An-Najah National University
Faculty of Graduate Studies

Photocatalytic Degradation of Organic Contaminants in the Presence of Graphite-Supported and Unsupported ZnO Modified with CdS Particles

By

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This Thesis is submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry, Faculty of Graduate Studies, An-Najah National University, Nablus, Palestine.

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Ghazi Y. M. Al-Nour

This thesis was defended successfully on Wednesday, June 24th, 2009, and approved by:

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Dedication

To my family, who offered me endless support ….

To those who are looking forward to enrich their knowledge

……...


I would like to thank and express indebtedness to my supervisor Prof. Hikmat Hilal, Ph.D., for his sincere encouragement, helpful guidance and close supervision which have been invaluable for me throughout all stages of the study. Financial support donated to this project by Palestinian-French University Cooperation Program is acknowledged. I also thank Birzeit-Palestine Pharmaceutical Company for gift of free chemicals.

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Finally I wish to express my sincere gratitude and thanks to my family for their endless support and help, with special appreciation and thanks to my wife.
Declaration

The work provided in this thesis, unless otherwise referenced, is the researchers own work and has not been submitted elsewhere for any other degree or qualification.
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### 3.4 Effect of pH on rate of methyl orange degradation reaction.

Under direct light (90000 Lux, 0.013 W/cm$^2$). All reactions were conducted at room temperature in a 250 mL solution of methyl orange (10 ppm) using 0.1 g ZnO. The pH values were: a) 4.7 b) 7 c) 9 d) 11.

### 3.5 Effect of pH value on photo-degradation under direct solar light.

(Radiation intensity: 127000 Lux, 0.01859 W/cm$^2$) of 300 mL methyl orange (20 ppm) using 0.1 g ZnO. Only basic range of pH values are: a) 8.1 b) 9.2 c) 10.4 d) 12.0.

### 3.6 Effect of temperature on photo-degradation of neutral 300 mL solution methyl orange (10 ppm) using 0.1 g ZnO.

Temp: a) 10°C b) 20°C c) 30°C d) 40°C. For better temperature control, radiation was conducted inside 100 mL thermostated neutral solution of methyl orange (10 ppm) with solar simulator (Radiation Intensity 0.0212 W/cm$^2$) and 0.05 g naked ZnO.
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3.10 Photo-degradation reaction profiles for fresh and recovered ZnO catalysts. Reactions were conducted at room temperature under direct solar light (intensity 0.0144 W/cm$^2$) using a fresh neutral 300 mL solution of methyl orange (10 ppm) in each run. The original catalyst loading was (a) 0.1 g fresh ZnO, (b) First recovery, (c) Second recovery, and (d) Third recovery.

3.11 Effect of amount of AC/ZnO on photo-degradation rate of methyl orange (25 ppm) inside 300 mL neutral solution at room temperature under direct solar light (0.0149 W/cm$^2$). Catalyst amounts were: a) net ZnO (0.5 g), b) net ZnO (0.6 g), and c) net ZnO (0.7 g).
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<tr>
<td>$E_c$</td>
<td>Conduction band</td>
</tr>
<tr>
<td>$E_v$</td>
<td>Valence band</td>
</tr>
<tr>
<td>$E_{bg}$</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>$eV$</td>
<td>Electron volts</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Fermi level</td>
</tr>
<tr>
<td>RED</td>
<td>Redox</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet light</td>
</tr>
<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>MO</td>
<td>Methyl orange</td>
</tr>
<tr>
<td>$N_C$</td>
<td>Effective density of energy level at conduction band edge</td>
</tr>
<tr>
<td>$N_V$</td>
<td>Effective density of energy level at valance band edge</td>
</tr>
<tr>
<td>$\Lambda_{bg}$</td>
<td>Wave length of band gap energy</td>
</tr>
<tr>
<td>$V_{V,S}$</td>
<td>Potential at the valance band edge</td>
</tr>
<tr>
<td>PEC</td>
<td>Photo-electro chemical</td>
</tr>
<tr>
<td>T.N.</td>
<td>Turnover number</td>
</tr>
<tr>
<td>nm</td>
<td>Nano-meter</td>
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<tr>
<td>ppm</td>
<td>Parts per million</td>
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Photocatalytic degradation of organic contaminants in the presence of graphite-supported and unsupported ZnO modified with CdS thin films

By
Ghazi Yousef Mustafa Al-Nour
Supervisor
Prof. Hikmat Hilal

ABSTRACT

ZnO is a wide-band gap (3.2 eV) semiconductor, with limited photocatalytic applications to shorter wavelengths only. However, it is suitable to use in solar light photo-degradation of different contaminants, due to a number of reasons, taking into account that the reaching-in solar radiation contains only a tail in the near UV region. The high absorptivity of ZnO makes it efficient photo-catalyst under direct solar light. Moreover, it is relatively safe, abundant and non costly. In this research, ZnO has been investigated as a potential catalyst for photo-degradation of methyl orange (a known dye) and phenazopyridine in aqueous solutions with direct natural solar light under different conditions. Xe lamp was used in a number of experiments. The major aim was to assess the efficiency and stability of ZnO under photo-electrochemical (PEC) conditions, and to suggest techniques to enhance such features. This will shed light on the
future applicability of ZnO as a candidate for economic and friendly processes in water purification.

Recovery of ZnO particles, after reaction completion, has been facilitated by supporting ZnO onto activated carbon, to yield AC/ZnO system. The AC/ZnO was used as catalyst for contaminant photo-degradation in water solutions under direct solar light.

Both catalytic systems, naked ZnO and AC/ZnO, were highly efficient in degrading both contaminants, reaching complete removal in reasonable times. The latter system showed higher efficiency. In both systems, the reaction goes faster with higher catalyst loading, until a maximum efficiency is reached at a certain concentration, after which the catalyst concentration did not show a systematic effect.

In both catalytic systems, the rate of degradation reaction increases with higher contaminant concentrations until a certain limit is used. The contaminant degradation reaction was studied, using both catalysts, at different pH values. The pH value 8.0 gave the highest catalyst efficiency. The tendency of naked ZnO to degrade into soluble zinc ions, under photo-degradation experiments, was studied under different pH values. Catalyst recovery and reuse experiments were conducted on both systems. The catalytic activity of the recovered systems was only slightly lower than the fresh system in each case. The fourth time recovered catalysts showed a considerable efficiency loss in each case, except when ZnO/AC system was used to photo-degrade MO, presumably due to ZnO
degradation and leaching out. However, fresh and recovered catalyst systems caused complete degradation of contaminants after enough time. Temperature showed a slight effect on rate of reaction, with immeasurably small activation energy value. Details of effects of other parameters on reaction rate and catalyst efficiency are described. Using CdS as sensitizing dye failed to enhance ZnO efficiency under direct solar light. The screening effect and tendency of CdS to leach out limit its use as ZnO sensitizer. Tendency of ZnO to leach out zinc ions into solution is discussed. The naked ZnO and AC/ZnO systems are promising photo-catalysts in future water purification technologies by direct solar light.
1.1 Semiconductor electrodes

1.1.1 Introduction

Semiconductor electrochemistry is a relatively new but mature branch of 
electrochemistry. The first paper on a well-defined semiconductor 
(germanium) appeared in 1955 [1]. During the fifteen years followed many 
workers contribute to the fundamental study of semiconductor electrodes, 
most of the study focused on silicon and germanium, although other 
semiconductors (ZnO, GaAs, CdS) were also investigated [2]. The chief 
attributes of semiconductor electrodes from these studies were:

1) The presence of two energy bands separated by a band gap, with charge 
transfer proceeding by either of the two energy bands.

2) The low concentration of mobile charge carriers within the 
semiconductor relative to the electrolyte.

3) The photo excitation of electrons from the valence band to the 
conduction band, leading to enormous photo effects in semiconductor 
electrochemistry.

The practical aspects of the photo-effects, i.e. solar energy conversion were 
not fully recognized until the seventies. In 1971 and 1972 Fujishama and 
Honda [3, 4] reported that water could be electrolyzed to oxygen and 
hydrogen in a simple cell using a platinum and TiO$_2$ electrode.
In 1977 Tributsch [5] introduced to the field a new class of semiconductor electrodes, tungsten and molybdenum chalcogenides. However, these semiconductors have problems related to the presence of structural defects at the surface, and thus to stability.

1.1.2 Energy bands in solids

With rare exception, the semiconductors of interest are net-work solids, not discrete molecules; the covalent bond net-work extends throughout the volume of the crystal. As required by molecular orbital theory, an energy level that exists for a discrete bond between a pair of atoms splits into a very large number of closely spaced energy levels in the microscopic solid. The ensemble of energy levels is called energy band gap ($E_{bg}$) [6].

