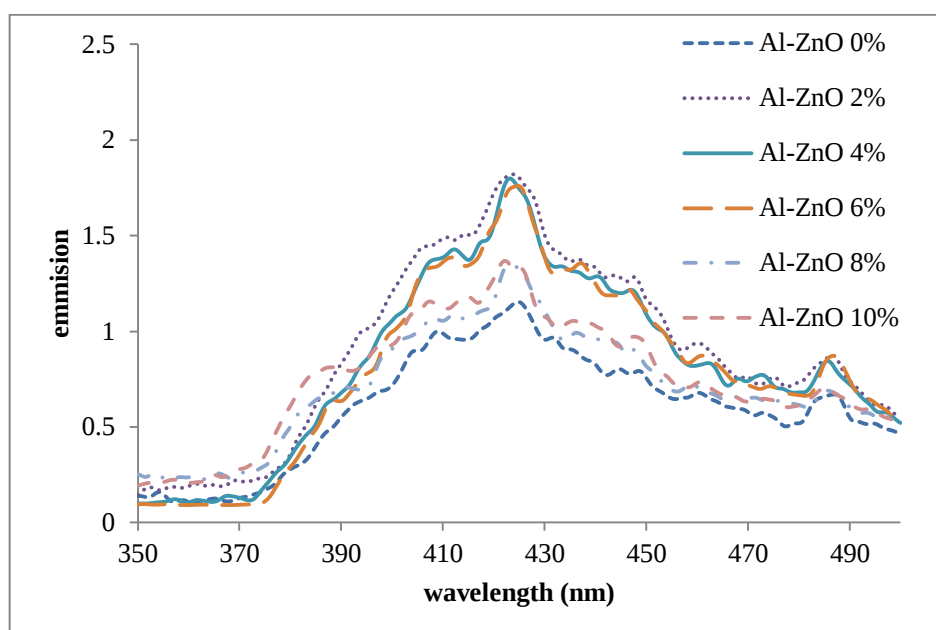


Figure (14): PL spectra for Al-ZnO nanoparticles with Al atomic% (0-10%).

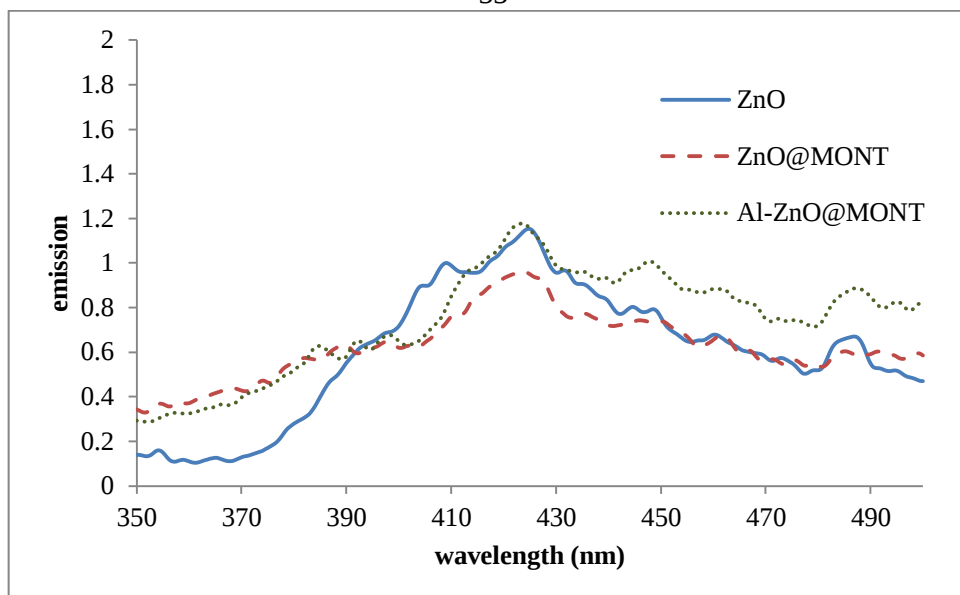


Figure (15): PL spectra for MONT, ZnO, ZnO@MONT and Al-ZnO@MONT.

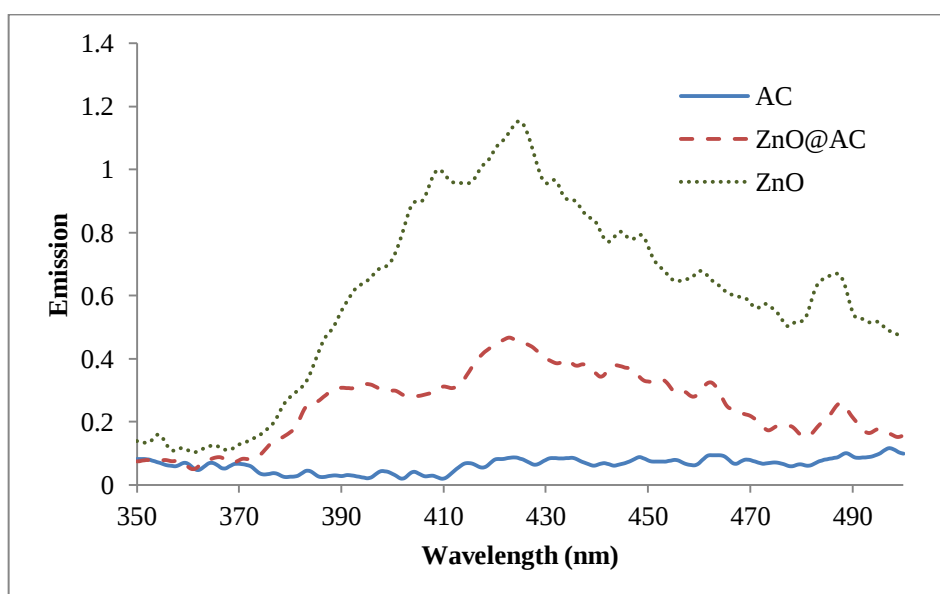


Figure (16): PL spectra for AC, ZnO and ZnO@AC.

Table (6): Values of PL maximum wavelengths and band gap energies for different catalysts.