An energy band is treated as a continuum of energy levels because the energy spacing between adjacent levels is so small. The energy level diagram of a net work solid consists of stacked series of energy bands some of which may overlap. The highest filled energy band and the lowest empty energy band are the most important in terms of charge transport and charge transfer. In a semiconductor or an insulator, these bands are separated by a gap devoid of energy levels, Figure (1.1) [6]. In a metal the two bands overlap, or a band is partially filled with electrons. The highest filled band is called the valence band (V.B.), and the lowest empty band the conduction band (C.B.) [6].
In most semiconductors the valence band is derived from a bonding molecular orbital and the conduction band from an anti-bonding molecular orbital. The band gap energy and the positions of \( E_v \) and \( E_c \) band edges on an electrochemical potential scale are the primary determinants of the properties and behavior of semiconductor electrodes. The preferred energy unit for \( E_{bg} \) is electron-volts (eV), since this unit translates readily into the electrochemical scale, Figure (1.2) [7].

**Figure (1.1):** The energy band diagram for a semiconductor in contact with an electrolyte. \( E_c \): conduction band; \( E_v \): valence band; \( E_{bg} \): band gap energy.
5

Figure (1.2): Band positions (top of valence band and bottom of conduction band) of several semiconductors together with some selected redox potentials.

1.1.3 Charge carrier generation

In a metal the empty energy levels are immediately above the occupied ones. Conduction of electricity occurs when electrons are thermally excited to the empty levels and acquire lateral mobility along the adjacent empty levels. A perfect semiconductor is a non-conductor at absolute zero, because the valence band is completely occupied and the conduction band totally empty. To impart electrical conduction, charge carriers can be generated by one of three mechanisms: thermal generation, doping, and photo-excitation. Figure (1.3) shows such mechanisms [8].

Two charge carriers are generated when photons at room temperature excite electrons from the valence band to the conduction band; the
electrons in the conduction band and the holes in the valence band. The concentration of electrons (n) and holes (p) depends on the absolute temperature and the energy band gap (n)(p)= N_c N_v \exp(-E_{bg}/KT).

N_t and N_v are the effective density of energy levels at the conduction band edge and the valence band edge their values are on the order of 10^{19}/cm.

of charge carrier generation (n) = (p) the total charge carrier concentration (and conductivity) drops rapidly with increasing E_{bg} at a given temperature. At room temperature KT is 0.0257 eV; consequently, intrinsic semiconductors with band gap energies greater than 0.5 eV are essentially insulators. In doping, energy levels are introduced into the band gap region by chemically altering the crystal lattice. When the doping entity is an electron donor, and is located within a few KT of the conduction band edge, a large population of electrons is donated into the conduction band by thermal excitation. Consequently, the hole-concentration drops as the electron concentration increases [8].

Electrical current is carried predominantly by the negative charge carriers in the conduction band. The semiconductor is therefore called n-type. In p-type semiconductor, electrons are captured from the valence band creating an excess population of positive charge carriers. By doping process useful conductivity can be imparted to semiconductors with E_{bg} as large as 3.5 eV.

In photo-excitation, a photon of light with suitable energy can excite an electron from the valence band to the conduction band. Recombination
between excited electrons and holes may occur, but they can be separated by means of electric field or diffusion. A useful relationship between $\lambda_{bg}$ and $E_{bg}$ is $\lambda_{bg} = 1240/E_{bg}$ [8]. Where $\lambda_{bg}$ in nanometers and $E_{bg}$ in electron volts

![Diagram A](image1.png)

![Diagram B](image2.png)

![Diagram C](image3.png)

![Diagram D](image4.png)

**Figure (1.3):** Mechanisms of charge carrier generation in a semiconductor, A: Thermal generation, B: n-type doping, C: p-type doping, D: Photo excitation.

### 1.1.4 Fermi level

The Fermi level is the energy at which the probability of an energy level being occupied by an electron is exactly $\frac{1}{2}$. For semiconductors the Fermi level resides in the band gap region. In case of an intrinsic semiconductor the Fermi level is approximately midway between $E_c$ and $E_v$. For n-type doping, the Fermi level shifts towards the conduction band edge, while p-type doping shifts it towards the valence band edge [9].
1.1.5 Photo-effect at the semiconductor

A doped semiconductor has a large difference in the concentration of the two types of charge carriers. So when the semiconductor excited holes and electrons are generated by light absorption. Little change in the concentration of the majority carriers occurs and the minority carrier concentration is greatly enhanced. Photo-generated minority carriers migrate towards the electrode/electrolyte interface, and affect both the photo-current and the photo-potential. The sensitivity of a semiconductor to photon energy is dictated by the band gap energy. When the wavelength of incident light decreases below $\lambda_{bg}$, the photo effects switch on. Another phenomenon, important to photo-effects, is recombination. Direct recombination may occur when the electrons descend from the conduction band edge to the hole at the valence band edge. Indirect recombination occurs via an intermediate energy level (bulk or surface state). This mode of recombination can be particularly effective because the intermediate energy level can capture the hole and electron. The magnitude of the photo-effect is reduced by recombination. Upon irradiation of a n-type semiconductor through the electrolyte with light ($\lambda$ shorter than $\lambda_{bg}$), large anodic photo currents appear as a result of the flux of holes (minority carriers) arriving at the surface [10].

When an electron-hole pair is generated by light absorption in the depletion layer, the electric field separates the two charge carriers, with the electron moving toward the bulk of the crystal and the hole migrating toward the
surface, Figure (1.4). The oxidation power of the holes are roughly equivalent to the potential of the valence band edge, and are capable of oxidizing a reduced (RED) molecule whose formal potential is less positive than that of the hole. In the wider band gap, materials e.g. TiO$_2$, the electrolyte (H$_2$O) is oxidized. The electron in the conduction band flows via an external circuit to another electrode where reduction takes place [10].

![Diagram of energy levels in a semiconductor](image)

**Figure (1.4):** Photocurrent generation at n-type semiconductor

### 1.2 Organic contaminants

Manufacture industries produce large amount of organic contaminants and dyes which are toxic and non biodegradable. The presence of these contaminants has caused severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase [11-12]. Examples of contaminants widely encountered in water are: chlorinated hydrocarbons, phenol derivative, insecticides, pesticides and pharmaceutical formulations [13-14].
Various chemical and physical processes such as adsorption, air stirring, flocculation, reverse osmosis and ultra filtration can be used for water purification. Because these techniques are non-destructive, a new type of pollution will arise which needs further treatment [15]. Recently, photo catalytic reactions induced by illumination of semiconductors in suspension has been shown to be one of the most promising processes for the waste water treatment due to its advantages over the traditional techniques, since they provide an interface with an aqueous medium and induce an advanced oxidation process (AOP$_5$), no formation of polycyclic products, oxidation of pollutants in the ppb range [16]. AOP$_5$ are based on generation of reactive species such as hydroxyl radicals obtained by the reaction of holes with surface hydroxyl or water and their attachment to organic compounds that oxidize abroad range of pollutants efficiently. AOP$_5$ include photo catalysis systems such as combination of semi conductors with light and semi conductor with oxidant [11, 13, 17].

1.3 ZnO and TiO$_2$ semiconductors

Many different SC materials, such as TiO$_2$ (Degussa), TiO$_2$ (Merck), ZnO, ZrO$_2$, SrO$_2$, Fe$_2$O$_3$, CdS, ZnS have been used to photo-degrade different pollutants [15]. TiO$_2$ and ZnO are known to be the best photo catalysts for the degradation of several environmental contaminants [11, 15]. TiO$_2$ nano particles have been extensively used on environmental applications due to lack of toxicity, low cost, photo-stability, and water insolubility under most conditions [18, 19].
ZnO has also been used to photo-degrade water contaminants in the UV region, but to a much lesser extent than TiO₂. ZnO has comparable band gap to that of TiO₂ (3.2) eV. However, the greatest advantage of ZnO is that it absorbs large fraction of solar UV light than TiO₂ does [11]. TiO₂ can utilize only about 3.0% of the solar light reaching the earth surface for an effective decomposition of organic compounds [20]. The major problem is that only about 4% of the solar spectrum falls in UV range. The efficient use of sun light became an appealing challenge for developing photo-catalysts [14, 21]. One approach is to sensitize TiO₂ and ZnO by using narrow band gap semi-conductors with higher conduction band, Figure (1.5). CdS with band gap energy of 2.41 eV is considered to be one of the many sensitizers used for large band-gap semiconductor [22]. This is due to the ideal position of its conduction and valence band edges. CdS alone however, may show lower photo-catalytic activity because of rapid electron hole pair (EHP) recombination rates. Studies have proven that with the appropriate particle interaction, CdS/TiO₂ nano-composites can efficiently decompose organics such as phenol and methylene blue under visible irradiation shorter than 495 nm. The reaction, Figure (1.5), occurs when a CdS particle is excited by a photon with a wavelength shorter than 495 nm. An EHP is formed and subsequently, the photo-generated electron is quickly transferred to the conduction band of a coupled TiO₂ particle that has a conduction band edge more positive than the CdS particle. The photo
generated holes in the quantum-sized CdS particles can theoretically migrate to the surface and participate in the oxidation of adsorbed organics.

![Diagram](image)

**Figure (1.5)** Schematic showing how TiO$_2$ sensitization occurs using CdS

The electrons that are transferred to the conduction band of TiO$_2$ have no holes to recombine with and therefore, participate in reduction reaction according to the conduction band energy level of TiO$_2$ [21, 23].

Deposition of metal particles may also enhance the degradation efficiency of photo-catalytic reactions, due to the rapid transfer of photo generated electrons from the semiconductors to the metal particles. This results in the effective separation of the electrons and holes. The photo-activity of TiO$_2$ is not only affected by the separation and life time of the photo-produced electron-hole pairs. It also relates to bulk, crystal phase surface area and distribution of the photo-active compounds [13, 18].

Activated carbon (AC)-TiO$_2$ showed high activity in the decomposition of polyvinyl alcohol in water under UV-irradiation and was able to use repeatedly. AC acts as an efficient adsorption trap to the organic pollutant and bringing them into close proximity to the catalytic site [14, 19].
Photo-catalysis is efficient in several fields. It can be used to induce mild and selective oxidation reactions or total oxidation reactions leading most elements to their higher oxidation state (complete mineralization). In case of organic carbon CO₂ is produced. What governs the photo-catalysis reaction to become mild oxidation or total oxidation catalyst is absence or presence of water. Total oxidation catalysis occurs in presence of water, because of the photo-generation of OH⁻ (second best universal oxidant) radicals. The OH⁻ radicals are created by neutralization of OH⁻ surface groups by positive holes which are generated when a semi-conductor is illuminated with suitable photons. In the absence of water, the active species are neutral atomic O* species. Their formation is summarized in Table (1.1) [24].
Table (1.1): Main features of photo-catalytically driven fine and environmental chemistry [21].

<table>
<thead>
<tr>
<th>Features</th>
<th>Fine chemicals</th>
<th>Environmental catalysis</th>
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<td>Main reaction</td>
<td>Mild oxidation</td>
<td>total oxidation</td>
</tr>
<tr>
<td>initial selectivity</td>
<td>100%</td>
<td>No selectivity</td>
</tr>
<tr>
<td>Final produced for organics</td>
<td>C=O</td>
<td>------</td>
</tr>
<tr>
<td>Medium</td>
<td>Dry medium</td>
<td>water, humid air</td>
</tr>
<tr>
<td>Active species</td>
<td>O*</td>
<td>OH⁻</td>
</tr>
<tr>
<td>Reaction of formation</td>
<td>(TiO₂)+hv→ e⁻ + h⁺</td>
<td>(H₂O→H⁺+OH⁻)+h⁺→</td>
</tr>
<tr>
<td></td>
<td>O*(ads)+h⁺→O*(ads)</td>
<td>H⁺+OH⁻</td>
</tr>
</tbody>
</table>

Selective photo-catalytic mild oxidation occurs in the following reactions: n-alkanes can be functionalized into carbonyl-containing molecules either in the gas or in liquid phase \((C \geq 2)\)

\[
C_nH_{2n+2} + O_2 + (TiO_2 + hv + air) \rightarrow C_nH_{2n}O + H_2O
\]

cyclo-alkanes \((C_nH_{2n})\) are selectivity oxidized in cyclo ketones. In alkyl tolenes the methyl group is selectively oxidized into alkyl benzaldehydes by irradiation of titania at room temperature.

\[
R-C_6H_4CH_3 + O_2 \rightarrow R-C_6H_4–CHO + H_2O
\]
Selective oxidation of primary and secondary alcohol are oxidized to their corresponding aldehydes and ketones 100% selectively. In thio-photo catalysis propene was converted selectively to 1-propanthiol

\[ \text{CH}_3 - \text{CH} = \text{CH}_2 + \text{H}_2\text{S} \rightarrow \text{CH}_3 \text{CH}_2 \text{CH}_2 - \text{SH} \]

Whereas secondary 2-propanthiol is preferentially obtained in conventional processes [21]. In environmental photo catalysis many toxic inorganic ions were oxidized in their harmless upper oxidized state. For example \( \text{PO}_3^{3-} \) is oxidized into \( \text{PO}_4^{3-} \), whereas \( \text{SO}_3^{2-} \), \( \text{HSO}_3^{-1} \), \( \text{S}_2\text{O}_3^{2-} \), \( \text{S}^2- \) and \( \text{HS}^- \) were oxidized into \( \text{SO}_4^{2-} \) [24, 25].

Because of the unselective attack of organics by OH\(^-\) radical, most of aliphatic and aromatic pollutants were totally mineralized into \( \text{CO}_2 \) and innocuous inorganic anions, more complex molecular such as pesticides or dyes are totally destroyed. Organics when attacked by OH\(^-\) radials unselectively oxidized a C-H bond into a carboxylic group, which decarboxylates according to the photo-Kolbe reaction:

\[ \text{R-COO}^- + \text{h}^+ \rightarrow \text{R-COO}^\circ \rightarrow \text{R}^\circ + \text{CO}_2(\text{g}) \rightarrow \text{C}_{n-1} \rightarrow \text{C}_{n-2} \rightarrow \text{C}_{n-3} \rightarrow \ldots \rightarrow \text{CO}_2 \]

In organic molecules containing azo group (-N=N-), the photo-catalytic degradation of azo group is 100% selective in generating nitrogen gas [24].
1.4 ZINC Oxide:

Zinc oxide, ZnO, is soluble in acids and alkalis, but nearly insoluble in water. In nature, it occurs as the mineral zincite. Crystalline zinc oxide exhibits piezoelectric behavior and is thermo-chromic. On heating, its color changes from white to yellow.

1.4.1 Chemical properties:

ZnO has a considerable stability. Decomposition of ZnO to zinc vapor and oxygen occurs only at around 1975°C. When ZnO is heated with carbon the oxide is converted to zinc

\[ \text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO} \]

Zinc oxide converts to Zinc sulfide when exposed to hydrogen sulfide.

\[ \text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \]

**Amphotericism:**

Zinc oxide is reactive toward both acids and bases, so it is considered as an amphoteric oxide. It reacts with acids as follows:

\[ \text{ZnO} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O} \]

\[ \text{ZnO} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2\text{O} \]

and with bases, it reacts as:
ZnO + 2NaOH + H₂O → Na₂[Zn(OH)₄]

The pH for ZnO suspension in water is 6.95 when it is produced by American process, and 7.37 when it is produced by the French process.

1.4.2 Applications of ZnO:

1.4.2.1 Medical application:

A mixture of zinc oxide with about 0.5% iron(III)oxide is called calamine and is used in calamine lotion. When zincite and hemi-morphite are mixed with eugenol the mixture is called zinc oxide eugenol, which has restorative and prosthodontic applications in dentistry. Zinc peroxide ZnO₂.1/2H₂O is used in antiseptic ointments.

1.4.2.2 Chemicals and biosensor applications:

ZnO nanostructures exhibited interesting properties including high catalytic efficiency and strong adsorption ability, in addition to its unique optical, semi-conducting, piezoelectric and magnetic properties. Due to its high isoelectric point (9.5), biocompatibility and fast electron transfer, interest has recently been focused onto the application of ZnO in biosensing.
1.4.2.3 Nutrition value of ZnO:

Zinc oxide is added to many breakfast cereals, as a source of zinc, a necessary nutrient.

1.4.2.4 Uses as pigment:

ZnO absorbs both UVA and UVB rays of ultraviolet light. Thus it can be used in creams, ointment and lotions to protect against sunburn. Zinc white is used as pigment in paints which are less opaque than TiO₂.

1.4.3 Electronic materials

The most common applications of ZnO are in laser diodes and light emitting diodes (LEDs) since it has as excited and biexciton energies of 60 meV and 15 meV, respectively. ZnO is a semiconductor with band gap energy of 3.37 eV at room temperature. Most ZnO powders have n-type character. Nature defects such as oxygen vacancies or zinc interstitials are often assumed to be the origin for this. n-type doped films are often used in thin film technology. ZnO is used in a transparent conducting oxide (TCO) productions. ZnO has also been considered for spintronic applications because of predications of room temperature ferromagnetism [26].

1.5 Earlier works on water purification from organic contaminants

MO photo-degradation has been widely studied [27-31]. Rashed et al used TiO₂ for photo-degradation of methyl orange dye under different irradiation
sources, such as Halogen lamp 1000 W, fluorescent lamp and natural sun light [12]. The effect of initial dye concentration, irradiation time and light intensity were also studied. The results revealed that the dyes undergo faster degradation with the natural sun light than with the halogen and fluorescent lamp sources. The rate of de-colorization was estimated from residual concentration spectro-photometrically.

Kansal et al. studied the photo-degradation of methyl orange (MO) and Rhodamine 6G (R6G) in aqueous phase using ZnO, SnO$_2$, ZnS, CdS, TiO$_2$ as photo-catalysts [11]. The experiments were carried out using UV and solar light as sources of irradiation. The rate of decolorization was estimated from residual concentration spectro-photometrically. Similar experiments were carried out using different pH values in the range 2–10. They used nominal amounts of catalyst 0.25–2.0 g/L, and initial dye concentrations 5–200 mg/L. The experimental results indicated that the maximum decolorization (more than 90%) of dyes occurred with ZnO catalyst in basic media. The performance of ZnO/solar light photo-catalytic system was higher than that for ZnO/UV system.