Catalyst	Wavelength (nm)	Band Gap (eV)
commercial ZnO	390	3.18
prepared ZnO	388	3.20
Al:ZnO (2:98)	394	3.15
Al:ZnO (4:96)	387	3.20
Al:ZnO (6:94)	387	3.20
Al:ZnO (8:92)	382	3.25
Al:ZnO (10:90)	384	3.23
ZnO@MONT	362	3.43
Al-ZnO@MONT	365	3.40
ZnO@AC	388	3.20

3.1.4. P_{ZC}

Point of zero charge values for catalysts were determined by pH drift method. At P_{ZC} value catalyst surface has no charge. Below that the catalyst surface has a positive charge and above that the catalyst surface has negative charge. Point of zero charge for commercial and prepared pristine-ZnO powders were 7.5 and 8.3 respectively, compared to reference value 9.3 [76]. With Al doping, P_{ZC} increases as Al atomic% increases, as shown in Table (7) and Figure (17). For MONT and AC supports, P_{ZC} values 11.00 and 5.00 respectively. The supported catalysts with nanoparticles have P_{ZC} value of ~ 10 -11.

To determine attraction between imidacloprid and catalysts, comparisons between catalyst surface charge and imidacloprid charge are shown in Figures (18), (19) and (20). For imidacloprid which has two pKa values,

the molecule charge is positive below pK_{a1} , negative above pK_{a2} and neutral between pK_{a1} and pK_{a2} . At pH value where degradation is studied (pH of nearly 7) no strong attraction is expected between catalyst surface positive charge and neutral imidcloprid molecule.

Table (7): Point of zero charge for catalysts.

Catalyst	P_{ZC}	Catalyst	P_{ZC}
commercial ZnO	7.5	Al:ZnO (10:90)	11.0
prepared ZnO	8.3	MONT	11.0
Al:ZnO (2:98)	8.0	ZnO@MONT	10.5
Al:ZnO (4:96)	8.6	Al-ZnO@MONT	10.7
Al;ZnO (6:94)	8.8	AC	5.0
Al;ZnO (8:92)	9.4	ZnO@AC	9.6

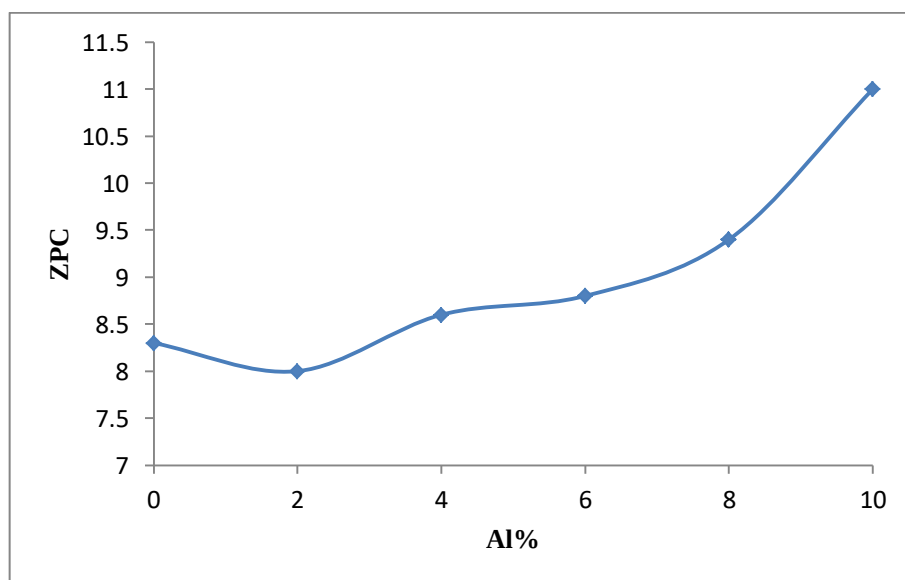


Figure (17): Variation of P_{ZC} of Al-ZnO with Al atomic% (0-10%).

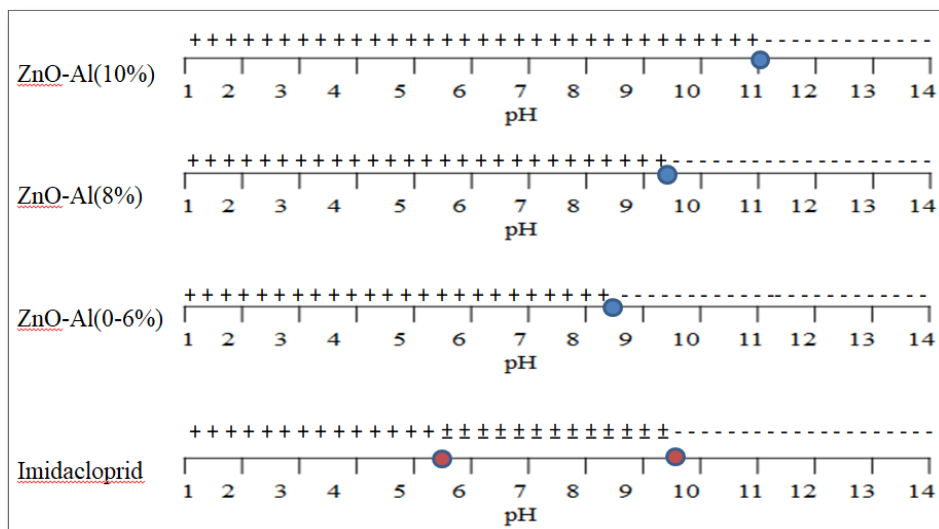


Figure (18): Values of P_{ZC} of imidacloprid and Al-ZnO with Al atomic% (0-10%).

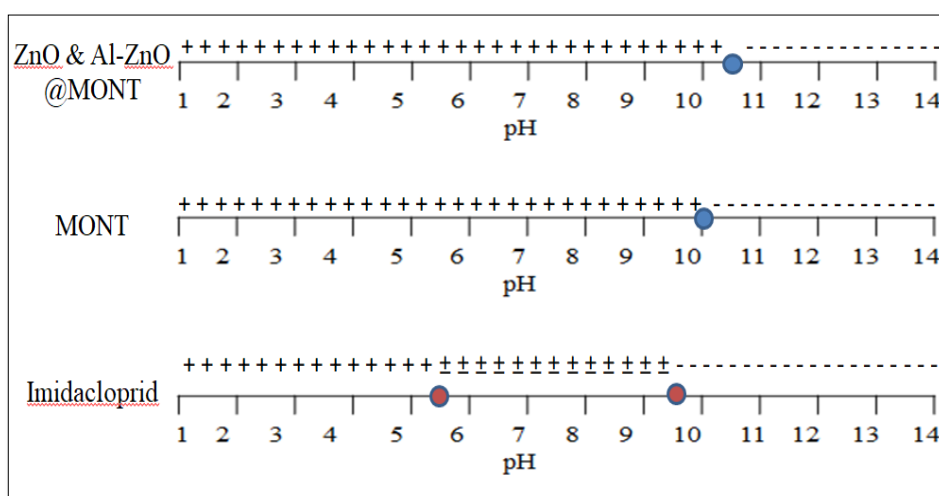


Figure (19): Values of P_{ZC} of imidacloprid, MONT, ZnO@MONT and Al-ZnO@MONT.

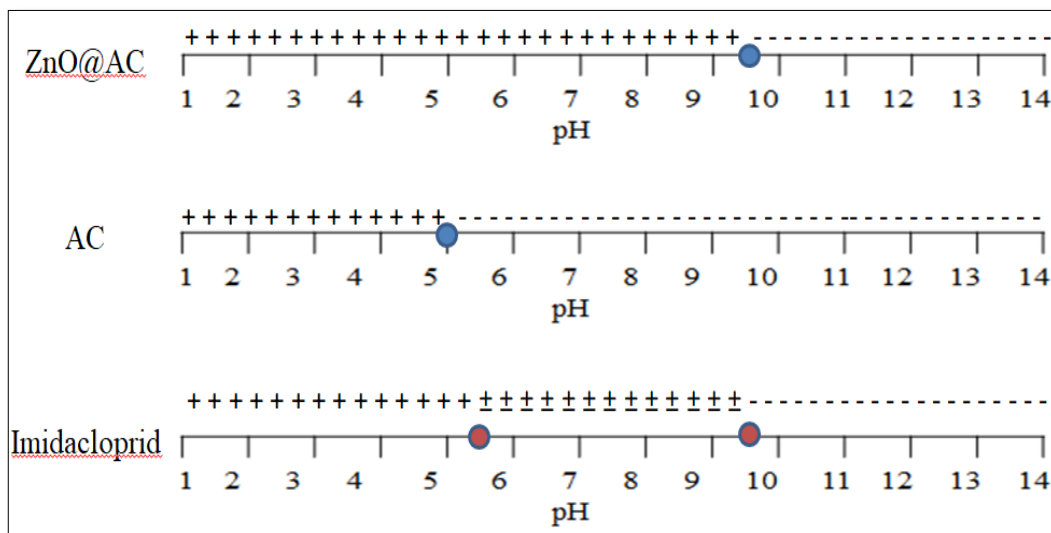


Figure (20): Values of P_{ZC} of imidacloprid, AC and ZnO@AC.

3.1.5. Catalyst composition

Actual ZnO% values in different catalysts were determined experimentally by energy-dispersive X-ray spectroscopy (EDX) analysis and atomic absorption spectroscopy (AAS). The values were compared to theoretical values in Table (8). Accepted trend in both EDX and AAS results is observed but these values are different from theoretical values.

Table (8): Experimental and theoretical ZnO% values in different catalysts.

Catalyst	ZnO%		
	EDX	AAS	Theoretical
commercial ZnO	86.12	95.32	100.00
Al:ZnO (0:100)	99.76	89.53	100.00
Al:ZnO (2:98)	91.81	88.77	98.74
Al:ZnO (4:96)	80.23	83.68	97.46
Al:ZnO (6:94)	75.48	89.70	96.15
Al:ZnO (8:92)	75.32	72.23	94.83
Al:ZnO (10:90)	68.92	63.30	93.49
MONT	0.00	0.17	0.00
ZnO@MONT	53.52	38.58	44.20
Al-ZnO@MONT	41.14	40.41	43.70
AC	-	0.13	0.00
ZnO@AC	-	69.33	50.00

3.2. Photocatalytic degradation experiments

Photocatalytic degradation experiments were carried out using prepared, pristine ZnO in imidacloprid solution under simulated solar radiation. To evaluate degradation process, degradation percentage (Deg.%), turnover number (TN), turnover frequency (TF), quantum yield (QY) and relative quantum yield (RQY) were calculated.

3.2.1. Control experiments

Two control experiments were carried out using 100 ml of 20 ppm imidacloprid solution. First control experiment was carried out under solar light radiation without catalyst to determine imidacloprid losses by photolysis process. As shown in Table (9), no losses of imidacloprid are observed over 1 hour by photolysis process. The other experiment were

carried out with 0.2 g of commercial and prepared ZnO powders in dark to control adsorption of imidacloprid on catalyst surfaces. No adsorption happened in both catalysts over 1 hour, as shown in Table (9).

Table (9): Contaminant removal % of imidacloprid over 1 hour by photolysis and by adsorption.

Control experiment	Contaminant Removal %
Photolysis (light without catalyst)	~ 0
Adsorption (commercial ZnO without light)	~ 0
Adsorption (prepared ZnO without light)	~ 0

*Experiments were done using 100 ml of 20 ppm imidacloprid at pH 5.6 and room temperature for 1 hour.

3.2.2. Commercial and prepared ZnO

By comparing efficiency of commercial and prepared ZnO in photocatalytic degradation of imidacloprid, commercial ZnO show higher activity than prepared one as shown in Table (10).

Table (10): Values of Deg.%, TN, TF, QY and RQY for degradation of imidacloprid using commercial and prepared ZnO.

Catalyst	Deg. %	TN (10^{-4})	TF (10^{-6}) min^{-1}	QY(10^{-4}) molecule/photon	RQY (10^{-25}) photon $^{-1}$
Commercial ZnO	27.98	9.479	15.798	2.451	1.632
Prepared ZnO	13.3	4.8	7.9	1.3436	0.8857

* Experiments were made using 0.2 g ZnO, 100 ml of 20 ppm imidacloprid solution, initial solution pH 5.6, room temperature, 1 hour and light intensity 100000 lux.

3.2.3. Effect of reaction parameters

3.2.3.1. Effect of imidacloprid concentration

To determine optimum imidacloprid concentration, degradation experiments were carried out using 10, 20 and 30 ppm imidacloprid solutions using prepared ZnO powders. Results shown in Tables (11) indicate that 20 ppm is the optimum concentration for photodegradation where lower deg.% but higher catalyst efficiency for ZnO are shown.

Table (11): Values of Deg.%, TN, TF, QY and RQY for degradation of different imidacloprid concentrations using prepared ZnO.

Imidacloprid concentration (ppm)	Deg. %	TN (10^{-4})	TF (10^{-6}) min^{-1}	QY(10^{-4}) molecule/photon	RQY (10^{-25}) photon^{-1}
10	22.5	4.3	7.2	0.9362	0.63261
20	13.3	4.8	7.9	1.3436	0.8857
30	9.2	4.7	7.7	1.148	0.776

* Experiments were made using 0.2 g ZnO, 100 ml of imidacloprid solution, initial solution pH 5.6, room temperature, 1 hour and light intensity 100000 lux.