Ke Dai et al. investigated the photo-degradation of (MO) in aqueous suspensions of meso-porous titania nano-particles under UV irradiation [16]. The experimental results showed that 98% MO can be mineralized in the 1.0 g/L meso-TiO$_2$ suspension (pH = 2.0) after 45 minutes illumination. A 20 ppm MO solution was used in this study.
Cheng Chen et al studied the photo-degradation of (MO) in the presence of Zn-doped TiO\(_2\) prepared by a stearic acid gel method using UV light source [18]. They found that the 0.1\% Zn/TiO\(_2\) nano-crystals exhibited the best photo-degradation. The photo-degradation of the dye was also carried out using 0.1 \% Zn/TiO\(_2\) nano-crystals calcinated at various temperatures. The optimized calcination temperature was 450\(^\circ\)C.

ZnO has been widely used to catalyze the photo-degradation of water contaminants such as: rhodamine B, methylene blue, acid red 14 and others [32-36]. N. Daneshvar et al prepared ZnO nano-crystals with mean diameter size 14 nm by precipitation method [37]. The resulting ZnO was examined as photo-catalyst for the UV–induced degradation of insecticide diazinon as deputy of organic pollutant in aqueous solution. The effect of various parameters, such as illumination time, amount of photo-catalyst, initial pH values and initial concentration of insecticide, on the photo-catalytic degradation of diazinon, were investigated to find desired conditions. The desired parameters were also tested for the treatment of real water containing the insecticide. Diazinon photo-degradation efficiency was studied using commercial and prepared ZnO. The results indicated that the prepared ZnO is more efficient than the commercial ZnO nano-crystals.

S. Sakthivel et. al investigated the activity of commercial ZnO powder, using acid brown 14 as the model pollutant [38]. Solar light was used as the
energy source for the catalytic experiments. Acid brown was converted completely into colorless intermediates within 120 and 300 minutes by ZnO and TiO$_2$ respectively. Complete degradation was observed within 360 minutes with ZnO and 420 minutes while using TiO$_2$. Complete mineralization was attained with the formation of carbon dioxide, water, nitrate, ammonia, sulphate and chloride. Comparison of photo-catalytic activity of different semi-conducting materials has indicated that ZnO is the most active photo-catalyst in the degradation of acid brown 14. The effect of initial dye concentration, catalyst loading, irradiation time, pH, adsorption of acid brown 14 on ZnO and TiO$_2$ have been investigated.

S. Sakthivel et al studied the photo-catalytic activity by semiconductor heterojunctions: $\alpha$-Fe$_2$O$_3$, WO$_3$ and CdS deposited on ZnO. Dichloro acetic acid (DCA) was used as a model pollutant. A medium pressure mercury lamp was used as a source of light [39]. The results showed that the mixture of ZnO with $\alpha$-Fe$_2$O$_3$ (0.5% wt), WO$_3$ (0.02% wt) and CdS (0.2% wt) exhibit higher photo-catalytic activity than pure ZnO.

H. Wang et al. prepared ZnO powders by two different preparation methods, with mean diameter size: 10, 50, 200 and 1000 nm. MO was used as a model of pollutant under UV irradiation. ZnO nano particle with diameter size 50 nm prepared by thermal evaporation method showed the highest photo-catalytic reactivity [40].
G. Zhou, et al. prepared Ag/ZnO nano composites by the coordination homogeneous co-precipitation method. MO was used as a model of pollutant and a single 15 W UV tube at 254 nm as a source of light. The results indicated that Ag/ZnO prepared by the method above, exhibited better photo-catalytic performance than the prepared by the photo reduction method, especially when the photo-catalyst was calcinated at 300°C. When the temperature was increased from 300-700°C, the photo-catalytic performance decreased [41].

1.6 Objectives of the present work:

In this work, we will study the photo-degradation of organic contaminants by direct sunlight and visible light region, using different ZnO surface systems as catalysts. Naked ZnO and CdS modified ZnO surfaces will be examined, moreover, we will support the ZnO particles onto activated carbon (AC) particles. The targeted organic contaminants include one known dye, namely methyl orange, which is commonly studied in literature. Moreover, one medically active organic compound, namely, phenazopyridine will be photo-degraded using the supported and unsupported ZnO catalytic systems. Thus the following technical objectives will be targeted in this study.

1- Studying photo-degradation of methyl orange and phenazopyridine by ZnO under direct sun light and under solar simulator light.
2- Preparation of nano-scale CdS particles onto ZnO particles. The CdS particles will be investigated as sensitizers for ZnO in the visible region.

3- Preparation of AC/ZnO systems and using them as photo-degradation catalytic systems in degradation of methyl orange and phenazopyridine.

4- Studying the effects of different parameters, such as pH, temperature, in addition to concentrations of contaminants and catalysts, on catalyst system efficiencies.

5- Calcinating the ZnO/AC system and using them in photo-degradation of methyl orange and phenazopyridine.

6- Recovering the ZnO and ZnO/AC systems and reusing them for multiple times.

Such study has not been conducted earlier, to the best of our knowledge, on phenazopyridine. Methyl orange has been degraded using naked ZnO in earlier literature. Other than that the objectives stated above have not been targeted on methyl orange by earlier studies. Phenazopyridine has not been degraded by ZnO in earlier studies. Calcination of ZnO on activated carbon was not done before. AC/ZnO has not been described in methyl orange in photo-degradation before.
1.7 Hypothesis:

1- Naked ZnO will catalyze organic contaminant degradation by UV light in water. This is due to the large band gap of ZnO $\approx 3.2$ eV. ZnO absorbs UV effectively. Thus naked ZnO may degrade contaminants with direct solar energy using the small fraction of UV light therein.

When ZnO is irradiated with UV, the highly energetic holes, with high positive potential and highly oxidizing power created in the valence band will oxidize all contaminants described here. The structural formula for methyl orange is shown in Scheme (I), and phenazopyridine is shown in Scheme (II). Due to its large band gap, naked ZnO will not be able to photo-degrade contaminants in the visible region.

![Scheme (I): Methyl orange](image)

2- CdS may efficiently sensitize ZnO surfaces in photo-degradation of contaminants to the visible region. This is because CdS has lower band
gap (2.5 eV) and absorbs in the visible. However, the CdS particles may have inhibiting effect by blocking the ZnO from UV light.

3- Semi-conductors supported onto activated carbon will exhibit higher activity in the photo-degradation processes. This is due to the ability of carbon to absorb organic contaminants from water and send them to the catalytically active sites.

4- Calcinations of ZnO/AC system will show higher efficiency than the non-calcinated ZnO/AC system in photo-degradation of contaminants. This is due to ZnO agglomeration which may take place in the AC pores and enhances ZnO and carbon interactions.
CHAPTER 2
EXPERIMENTAL

2.1 Materials and reagents
ZnO was purchased from Merck. Activated carbon was purchased from Aldrich. Organic solvents (ethanol, acetone, acetic acid) were obtained from Reidel–DeHaen. All these materials were analytical grade and were used without further treatment.

2. 2 Photo-catalytic reactors and degradation experiment

2. 2.1 Photo-catalytic reactor with direct solar light:

Outdoor experiments were carried out with a 7 cm height and 13.2 cm in diameter dish placed out side under direct sun light. A 250 mL sample of the contaminant solution of known concentration and 0.1 g of ZnO was placed in the reaction vessel. A 300 mL pyrex glass was also used. The incident solar radiation was measured with a lux-meter. The sunlight intensity at the beginning and end of the experiment was estimated. The main daily temperature was 35°C.

The suspension was constantly stirred for 20 minutes in the dark before irradiation reached equilibrium absorption of the ZnO in the organic substance solution. During irradiation the photo-reactor was maintained having a homogeneous suspension, to promote the adsorption on the surface of ZnO and sunlight absorption. The degraded solution was taken for spectra-measurement at various time intervals after centrifugation.

2. 2.2 Photo catalytic reactors with Xe light source

The experiments were carried out in a photo-reactor vessel equipped with a water jacket. Illumination in the visible range was carried out using a 50 W xenon lamp equipped with a housing and a concentration lens (Leybold Didactic Co., Model 45064). The lamp has a high stability and an intense
coverage of wide spectrum [42]. The light intensity at the electrode surface was measured and was 70000 lux. The light source was assembled above the sample. The intensity level of the light is controlled by fixing the distance between the source of light and the specimen.

A 100 mL dye samples and (0.05-0.25 g) ZnO were added inside the reactor vessel under constant stirring for 20 minutes in the dark before irradiation to reach equilibrium absorption of the ZnO in the organic substance solution. During irradiation the photo-reactor was maintained under magnetic stirring for having always a homogeneous suspension to promote the adsorption on the surface of ZnO. The degraded solution was taken for spectral measurement at various times intervals after centrifugation.

2.3 Measuring Devices

2.3.1 UV/ Vis Spectrophotometry

A Shimadzu UV-1601 spectro-photometer was used for electronic absorbance measurements.

2.3.2 Polarograph

Anodic stripping differential pulse polarography (ADPP) was conducted using a dropping mercury electrode (MDE 150) on a PC controlled polarograph (POL 150) to analyze Zn\(^{2+}\) and Cd\(^{2+}\) ions.