3.2.3.2. Effect of catalyst loading

To determine optimum mass of ZnO needed for degradation of imidacloprid solution, different masses of ZnO (0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g) were used for degradation of 20 ppm imidacloprid. As shown in Table (12), 0.2 g is the optimum amount of catalyst as this mass has highest degradation percentage and other catalyst parameters.

Table (12): Values of Deg.%, TN, TF, QY and RQY for degradation of imidacloprid solution using different masses of ZnO.

ZnO mass (g)	Deg. %	TN (10^{-4})	TF (10^{-6}) min ⁻¹	QY(10^{-4}) molecule/photon	RQY (10^{-25}) photon ⁻¹
0.05	2.20	3.075	5.124	0.2010	0.5431
0.10	5.52	3.776	6.293	0.4985	0.6710
0.15	6.42	3.035	5.058	0.5950	0.5362
0.20	13.30	4.810	7.900	1.3436	0.8857
0.25	7.74	2.182	3.637	0.7132	0.3855
0.30	6.70	1.517	2.529	0.5950	0.2681

*Experiments were made using 100 ml of 20 ppm imidacloprid solution, initial solution pH 5.6, room temperature, 1 hour and light intensity 100000 lux.

3.2.3.3. Effect of time of irradiation

To study time of irradiation needed for highest degradation efficiency of imidacloprid sample, 0.2 g prepared ZnO was used for degradation of 20 ppm imidacloprid. Values of deg.% increases with time and reached 53% after 5 hours. Results are shown in Table (13).

Table (13): Values of Deg.%, TN, TF, QY and RQY for degradation of imidacloprid using different times of irradiation.

Time of irradiation (min)	Deg. %	TN (10^{-4})	TF (10^{-6}) min ⁻¹	QY(10^{-4}) molecule/photon	RQY (10^{-25}) photon ⁻¹
30	6.20	0.190	0.632	1.186	0.318
60	10.9	3.316	5.526	1.038	0.278
120	25.6	7.895	6.579	1.233	0.331
180	37.0	11.527	6.404	1.202	0.322
240	46.7	14.527	6.053	1.136	0.305
300	53.0	16.421	5.474	1.028	0.276

*Experiments were made using 0.2 g ZnO, 100 ml of 20 imidacloprid solution, initial solution pH 5.6, room temperature and light intensity 100000 lux.

3.2.3.4. Effect of pH

To study the effect of pH on degradation process, imidacloprid solution with different pH values in the range 1.97-12 were used for degradation using prepared ZnO. As shown in Table (14), good degradation efficiency values are shown at pH 5.6, (the pH of this work). Slight decreases in degradation efficiency were observed in acidic and basic media. An increase in removal efficiency appears at higher basicity (pH 12).

Table (14): Values of Deg.%, TN, TF, QY and RQY for degradation of imidacloprid solution using prepared ZnO at different pH values.

pH of imidacloprid solution	Deg. %	TN (10^{-4})	TF (10^{-6}) min ⁻¹	QY(10^{-4}) molecule/photon	RQY (10^{-25}) photon ⁻¹
1.97	3.87	1.285	2.143	0.3395	0.2272
4.12	5.94	2.059	3.431	0.5409	0.3637
5.60	13.3	4.8	7.9	1.3436	0.8857
8.10	6.21	2.134	3.557	0.5608	0.377
9.93	1.18	3.523	5.872	0.9213	0.622
12.04	15.72	4.589	7.648	1.212	0.8107

* Experiments were made using 0.2 g ZnO, 100 ml of 20 ppm imidacloprid solution, room temperature, 1 hour and light intensity 100000 lux.

3.2.3.5. Effect of light intensity

To determine effect of light intensity, degradation experiment were carried out under 50000 and 100000 lux. As shown in Table (15), increasing light intensity enhances degradation process.

Table (15): Values of Deg.%, TN, TF, QY and RQY for degradation of imidacloprid using prepared ZnO under 50000 and 100000 lux.

light intensity (lux)	Deg. %	TN (10^{-4})	TF (10^{-6}) min^{-1}	QY(10^{-4}) molecule/photon	RQY (10^{-25}) photon^{-1}
50000	4.6	1.1	1.8	0.5577	0.3749
100000	13.3	4.8	7.9	1.3436	0.8857

* Experiments were made using 0.2 g ZnO, 100 ml of 20 ppm imidacloprid solution, initial solution pH 5.6, room temperature and 1 hour.

3.2.3.6. Effect of Al doping to ZnO

ZnO were doped with different Al atomic% values (2.0, 4.0, 6.0, 8.0 and 10%) in order to enhance its efficiency. Figure (21) and Table (16) indicate that the presence of Al decrease photocatalytic degradation efficiency of imidacloprid.

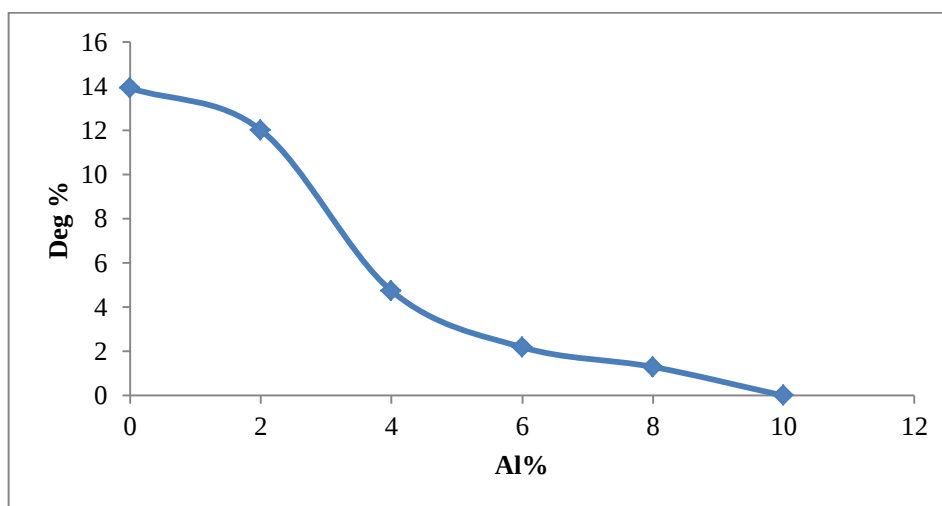


Figure (21): Degradation% of Al-ZnO with Al atomic% (0-10%).