2.3.3 Lux-meter
A Lux meter (Lx-102 light meter) was used to measure the intensity of solar radiation.

2.4 Solution preparation:
The following solutions were prepared and used:
* Sodium hydroxide solution (NaOH, 0.2 N) 4 g of NaOH was dissolved in distilled water and was then diluted to 0.5 liter
* Hydrochloric acid solution (HCl, 0.2 N) 10.5 mL of 32% HCl were diluted to 0.5 liter with distilled water
* Zinc ion (Zn^{2+}) solution (100 ppm, 1.53\times10^{-3}M): 0.4395 g of ZnSO_{4}.7H_{2}O was dissolved in distilled water and diluted to 1.0 liter with distilled water.
* Cadmium chloride solution: (0.12M) 1.32 g of CdCl_{2}.2H_{2}O were dissolved in distilled water and diluted making final volume 50 mL.
* Ammonium chloride solution: (0.2M) 0.535 g of NH_{4}Cl were dissolved in distilled water and diluted making final volume 50 mL.
* Thiourea solution: (0.6M) 2.283 g of H_{2}NCSNH_{2} were dissolved in distilled water and diluted making final volume 50 mL.

2.5 Surface area measurement
The surface area of ZnO was measured using the method of acetic acid adsorption on the surface of ZnO [43]. Seven dry clean flasks were used. To each flask 1.0 g of ZnO was added. A standardized solution of approximately 0.2 M acetic acid was prepared. Then 100 mL solutions with different molarities of acetic acid were prepared by dilution (0.1569,
0.12555, 0.094, 0.0784, 0.0627, 0.0313, 0.01569 M) and added to the flasks. The flasks were covered with stoppers and shaken in a thermostat at 25 °C for one hour to reach equilibrium. The samples were filtered and then a known volume of the filtrate was titrated with a 0.093 M standardized NaOH solution. Phenolphthalein indicator, KHP was used for standardization of NaOH. The surface area result for ZnO was calculated to be 47.2 m²/g according to Table (2.1).

Table (2.1): Data for ZnO surface area measurement.

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>N1</th>
<th>N2</th>
<th>N</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>0.15345</td>
<td>0.015345</td>
<td>0.01569375</td>
<td>0.0003487</td>
<td>440.063</td>
</tr>
<tr>
<td>26.3</td>
<td>0.122295</td>
<td>0.0122295</td>
<td>0.012555</td>
<td>0.0003255</td>
<td>375.513</td>
</tr>
<tr>
<td>19.6</td>
<td>0.09114</td>
<td>0.009114</td>
<td>0.00941625</td>
<td>0.0003022</td>
<td>301.58835</td>
</tr>
<tr>
<td>16.2</td>
<td>0.07533</td>
<td>0.007533</td>
<td>0.00784687</td>
<td>0.0003138</td>
<td>240.0573</td>
</tr>
<tr>
<td>12.8</td>
<td>0.05952</td>
<td>0.005952</td>
<td>0.00627749</td>
<td>0.0003254</td>
<td>182.9133</td>
</tr>
<tr>
<td>6.2</td>
<td>0.028883</td>
<td>0.0028883</td>
<td>0.00313</td>
<td>0.0002417</td>
<td>119.4993</td>
</tr>
<tr>
<td>3</td>
<td>0.01395</td>
<td>0.001395</td>
<td>0.00156937</td>
<td>0.0001743</td>
<td>80.03442</td>
</tr>
</tbody>
</table>

V: Volume of NaOH used in the titration

C: Concentration of acetic acid (calculated using $M_1V_1 = M_2V_2$)

N₁: Number of moles of free acetic acid that remain after adsorption

N₂: Number of moles of acetic acid before adsorption

N: Number of moles of acetic acid adsorbed per 1.0 g ZnO

Langmuir adsorption isotherms were used according to the equation:

$$\frac{C}{N} = \frac{C}{N_m} + \frac{1}{KN_m}$$
Where \( N_m \) Number of moles of acetic acid per gram required to form a monolayer.

A plot \( C/N \) vs. \( C \) was constructed for the ZnO, Figure (2.1). From the graph the slope \( (1/N_m) \) was calculated.

From the calculated number of moles of acetic acid adsorbed onto 1.0 g ZnO, the number of molecules per gram ZnO was then calculated assuming a mono-layer. The surface area of ZnO was obtained by multiplying the area of 1.0 molecule acetic acid by the number of molecules per gram ZnO. The measured surface area for ZnO was \( (47.2) \) m\(^2\)/g, Table (2.2).
Table (2.2): Surface area data measured for ZnO based on Langmuir plots.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Slope</th>
<th>1/slope (number of moles) (M)</th>
<th>Molecule (6.02E23*M)</th>
<th>Area of acetic acid molecule (m²/molecule)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>2678.541</td>
<td>0.0003733</td>
<td>2.25E+20</td>
<td>2.10E-19</td>
<td>47.20</td>
</tr>
</tbody>
</table>

2:6 Photolysis experiments

2:6:1 Naked ZnO as catalyst

(0.05-0.3) g ZnO was added to 100 mL of pollutant aqueous solution with a known concentration. The photo-degradation reaction was investigated using Xe lamp. ZnO (0.1-1.2 g) was added to 250 or 300 mL of pollutant aqueous solution with known concentration. Direct sun light was used for degradation.

The pollutant aqueous solution was centrifuged for 15 minutes to obtain a good dispersion of the catalyst. It was then exposed to the light source. Aliquots (5 mL) were withdrawn from the pollutant solution at various time intervals for analysis after removal of the catalyst by centrifuging at 4000 rev/min for 5 minutes.

2:6:2 ZnO/CdS catalyst

ZnO (2.0 g) and 25 mL distilled water were added to a cylindrical double faced reactor. The reactor was equipped with a water jacket and was heated to 80°C using a thermostat. Then 2.5 mL CdCl₂ (1.2 M) was added to the reactor followed by the addition of 10 mL NH₄Cl (0.2 M). The system was
closed after the temperature reached $80^0 \text{C}$. 15 mL NH$_3$ (2.0 M) was syringed in, followed by addition of 2.5 mL thiourea (0.6 M).

After one hour, the sample was filtered, washed with acetone, water and absolute ethanol and then dried at $110^0 \text{C}$ four 8 hours. The powder was heat-treated at $400^0 \text{C}$ for 1 hour. After cooling, known amount of the solid was placed in the reactor, together with 300 mL of pollutant solution with known concentration. Photo-catalytic experiments were performed under direct sun light after stirring the mixture for 20 minutes.

2.6.3 ZnO/AC

ZnO (10.0 g) was mechanically stirred with AC (2.0 g) in aqueous solution for 40 minutes in the dark. The resulting ZnO/AC was filtered and dried. Part of the dried ZnO/AC was calcined at $450^0 \text{C}$. Known amount of the solid was placed in the reactor in which aliquot of pollutant solution of known concentration was added. The mixture was centrifuged for 30 minutes in the dark in order to reach the ZnO/AC equilibrium absorption

2.7 Control experiments:

Control photolysis experiments were conducted with no catalyst under direct sun light. Other experiments were conducted in the presence of a catalyst in the dark. In these experiments contaminant concentration did not change after 30 minutes. In the presence of activated carbon the concentration of contaminant significantly change after 30 minutes, indicating adsorption of contaminant onto activated carbon.
2.8 Reuse experiments

After the end of the photo-degradation experiment the catalyst was filtered and washed with distilled water and then reused as a catalyst for a new experiment. The reuse procedure was repeated for four times.
CHAPTER 3
PHOTO-DEGRADATION OF
METHYL ORANGE
3.1 Methyl Orange (MO).

MO has the chemical formula $\text{C}_{14}\text{H}_{14}\text{N}_{3}\text{NaO}_{3}\text{S}$, its molar mass is 327.33 g/mole. The IUPAC name of MO is 4-dimethyl amino azo benzene-4-sulfonic acid sodium salt. Another name is p-dimethyl amino azo benzene sulfonic acid. It is also known as C. I. Acid orange 52, C.I. 13025, helianthine B, Orange III, Gold Orange and Tropaeolin D.

The density of methyl orange is 1.28 g/cm. Its melting point is 102.0°C. MO is a pH indicator frequently used in titration, because its clear color change at the pH of amid-strength acid. It is used as an indicator in the titration of weak bases with strong acids. It changes from red (at pH 3.1) to orange-yellow (at pH 4.4) [45, 46].

Modified MO, an indicator consisting of a solution of MO and Xylene Cyanol, changes from grey to green as the solution becomes more basic. MO is prepared by a reaction between the sulfanilic acid, sodium nitrite and dimethyl aniline. The reaction involves two steps. In the first step a diazonium salt is formed by a reaction between the sulfanilic acid dissolved in dilute aqueous acid and sodium nitrite. Secondly: a coupling reaction between the diazonium salt and dimethyl amine takes place in the opposite para- position from the $-\text{N(CH}_3\text{)}_2$ group. The hydrogen removed from the dimethyl aniline ring is accepted by the acetate ion.
Methyl Orange is used in dying and textile industries causing large volume of dye pollutant ion which are difficult to degrade by conventional chemical and/or biological methods in water. That is due to the stability of modern dyes. Thus photo-electrochemical methods are used to degrade such compounds.