Table (16): Values of Deg.%, TN, TF, QY and RQY for degradation of imidacloprid using Al-ZnO catalysts with different Al atomic% values.

Al%	Deg. %	TN (10 ⁻⁴)	TF (10 ⁻⁶) min ⁻¹	QY(10 ⁻⁴) molecule/photon	RQY (10 ⁻²⁵) photon ⁻¹
0	13.30	4.80	7.90	1.344	0.886
2	12.02	4.45	7.42	1.150	0.787
4	4.74	1.58	2.63	0.408	0.279
6	2.19	0.73	1.21	0.187	0.129
8	1.30	0.49	0.82	0.122	0.087
10	0.00	0.00	0.00	0.000	0.000

*Experiments were made using 0.2 g catalyst, 100 ml of 20 ppm imidacloprid solution, initial solution pH 5.6, room temperature, 1 hour and light intensity 100000 lux.

3.2.3.7. Effect support type

To facilitate separation process of catalyst, and to enhance its degradation efficiency, ZnO particles were supported at glass, MONT and AC. Table (17) shows inhibition of degradation efficiency in glass and MONT cases, and enhancement of degradation efficiency in AC case. For AC the adsorption capacity for 20 ppm imidacloprid solution is 21.739 mg imidacloprid/g AC.

Table (17): Values of Deg.%, TN, TF, QY and RQY for degradation of imidacloprid using ZnO@glass, MONT and AC.

Catalyst	Deg. %	TN (10 ⁻⁴)	TF (10 ⁻⁶) min ⁻¹	QY(10 ⁻⁴) molecule/photon	RQY (10 ⁻²⁵) photon ⁻¹
Glass	0	-	-	-	-
ZnO@Glass	0	0	0	0	0
MONT	0	-	-	-	-
ZnO@MONT	0	0	0	0	0
AC	100	-	-	-	-
ZnO@AC	100	32	53	8.319	5.621

*Experiments were made using 0.2 g catalyst, 100 ml of 20 ppm imidacloprid solution, initial solution pH 5.6, room temperature, 1 hour and light intensity 100000 lux.

3.2.4. HPLC analysis

To study degradation process products, HPLC analysis of samples after different periods of irradiation time were run. Figure (22) shows that different peaks (at 1.174, 1.837 and 2.142 min) for intermediates appeared and their peaks areas increased with increase degradation time. The imidacloprid peak at 2.486 min area decrease with time. The values are shown in Table (18).

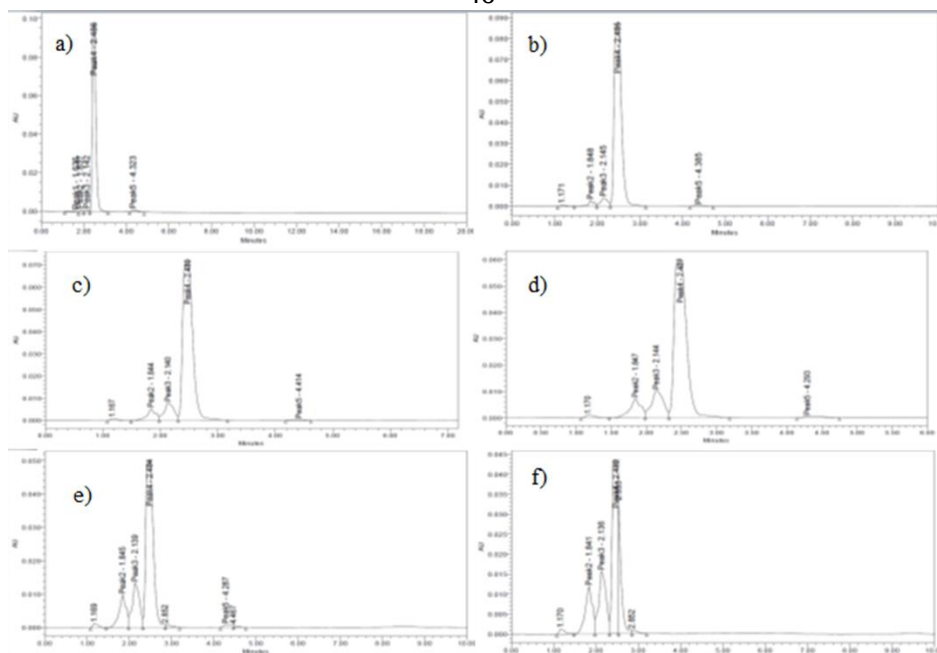


Figure (22): HPLC chromatograms for imidacloprid sample after degradation with ZnO after different period of time (a) 0 (b) 60 (c) 120 (d) 180 (e) 240 and (f) 300 min. Experiments were made using 0.2 g ZnO, 100 ml of 20 ppm imidacloprid solution, initial solution pH 5.6, room temperature and light intensity 100000 lux.

Table (18): Values of peak areas for imidacloprid and its degradation intermediate after degradation experiment with ZnO with different time of irradiation.

Time (min)	Peak area for different retention time ($\mu\text{V}\cdot\text{S}$)			
	1.174 min	1.837 min	2.142 min	2.486 min**
0	0	10444	14494	1156216
30	2289	11766	25634	1084586
60	4519	23649	44249	1030495
120	7166	53416	91068	859969
180	9430	77771	121756	727574
240	11075	111945	160362	615927
300	11128	138050	189652	405802

*Experiments were made using 0.2 g ZnO, 100 ml of 20 ppm imidacloprid solution, initial solution pH 5.6, room temperature and light intensity 100000 lux.

**This belong to original contaminant

3.2.5. Zn^{2+} residue

To determine stability of the catalyst, amounts of dissolved ZnO were determined by measuring Zn^{2+} concentration by AAS in degradation solutions after degradation process for commercial, prepared, Al-ZnO and supported catalysts. Table (19) shows the mass percentage of ZnO dissolved in solution. The percentages are higher for Al doped ZnO than for pristine prepared ZnO powder. However, commercial ZnO shows higher solubility than prepared one. For supported systems MONT supported systems shows higher solubility of ZnO than AC.

Table (19): Values of ZnO% for dissolved ZnO after degradation experiment of 100 ml solution using 0.2 g catalyst.

Catalyst	ZnO%	Catalyst	ZnO%
commercial ZnO	0.906	Al:ZnO (10:90)	0.703
prepared ZnO	0.43	MONT	0.006
Al:ZnO (2:98)	0.675	ZnO@MONT	4.33
Al:ZnO (4:96)	0.862	Al-ZnO@MONT	4.13
Al:ZnO (6:94)	0.882	AC	0.14
Al:ZnO (8:92)	0.743	ZnO@AC	0.14

Effect of pH on solubility was also studied. As shown in Table (20) solubility increased at lower pH.