3.2 Experimental

3:2.1 Chemicals

Methyl orange and activated carbon were purchased from Aldrich. ZnO was purchased from Merck (catalog no. 8849, with average particle size 230 nm). Zinc sulfate, Thiourea, CdCl₂ and organic solvents were all purchased from either Aldrich-Sigma Co. or Frutarom Co. in pure form.
**Stock solution preparations**

The following solutions were needed and prepared

* Stock methyl orange solution: 0.1 g of methyl orange was dissolved in hot deionized distilled water. The solution was then diluted to 1.0 liter to make the final concentration 100 ppm (3×10⁻⁴M).

* Sodium hydroxide solution (NaOH\(_{\text{aq}}\), 0.2 N): 4 g of NaOH was dissolved in distilled water and was then diluted to 0.5 liter.

* Hydrochloric acid (HCl\(_{\text{aq}}\), 0.2 N): 10.5 mL of 32% HCl were diluted to 0.5 liter with distilled water

* Zinc ion (Zn\(^{2+}\)) solution: 0.4395 g of ZnSO\(_4\).7H\(_2\)O were dissolved in distilled water and diluted to 1.0 liter to make the final concentration 100 ppm (1.53×10⁻³M).

* Acetate buffer solution: 6 g (0.1 mole) of acetic acid (CH\(_3\)COOH) and 8.2 g (0.1 mole) of sodium acetate were dissolved in distilled water and diluted making final volume 1.0 liter (pH = 4.7).

**3.2.2 Equipment**

Methyl orange concentration were spectro-photometrically measured on a shimadzu UV-1601 spectro-photometer at wavelength 480 nm. To analyze dissolved Zn\(^{2+}\) ions. Anodic Stripping Differential Pulse Polaroigraphy (ADPP) was conducted using a dropping mercury electrode (MDE 150) on a PC-controlled Polarograph (POL 150). The Hanging Mercury Drop Electrode (HMDE) method was followed. The analysis parameters were: initial potential–1200 mV, final scan rate 20 mV/sec, pulse height 25 mV.
To measure the intensity of solar radiation a Lux-meter (Lx-102 light meter) was used

**3.2.3 Concentration measurements**

A spectro-photometer was used to measure methyl orange remaining during photo-degradation experiments. Aqueous solutions with different nominal methyl orange concentrations: 1 ppm, 5 ppm, 10 ppm, 15 ppm, 20 ppm, and 25 ppm were prepared. An absorbance vs. concentration calibration curve was used to analyze remaining MO throughout the course of degradation reaction.

**3.3 Results**

**3.3.1 Calibration curve**

The absorbance vs. concentration calibration curve was used to measure the un-reacted methyl orange concentrations with time during degradation experiments. Figure (3.1) shows the constructed.
Figure (3.1): A calibration curve showing a plot of absorbance vs. methyl orange concentration (ppm). Measurements were conducted in aqueous media, at room temperature.

3.3.2 Control experiments

Control experiments were conducted using aqueous methyl orange solutions, in the absence of light and/or catalyst. Control experiments were also conducted using aqueous methyl orange solutions in the absence of catalyst while using activated carbon (AC). It was found that in all photolysis experiments, carried out with no catalyst, or no light, no methyl orange concentration loss occurred after prolonged time when naked ZnO was used. ZnO/AC system exhibited relatively slight adsorption onto the AC surface, which accounted for about 10 ppm/200ml solution of contaminant concentration on the AC surface (0.02 g).

3.3.3 Naked ZnO catalyst system:

3.3.3.1 Effect of added CdS dye:

The ZnO/CdS system showed lower efficiency, under direct solar light, than the naked ZnO system. Figure (3.2) shows that the degradation
reaction rate was slightly lowered by using small CdS uptakes. CdS exhibited inhibition effect which increased with higher uptakes. Similar behavior was observed from values of quantum yield (molecules contaminant removed per photon after 15 minutes). Quantum yield values (0.01276, 0.01137, 0.01082 and 0.002) were observed for samples with CdS uptakes: 0.0% CdS, 0.4%, 0.8% and 4%, respectively. In the case of using a filter, where UV is not allowed, the naked ZnO did not function, but the ZnO/CdS system caused less than 15% degradation of methyl orange after one hour, as shown in Figure (3.3).

![Graph showing the effect of CdS on ZnO photo-degradation of methyl orange under direct solar light](image)

**Figure (3.2):** Effect of CdS on ZnO photo-degradation of methyl orange under direct solar light (intensity 128000 Lux, 0.0187 W/cm²). All reactions were conducted in a neutral 250 mL contaminant solution (10 ppm) at room temperature using 0.1 g ZnO/CdS with different CdS uptakes: a) 0.0% CdS b) 0.4% CdS, c) 0.8% CdS, and d) 4% CdS
Figure (3.3): Effect of CdS on ZnO photo-degradation of MO under Xe lamp (intensity: 0.01 W/cm²). Using a cut off filter eliminating 400 nm and shorter light. The reaction was conducted in a neutral 100 mL contaminant solution (10 ppm) at room temperature using 0.075 g ZnO with CdS uptake 0.8%.

3.3.3.2 Effect of pH:

Effect of pH on reaction rates of methyl orange degradation with direct solar light was investigated. The rate of reaction was not much affected with the value of pH. At high basicity a slightly different behavior occurred as shown in Figures (3.4) and (3.5). Turnover number (T.N.) values calculated after 15 minutes at different pH values (4.7, 7, 9, 11) were: (0.00529, 0.00536, 0.00538, 0.00496), respectively. The T.N. values indicate that the rate is not much affected with the value of pH and the photo-degradation reaction rate decreases at low or high pH values.
**Figure (3.4):** Effect of pH on rate of methyl orange degradation reaction. Under direct light (90000 Lux, 0.013 W/cm²). All reactions were conducted at room temperature in a 250 mL solution of methyl orange (10 ppm) using 0.1 g ZnO. The pH values were: a) 4.7  b) 7  c) 9  d) 11.

**Figure (3.5):** Effect of pH value on photo-degradation under direct solar light (Radiation intensity: 127000 Lux, 0.01859 W/cm²) of 300 mL methyl orange (20 ppm) using 0.1 g ZnO under basic conditions only. The pH values are: a) 8.1  b) 9.2  c) 10.4  d) 12.0.
3.3.3.3 Effect of temperature:

The effect of temperature on the rate of MO degradation was studied over the temperature range, (10-40°C). There was no significant temperature effect on catalyst efficiency. Temperature 40°C was slightly more favorable, Figure (3.6). Activation energy ($E_a$) calculated was very low (6 kJ/mole). The equation used to calculate the activation energy was

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right].$$

Figure (3.6): Effect of temperature on photo-degradation of neutral 100mL solution methyl orange (10 ppm) using 0.05 g ZnO temp: a) 10°C  b) 20°C  c) 30°C  d) 40°C. For better temperature control, radiation was conducted inside 100 mL thermostated neutral solution of methyl orange (10 ppm) with solar simulator (Radiation Intensity 0.0212 W/cm²) and 0.05 g naked ZnO.

3.3.3.4 Effect of catalyst concentration:

The effect of concentration of ZnO on photo-degradation of MO was investigated by varying its amount from 100 to 1200 mg/300 mL of MO solution. The rate of reaction increased with increasing catalyst amount as shown in Figure (3.7). At higher concentrations, 600-1200 mg, the rate was
independent of catalyst concentration as shown in Figure (3.8). These results indicate that the optimum catalytic amount is between 0.15-0.2 g/100 mL MO solution. Turnover number values relatively decreased with higher catalyst nominal concentrations. For the lower catalyst amount system, 0.6 g/300 mL, it was 0.00224 and for the higher catalyst amount, 1.2 g/300 mL, it was 0.00111.