Table (20): ZnO% solubility for prepared ZnO at different pH

pH	1.97	4.12	5.6	8.1	9.93	12.04
ZnO%	2.045	0.47	0.43	0.55	0.47	0.19

3.2.6. Catalyst reuse

To determine the ability to reuse the catalyst, ZnO catalyst sample were used for 2 times in degradation of fresh 20 ppm imidacloprid solutions. Degradation percentage for each time was calculated as shown in Table (21). The value is decreased nearly to the half in the second time.

Table (21): Values of Deg.% of imidacloprid using recovered ZnO catalyst for 2 times.

Trial Number	Deg. %
1	8.9
2	4.8

3.2.7. Degradation under visible light irradiation

Cut off filter was used to filter UV radiation fraction from simulated solar light radiation. This was to determine efficiency of catalyst under visible light fraction. Results for pristine and Al doped ZnO catalysts shown in Table (22) indicate that these catalysts have activity in visible light but its lower than in complete solar light radiation.

Table (22): Values of Deg.%, TN and TF for degradation of imidacloprid under visible light fraction of solar light irradiation.

Catalyst	Deg.%	TN (10^{-4})	TF (10^{-6}) min ⁻¹
commercial ZnO	18.81	5.92	9.87
prepared ZnO	10.64	3.74	6.24
Al:ZnO (2:98)	1.52	0.992	1.65
Al:ZnO (4:96)	1.70	0.557	0.927
Al:ZnO (6:94)	2.35	0.81	1.35
Al:ZnO (8:92)	0.33	0.111	0.186
Al:ZnO (10:90)	0	0	0
MONT	0	0	0
ZnO@MONT	0	0	0
Al-ZnO@MONT	0	0	0
Glass	0	0	0
ZnO@Glass	0	0	0
AC	-	-	-
ZnO@AC	-	-	-

*Experiments were made using 0.2 g catalyst, 100 ml of 20 ppm imidacloprid solution, initial solution pH 5.6 and room temperature.

Chapter Four

Discussion

Commercial and prepared ZnO particles were examined for photodegradation of imidacloprid in water under simulated solar light radiation. Al doped ZnO and supported ZnO on MONT, AC and glass were prepared and used as photocatalysts. All the catalysts were characterized. Different factors affecting photocatalysis were studied. Results showed in chapter 3 will be discussed here.

4.1. Catalysts characterization

Structural and optical properties in addition to surface charge and composition of different catalyst systems were studied.

4.1.1. Crystal structures

XRD patterns for commercial and prepared ZnO nanoparticle show crystallinity with pure hexagonal wurtzite crystal and smaller particle size for prepared one indicated by broadening in XRD signals. Al doped ZnO with different Al percentage shows high crystallinity with XRD pattern matching ZnO hexagonal wurtzite structure with absence of any signal for Al_2O_3 . This indicates that Al^{3+} ions are homogenously distributed in ZnO crystal structure where Al^{3+} substitute Zn^{2+} ion in the crystal. The results means that Al is successfully doped with ZnO as reported earlier [43, 49, 77]. For particle size an increase appears with increasing of Al%. This is contrary to references where through doping some Al atom are expected to

located near to ZnO nanoparticle boundaries which reduce ZnO diffusion rate and prevent the growth of nanoparticles, it also explained by different in size of Al^{3+} and Zn^{2+} ions where Al^{3+} has smaller size [39]. One reference show the same tendency and explain it by coarsening result from Al doping that reduces retarding force prevent crystal growing [51]. For MONT supported systems with ZnO and Al-ZnO, XRD pattern indicates that pure hexagonal wurtzite crystals are supported at MONT with smaller particle sizes that could be related to lamellae structure of MONT where silicate group at layer prevent nanoparticles from aggregation [78]. The decrease in MONT particle size in case of supporting with ZnO could be due to crystal distortion in presence of ZnO. However, the increase in its size in case of supporting with Al-ZnO indicate that thin film of Al_2O_3 (signal at $2\theta = 28^\circ$) at MONT was formed and prevent its distortion [79].

4.1.2. Micrographs

By comparing prepared and commercial ZnO, the prepared one show larger agglomerate than commercial one. Each agglomerate contains many ZnO nanoparticles, which indicates that commercial one could have larger exposed surface area during photodegradation process. Larger agglomerates for the prepared ZnO is related to smaller particle size that increase active surface area and so increase its agglomerate formation ability.

The effect of Al doping on morphology were shown in Figure (7), where an increase in grain size with high Al doping amount is observed. This indicates that grains grow easily in presence of Al [80].

For MONT supported systems, SEM images show plate like shape for supported and unsupported systems with smaller particles for nano size scale of ZnO and Al-ZnO at the surface of supported system. The micrographs confirm the formation of ZnO and Al-ZnO at the support surface.

Based on XRD (particle size) and SEM (agglomerate size) results we can conclude that ZnO particles exists in larger agglomerates [81].

4.1.3. Spectral study

Band gap for different used catalysts were determined using PL and UV-visible spectra. From UV-Vis spectra, no difference between commercial and prepared ZnO nanoparticles occurred. Slight blue shift appeared in Al-doped systems. This is explained by Moss-Burstein effect where electron donor Al atom state is close to conduction band and donates e^- to it, so higher energy is needed by e^- in ZnO valence band to move to higher energy state in valence band [82, 83]. The small blue shift in MONT supported systems could be related to decrease in particle size of ZnO at MONT clay surface [84].

From PL spectra, band gap values show similar behavior to UV-Vis values except for commercial and prepared ZnO samples. The prepared one shows slightly larger band gap due to smaller particle size [84].

4.1.4. P_{ZC}

P_{ZC} was determined for all prepared catalyst systems. In case of Al doping, the increase in P_{ZC} values with Al% could be related to trace Al_2O_3 formation. For MONT supported systems, the P_{ZC} value increase is due to presence of MONT which has high P_{ZC} value.

The determination of this value is very important for adsorption of imidacloprid at catalyst surface where degradation process happen. As shown in Figures (18), (19) and (20) no strong interaction occurred between catalyst surface and imidacloprid at pH near 6. Its adsorption at catalyst surface is thus minimal. This lowers degradation process as explained below.