![Graph](image.png)

**Figure (3.7):** Effect of catalyst ZnO amount on rate of photo-degradation of methyl orange (250 mL solution, 10 ppm), at room temperature under neutral conditions using direct solar light (radiation intensity 0.01815W/cm²). Catalyst ZnO amounts were: a) 0.05 g, b) 0.1 g, c) 0.2 g, d) 0.4 g
**Figure (3.8):** Effect of high catalyst amount on photo-degradation of methyl orange (300 mL solution, 20 ppm), at room temperature under neutral conditions, using direct solar light (radiation intensity 0.01625 W/cm²). Catalyst ZnO amounts were: a) 0.6 g   b) 0.8 g  c) 1.0 g  d) 1.2 g

### 3.3.3.5 Effect of contaminant concentration:

Effect of initial MO concentration on initial rate of MO degradation was studied under direct solar light. The initial dye concentration was varied from 5 ppm to 20 ppm, with constant catalyst loading 0.1 g/300 ml. The degradation rate was higher with higher contaminant concentration as shown in Figure (3.9). T.N. values calculated after 20 minutes at different concentrations of MO (5, 10, 15 and 20 ppm) were: (0.004345, 0.00721, 0.008557 and 0.00912), respectively. The T.N. values indicate that the rate of photo-degradation increases as the initial concentration of MO increases. Plots of ln(initial rate) vs. ln(initial conc.) showed linear relation and the calculated reaction order was 0.7 with respect to the methyl orange concentration.
Figure (3.9): Effect of contaminant concentration on photo-degradation reaction using 0.1 g ZnO in 300 mL neutral solution at room temperature under direct solar light (0.0149 W/cm²). Methyl orange concentrations were: a) 5 ppm  b) 10 ppm  c) 15 ppm  d) 20 ppm

3.3.3.6 Catalyst reuse:

Naked ZnO catalyst samples were recovered for reuse in MO photo-degradation, first and second recovery sample showed almost similar activity as fresh samples. Quantum yield values for the first and second recovered systems in methyl orange degradation estimated after 40 minutes showed Quantum yield (0.0237) almost the same as that for the fresh sample (0.0246), and up to 4% loss of activity occurred. The third recovered catalyst system lost up to 35% of its activity compared to the fresh sample. Its quantum yield was 0.0159. This result is shown in Figure (3.10).
Figure (3.10): Photo-degradation reaction profiles for fresh and recovered ZnO catalysts. Reactions were conducted at room temperature under direct solar light (intensity 0.0144 W/cm²) using a fresh neutral 300 mL solution of methyl orange (10 ppm) in each run. The original catalyst loading was (a) 0.1 g fresh ZnO, (b) First recovery, (c) Second recovery, and (d) Third recovery.

3.3.4 AC-Supported ZnO System:

3.3.4.1 Effect of catalyst amount

The MO degradation reaction was studied using different AC/ZnO nominal amounts, as shown in Figure (3.11), using more than 0.72 g of ZnO/AC was useless, the highest AC/ZnO amount showed lower Quantum yield than using 0.72 g ZnO/AC, Quantum yields calculated for methyl orange photo-degradation after 15 minutes, using different catalytic amounts of ZnO/AC (0.6 g, 0.72 g, 0.84 g) were: (0.05928, 0.08928, 0.0872), respectively. These Quantum yields indicate that the best catalytic loading of ZnO/AC system is 0.72 g (net ZnO 0.6 g) per 300 mL of MO solution.
Figure (3.11): Effect of amount of AC/ZnO on photo-degradation rate of methyl orange inside 300 mL neutral solution at room temperature under direct solar light (0.0149 W/cm²). Catalyst amounts were: a) net ZnO 0.5 g, b) net ZnO 0.6 g), and c) net ZnO 0.7 g).

3.3.4.2 Effect of contaminant concentration:

The effect of contaminant concentration on the AC/ZnO catalyzed reaction was studied using wide range of contaminant concentrations (30-100) ppm as shown in Figure(3.12). It is obvious that the AC/ZnO system function efficiently in this range. T.N. values measured after 30 minute photo-degradation time, using contaminant concentrations (30, 40, 50, 100 ppm), were: (0.002, 0.007224, 0.009385 and 0.006426), respectively. These turnover number values indicate that the reaction was faster with higher contaminant concentrations up to 50 ppm.
Figure (3.12): Effect of contaminant concentration on photo-degradation reaction of methyl orange in neutral solutions (300 mL) at room temperature under direct solar light (intensity 0.0164 W/cm²) using AC/ZnO (0.24 g, containing 0.2 g ZnO). Contaminant concentrations were: a) 100 ppm  b) 50 ppm  c) 40 ppm  d) 30 ppm. T.N. values (moles reacted per mol ZnO after 30 min) are: 0.006426, 0.009385, 0.007224 and 0.002, respectively.

3.3.4.3 Effect of temperature:

MO degradation was studied using AC/ZnO system at different temperatures. A systematic effect for temperature on reaction rate was observed, as shown in Figure (3.13). T.N. values calculated after 40 minutes, for MO degradation at temperatures 19°C, 29°C and 38°C were (0.0022, 0.0019, 0.00089) respectively. Based on these T.N. values, the efficiency of photo-degradation was increased as the temperature was decreased.
Figure (3.13): Effect of temperature on photo-degradation of neutral 100 mL of methyl orange (40 ppm) using 0.12 g ZnO/AC (containing 0.1 g pure ZnO) under solar simulator radiation (0.0212 W/cm²). The reaction temperature was thermostated at: a) 19°C  b) 29°C  c) 38°C.

3.3.4.4 Effect of pH:

Methyl orange degradation reaction using AC/ZnO system was investigated in solutions with different pH values. The catalytic efficiency did not vary with value of pH in the range 4-10. At high pH values, the reaction rate was slightly lower as shown in Figure (3.14). T.N. values calculated after 40 minutes at pH values (4.2, 8.4, 10, 12) for MO degradation were: (0.0114, 0.0122, 0.0123, 0.0107), respectively. These T.N. values indicate that slightly basic conditions are more favorable.
Figure (3.14): Effect of pH on photo-degradation of 300 mL solution of methyl orange (25 ppm) using 0.12 g ZnO/AC (with 0.1 g net ZnO) at room temperature under direct solar light (0.0171 W/cm²). The solution pH values were: a) 4.2  b) 8.4  c) 10  d) 12

3.3.4.5 Catalyst recovery and reuse

The catalyst AC/ZnO was recovered from methyl orange degradation reaction and reused for three successive times, no efficiency loss occurred in all recovered catalyst systems as shown in Figure (3.15). Quantum yield values for the fresh, first, second and third recovery samples in MO degradation were: (0.03515, 0.04606, 0.03661, 0.03865), respectively. The quantum yield values show that a slight efficiency loss on recovery was observed. This will be discussed later in Chapter 5.
Figure (3.15): Reaction profiles showing photo-degradation of methyl orange in 300 mL neutral solutions at room temperature under direct solar light (0.01427 W/cm²) using: (a) 0.12 g fresh AC/ZnO catalyst (containing 0.1 g ZnO), (b) First recovery, (c) Second recovery, and (d) Third recovery.

3.3.4.6 Effect of calcinations

Effect of AC/ZnO catalyst pre-calcination on its efficiency was studied in methyl orange photo-degradation reactions. The degradation rate for calcinated AC/ZnO system was higher than that for untreated counterpart, as shown in Figure (3.16). Calcinations increased efficiency of photo-degradation of MO by 30%. T.N. values calculated after 60 minutes for calcinated ZnO/AC system and non-calcinated ZnO/AC system, were: (0.00242, 0.001631), respectively. The T.N. values indicate higher efficiency for the calcinated ZnO/AC system.
**Figure (3.16):** Comparison between calcinated ZnO/AC at 450°C and none calcinated ZnO/AC using 100 mL MO solution at room temperature under neutral condition using Xe lamp (Radiation intensity 0.01 W/cm²). Catalyst ZnO/AC amount was 0.12 g (containing 0.1 g ZnO).
CHAPTER 4
PHOTO-DEGRADATION OF PHENAZOPYRIDINE
4.1) Phenazopyridine

Phenazopyridine has the chemical formula C\textsubscript{11}H\textsubscript{11}N\textsubscript{5}.HCl, its structural formula is:

\[ \text{\includegraphics[width=0.2\textwidth]{phenazopyridine_structure.png}} \]

Its molecular weight is 249.7 g/mole, and it is chemically designated 2,6–pyridine diamine, 3–(phenyl azo), mono-hydrochloride. Brand names of phenazopyridine are: Azo–Gesic, phenazo, Prodim Azo–standard, Baridium, Pyridium, Pyridiate, Pyridium, Re–Azo, Uricalm, Uristal, Viridium, Eridium, Urogesc, Urodol, Urinary Analgesic.

Phenazopyridine is used as a pain reliever that affects the lower part of urinary tract. It also treats the symptoms of urinary tract like pain, burning, increased urination which are usually caused by infection, injury, surgery. The actual infection will not be treated by phenazopyridine but by any antibiotic that a doctor prescribes to treat the infection.

Phenazopyridine should not be taken by persons who are allergic to it or have kidney disease. It is taken with food to avoid stomach upset.

Before taking phenazopyridine the patient should inform the doctor if he/she is allergic to any drugs or if he/she has liver disease, diabetes or a condition called G6PD (glucose–6–phosphate dehydrogenase) deficiency.

The maximum time to use phenazopyridine is two days unless otherwise stated by the doctor. The patient should stop taking the medicine and call the doctor if he/she has a pale skin, fever, yellowing of skin or eyes,
increased thirst, swelling, or if he/she urinates more or less than usual. Less serious side effects may include headache, stomach pain, stomach upset or skin itching.

Phenazopyridine may interact with other drugs. Therefore the doctor should be told if the patient takes other drugs, vitamins, minerals or herbal products [47, 48]. Phenazopyridine will most likely darken the color of the urine. This is a normal effect. Darkened urine may also cause stains to underwear, which may not be removed by laundering.

Phenazopyridine is an example of the compounds that are difficult to degrade by conventional methods in water. Naked ZnO and ZnO supported onto activated carbon AC were used here as catalysts for photo–degradation of phenazopyridine.