4.1.5. Catalyst composition

ZnO% in each catalyst determined by EDX and AAS show accepted trend compared to theoretical one with some differences related to high error percentage in the methods and low purity of catalysts.

4.2. Photocatalytic degradation study

In photodegradation experiments of imidacloprid under solar light radiation commercial ZnO shows better efficiency than prepared one. To improve

degradation efficiency of prepared ZnO doping with Al and supporting it at different system were done. Doping has inverse effect on ZnO degradation efficiency. The AC support enhanced degradation process whereas MONT and glass did not.

4.2.1. Control experiments

Control study for photolysis indicated that imidacloprid is stable to sun light as no photolysis happened under solar light radiation [65]. Adsorption control experiments indicated that no adsorption at ZnO surface happened. According to P_{ZC} results, no attraction of neutral imidacloprid occurred with positive ZnO surface at pH 6-7 as shown in Figure (18).

4.2.2. Commercial and prepared ZnO

Higher efficiency for commercial ZnO compared with prepared one is due to smaller band gap of commercial ZnO sample and higher expected surface area. This is because it has smaller agglomerate size as shown from SEM image.

4.2.3. Effect of reaction parameters

To determine optimum system for degradation process, different parameters were studied. Using different imidacloprid concentrations, at low concentration 10 ppm low degradation efficiency is shown where higher values shown for higher concentration 20 ppm. At higher concentration of imidacloprid > 20 ppm a decrease in degradation

efficiency (TN) appeared due to screening of radiation away from ZnO surface by excess imidacloprid. Competition of imidacloprid with oxygen molecules and other intermediates at catalyst surface is also possible [84-91].

Using different catalyst loading amounts, degradation efficiency increased as catalyst amount increase to a certain limit due to increase in catalyst surface available for degradation process while at higher catalyst loading amount degradation efficiency decrease due to screening effect of excess catalyst that screen light from catalyst surface [85, 92].

As the pH for imidacloprid solution was higher or lower than optimum one, degradation efficiency decreased due to repulsion between catalyst surface and imidacloprid molecule. This is due to P_{ZC} values as shown in Figure (18). However, at high pH value 12 losses of imidacloprid is due to hydrolysis of imidacloprid in basic media as shown in Figure (23) [93, 94]. Value of pH also affected ZnO stability, which was lower at high and low pH. At low pH, ZnO dissolves into Zn^{2+} while at high pH value it dissolves into $Zn(OH)_4^{2-}$ [87, 95-97].

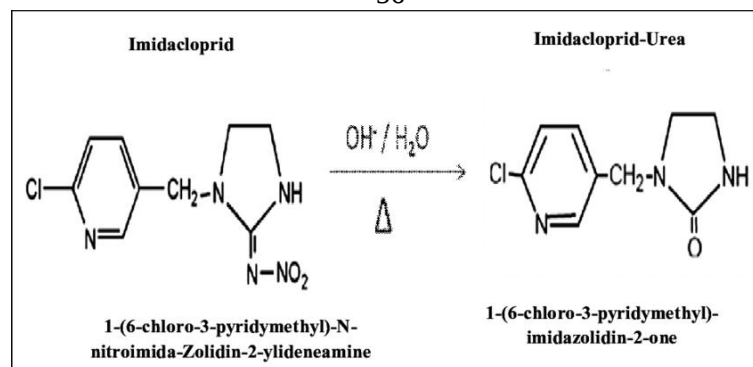


Figure (23): Hydrolysis of imidacloprid in basic media [93].

Increase in degradation efficiency with increasing light intensity is due to higher number of photon that excite electron to conduction band.

Doping ZnO with Al decreased its efficiency in degradation. This is due to increase in band gap where higher energy photons (shorter wavelength) are needed to excite electron to upper state. Increase in P_{ZC} were repulsion of imidacloprid and catalyst surface increase as shown in Figure (18) and decrease in surface area due to increase in agglomerate size as shown in Figure (7) for SEM results.

Supporting ZnO on glass and MONT showed no degradation of imidacloprid, where no adsorption happened at their surfaces. High adsorption and degradation occurred on AC as high absorption happened because of high carbon contents of AC [98]. The degradation efficiency of ZnO@AC needs to be confirmed by re-dissolving imidacloprid remains at system surface and analyzing its amount. P_{ZC} also affected adsorption and photodegradation process as shown in Figure (20).

4.2.4. HPLC analysis

The decrease in imidacloprid peak area confirmed the degradation of imidacloprid. Whereas the appearance of other peaks indicated the formation of intermediates from imidacloprid degradation. The area of intermediate peaks increased with time as degradation process increase continued.

4.2.5. Zn^{2+} residue

The increase in ZnO solubility as Al atomic% increase is related to surface coarsening in Al-ZnO particles. Acidic pH shows high solubility of ZnO as it reacts with acid to produce Zn^{2+} ions [99].

For supported systems, low solubility of ZnO@AC compared to ZnO@MONT could be explained based on surface charge. At pH near 6, ZnO has positive surface while AC has negative surface. High interaction occurred between ZnO and AC. In case of MONT at pH 6 MONT has positive charge which does not protect ZnO from dissolution.

4.2.6. Catalyst reused

The decrease in catalyst reuse ability is related to tendency of ZnO powder to coagulate which result from interaction with contaminant and intermediate and these aggregate lower effective surface area of catalyst [100].

4.2.7. Degradation under visible light irradiation

In cut-off filter experiments, the degradation activity under visible light for imidacloprid (despite the large band gap of ZnO that absorbs UV light) could be explained by sensitization effect of some impurities. Impurity molecules itself excited by visible light and electron transfers to ZnO conduction band where it reduce other species in solution [92, 101, 102]. However, imidacloprid has no sensitization effect where no light absorption in visible region appears as shown in Figure (24).

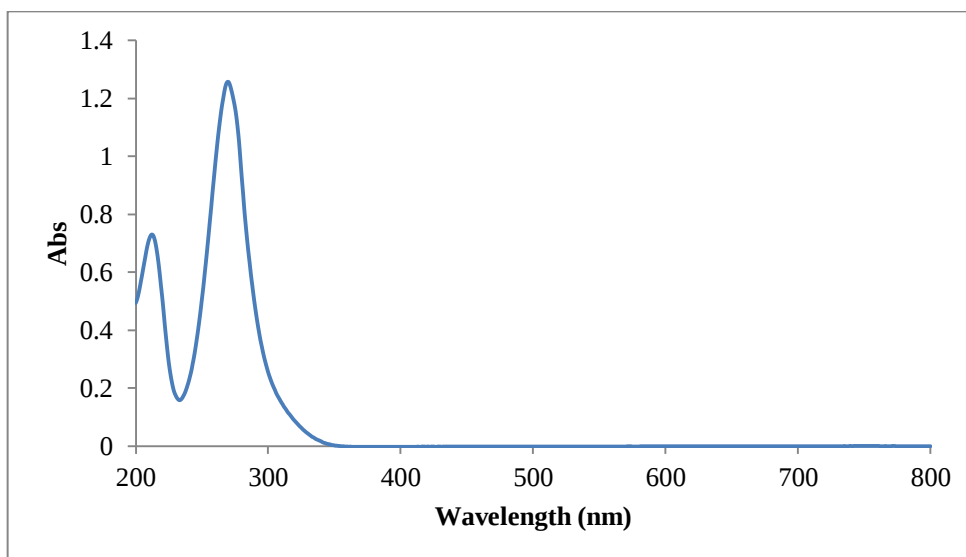


Figure (24): UV-Vis spectrum for imidacloprid.

Conclusion

1. Commercial ZnO showed larger particle size and smaller agglomerates than prepared one.
2. Al-doping causes increased in particle size while supporting cause decrease in particle size.
3. Nearly no change in crystal structure and band gap occurred for different systems.
4. Values of P_{ZC} for ZnO increased by Al doping and supporting.
5. Commercial ZnO was more effective in imidacloprid photodegradation than prepared one.
6. Al doping caused decrease in catalyst efficiency.
7. ZnO@MONT was not effective for imidacloprid degradation where ZnO@AC was more effective.
8. Degradation needed long period of time (5 hours) for 50%.
9. Stability of the system decreased as Al% increased.
10. AC supported ZnO particles are more stable to dissolution than MONT supported ZnO particles.

Recommendations for future work

1. Apply catalyst systems in degradation of other pesticides used in Palestine.
2. Study ability to reuse ZnO for more than 2 times in photodegradation.
3. Confirm degradation of imidacloprid on ZnO@AC surface.
4. Use photodegradation to purify natural contaminated waters.
5. Use other metals as dopants to enhance degradation efficiency of ZnO.
6. Study the mechanism for imidacloprid degradation.
7. Using other treatment systems for imidacloprid degradation like electroreduction.

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كلية الدراسات العليا

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الزنك المدعم بالألمنيوم والمثبت على سطوح مختلفة

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

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الملخص

تستخدم حبيبات أكسيد الزنك النانوية بشكل واسع كأشباه موصلات لمعالجة المياه من الملوثات العضوية. في هذا البحث تم استخدام حبيبات أكسيد الزنك النانوية التجارية والمحضرة مخبرياً وتم محاولة تحسينها من خلال تطعيمها بالألمنيوم بنسب مولارية مختلفة ومن خلال تثبيتها على الكربون المنشط وعلى فخار المنتموريلونيت وعلى الزجاج. تم دراسة نشاط هذه الحفازات المختلفة باستخدام ضوء الشمس في تخطيط مبيد الحشرات الايميداكلوبريد المستخدم بشكل واسع في القطاع الزراعي الفلسطيني.

بينت النتائج أن تطعيم أكسيد الزنك بالألمنيوم وتثبيته على سطح مواد داعمة ليس له تأثير على طاقة فجوة أكسيد الزنك (3.2 – 3.3 إلكترون فولت) والتي تم قياسها باستخدام مطياف الضوء المرئي والفوق البنفسجي ومطياف الوميض. من نتائج الأشعة السينية تبين أن جميع الحفازات التي تم تحضيرها تمتلك شكل فورتزيت سداسي ولم تظهر أي إشارة مستقلة للألمنيوم في حال الأكسيد الزنك المطعم بالألمنيوم ولكن في حال تثبيته على المنتموريلونيت فإشارته كانت تظهر. ولوحظ زيادة في حجم الجزيئات مع زيادة نسبة الألمنيوم ونقصان في حجمها في حال التثبيت على سطح المونتموريلونيت. من صور مسح المجهر الإلكتروني تبين أن شكل حبيبات أكسيد الزنك وأكسيد الزنك المطعم بالألمنيوم كروي غير منتظم، وأن حبيبات أكسيد الزنك المدعم على المنتموريلونيت تحمل شكلاً كروياً موزعاً على صفائح المنتموريلونيت. بالنسبة لدرجة الحموضة التي تتعدم عندها

شحنة سطح الحفاز تزداد بزيادة نسبة الألمنيوم المطعم وبالتثبيت على سطح المنتموريلونيت والكربون المنشط.

بالنسبة للعوامل المؤثرة على فاعلية التحطيم الضوئي للايميداكلوبريد فقد تمت دراسة مجموعة منها تركيز محلول الايميداكلوبريد، كمية أكسيد الزنك المستخدمة، مدة تعرض المحلول لضوء الشمس و شدة الضوء المستخدم بالإضافة لدرجة حموضة المحلول. حيث تم استخدام 0.2 غم من الحفاز لكل 100 مل من محلول الايميداكلوبريد بتركيز 20 ميكروغم/مل ودرجة حموضة 5.6 باستخدام شدة ضوء مماثلة لضوء الشمس كأفضل نظام.

بالنسبة لتأثير التطعيم بالألمنيوم فإن زيادة نسبة الألمنيوم أدت الى تثبيط نشاط أكسيد الزنك حيث انعدمت فاعليته عند نسبة ألمنيوم 10%. وفسر ذلك بناءً على شحنة سطح الحفاز. بالنسبة لتأثير التثبيت على سطح داعم لم يلاحظ أي نشاط لأكسيد الزنك في حال تثبيته على سطح المنتموريلونيت بينما لوحظ نشاط أكبر في حال تثبيته على سطح الكربون المنشط.

ذائبية أكسيد الزنك في المحلول تزداد بزيادة نسبة الألمنيوم المطعم وبوجود المنتموريلونيت بينما تقل بوجود الكربون المنشط. تم دراسة نشاط هذه الحفازات تحت الضوء المرئي حصرياً وأظهرت جميعها نشاطاً أقل مما يدل على إمكانية محلول الايميداكلوبريد بتحسين الحفاز للضوء المرئي.

كان أكسيد الزنك التجاري أكثر فاعلية من المحضر مخبرياً، وأكسيد الزنك أكثر فاعلية من استخدام أكسيد الزنك المطعم في معالجة المياه من الايميداكلوبريد، وكذلك استخدام الكربون المنشط كسطح داعم لأكسيد الزنك أفضل من استخدام المنتموريلونيت والزجاج.