4.2 Experimental
4:2.1 Chemicals

Phenazopyridine was kindly donated by Birzeit-Palestine Pharmaceutical Company. Organic solvents were purchased from either Aldrich-Sigma Co. or Frutarom, and ZnO from Merck.

Stock solution

The following solutions were needed and prepared:

*100 ppm phenazopyridine solution was prepared by dissolving 0.1 g phenazopyridine in distilled water then diluting to 1.0 liter.

*Approximately 0.2 M HCl solution was prepared by diluting 10.5 mL of 32% HCl to 500 mL with distilled water.

*Sodium hydroxide solution (NaOH_{aq}, 0.2 N): 4 g of NaOH was
dissolved in distilled water, and the solution was then diluted to 0.5 liter

*Cadmium ion (Cd\(^{2+}\)) solution: A solution (100 ppm) of Cd\(^{2+}\) was prepared by dissolving 0.195 g of CdCl\(_2\) in a certain amount of distilled water, and the solution was then diluted to 1.0 liter.

4.2.2 Equipment

Phenazopyridine concentrations were spectrophotometrically measured on a Shimadzu UV-1601 spectrophotometer at wavelength 480 nm. To analyze dissolved Zn\(^{2+}\) ions, anodic stripping differential pulse Polarography (ADPP) was conducted using a dropping mercury electrode (MDE 150) on a PC controlled Polarograph (POL 150). The analysis parameters were: initial potential -700 mV, final potential –400mV, purging time 30 sec, deposition time 20 sec, scan rate 20 mV/sec, pulse height 25mV.

4.2.3 Concentration measurements

A spectrophotometer was used to measure phenazopyridine remaining during photo-degradation experiments. Aqueous solutions with different nominal phenazopyridine concentrations, 1 ppm, 2 ppm, 5 ppm, 10 ppm, 15 ppm and 20 ppm, were prepared. An absorbance vs. concentration calibration curve was used to analyze remaining phenazopyridine throughout the course of degradation reaction.
4.3 Results

4.3.1 Calibration curve

The absorbance vs. concentration calibration curve was used to measure the un-reacted phenazopyridine concentrations with time during degradation experiments. Figure (4.1) shows the calibration curve used

![Calibration curve for PhenazoPyridene](image)

Figure (4.1): A calibration curve showing a plot of absorbance vs phenazopyridine concentration (ppm). Measurements were conducted in aqueous media, at room temperature.

4.3.2 Control experiments

Control experiments were conducted using aqueous phenazopyridine solutions in the dark, or in the absence of catalyst. AC adsorption of phenazopyridine was also studied. In control experiments, phenazopyridine concentrations did not change after prolonged time. ZnO/AC system exhibited relatively high adsorption onto AC surface which accounted to about 10 ppm of contaminant concentration on the AC surface (0.02 g).
4.3.3 Naked ZnO catalyst system:

4.3.3.1 Effect of pH

The effect of pH on reaction rates of phenazopyridine degradation with solar simulator was investigated. The rate of reaction was not much affected with the value of pH. At high basicity, a slightly different behaviour occurred as shown in Figure [4.2]. T.N. values calculated after 30 minutes at different pH values, 3.3, 6.4, 8 and 11.4, were: (0.00597, 0.00797, 0.00978, 0.00752), respectively. The T.N. values indicated that at low or high basicity the reaction was slower than in slightly basic or slightly acidic media.

Figure (4.2): Effect of pH value on photo-degradation of 100 mL phenazopyridine solution (12 ppm) under Xe solar simulator lamp (Radiation intensity: 70000 Lux, 0.01 W/cm²) using 0.15 g ZnO at room temperature. The solution pH values were: a) 4.9  b) 6  c) 8  d) 11.6
4.3.3.2 Effect of temperature:
The effect of temperature on rate of phenazopyridine degradation was studied with solar simulator radiation over the temperature range, 10-40°C. There was no significant temperature effect on catalyst efficiency with a slight increase in the rate at the highest temperature, as shown in Figure [4.3]. The calculated activation energy was negligible, (~6.1 kJ/mole).

![Figure (4.3): Effect of temperature on photo-degradation of neutral 100 mL solution phenazopyridine (10 ppm) using 0.05 g ZnO temp: a) 10°C  b) 20°C  c) 30°C  d) 40°C. For better temperature control, radiation was conducted inside 100 mL thermostated neutral solution of phenazopyridine (10 ppm) with solar simulator (Radiation Intensity 0.01 W/cm²).](image)

4.3.3.3 Effect of catalyst concentration
The effect of ZnO catalyst concentration on degradation of phenazopyridine was investigated. The rate of reaction increased with
increasing catalyst amount as shown in Figure [4.4]. At much higher concentration the rate became independent of catalyst concentration. Turnover number values calculated after 60 minutes using different catalyst amounts (0.09 g, 0.15 g, 0.2 g, 0.25 g) were: (0.00125, 0.00135, 0.000758, 0.000613), respectively. The T.N. values indicate the uselessness of increasing the amount of ZnO over 0.15 g/100 mL solution of phenazopyridine.

Figure (4.4): Effect of catalyst ZnO amount on rate photo-degradation of phenazopyridine (100 mL solution, 12 ppm), at room temperature under neutral conditions using Xe lamp (radiation intensity 0.01 W/cm²). Catalyst ZnO amounts were: a) 0.09 g  b) 0.15 g  c) 0.20 g  d) 0.25 g

4.3.3.4 Effect of contaminant concentration:
Effect of initial phenazopyridine concentration on initial rate of degradation was studied under direct solar light. The degradation rate was higher with higher contaminant concentration as shown in Figure (4.5). T.N. values calculated after 20 minutes at different phenazopyridine concentration (10,
15, 20) ppm were: (0.00755, 0.00941, 0.01), respectively. Plots of (ln initial rate) vs. (ln initial concentration) showed linear relation and the calculated reaction order was 0.4 with respect to the phenazopyridine concentration.

![Figure (4.5): Effect of contaminant concentration on photo-degradation reaction using 0.1 g ZnO in 250 mL neutral solutions at room temperature under direct solar light (0.0168 W/cm²) phenazopyridine concentrations were: a) 5 ppm b) 10 ppm c) 15 ppm d) 20 ppm.](image)

4.3.3.5 Catalyst reuse:

Naked ZnO catalyst samples were recovered for reuse in phenazopyridine photo-degradation. First, second and third recovery samples showed 13%, 21% and 63% catalyst efficiency losses, respectively, compared to the fresh sample. Figure (4.6) summarizes these findings. Quantum yield values for fresh sample and for first, second and third recovery samples, were: (0.00582, 0.00501, 0.00455, 0.00215), respectively.
Figure (4.6): Photo-degradation reaction profiles for fresh and recovered ZnO catalysts. Reactions were conducted at room temperature under Xe lamp solar simulator (intensity 0.01 W/cm²) using a fresh neutral 100 mL solution (10 ppm) in each run. The original catalyst loading was (a) 0.09 g fresh ZnO (b) First recovery (c) Second recovery and (d) Third recovery.

4.3.4 AC-Supported ZnO system:

4.3.4.1 Effect of catalyst amount

The phenazopyridine degradation reaction was studied using different AC/ZnO nominal amounts, as shown in Figure (4.7). Using high amounts of the catalyst did not increase the rate of the reaction. Highest AC/ZnO amounts showed lowest Quantum yield. Quantum yields calculated after 10 minutes, using different catalyst amounts of ZnO/AC system (0.84 g, 0.96 g, 1.08 g, 1.2 g) were: (0.05, 0.0575, 0.0575, 0.0478), respectively. These Quantum yields indicated that using more than net 0.8 g ZnO/400 mL phenazopyridine solution is useless.
4.3.4.2 Effect of contaminant concentration:

The effect of contaminant concentration on the AC/ZnO catalyzed reaction was studied. The rate of reaction increased as the initial concentration of the contaminant increased up to initial concentration 30 ppm, as shown in Figure (4.8). T.N. values measured after 20 minutes for different contaminant concentrations (20 ppm, 25 ppm, 30 ppm, 35 ppm) of phenazopyridine were: (0.00495, 0.00862, 0.008944, 0.00828), respectively. The T.N. indicated that the reaction was faster with higher contaminant concentration up to 30 ppm. Using higher contaminant amounts lowered down the reaction rate.
Figure (4.8): Effect of contaminant concentration on photo-degradation reaction of phenazopyridine in neutral solutions (300 mL) at room temperature under direct solar light (intensity: 0.0165 W/cm²) using AC/ZnO 0.15 g (containing 0. 0.125 g ZnO). Contaminant concentrations were: A) 20 ppm  b) 25 ppm  c) 30 ppm  d) 35 ppm.

4.3.4.3 Effect of temperature:
Phenazopyridine degradation reaction using AC/ZnO system was investigated. A systematic effect for temperature on reaction rate was observed up to a temperature 30°C as shown in Figure (4.9). T.N. values calculated after 60 minutes at temperatures 10, 20, 30 and 40°C were: (0.00264, 0.00233, 0.00182, 0.00212), respectively. These T.N. values showed that the efficiency of photo-degradation was decreased as the temperature increased until reaching temperature 30°C. Increasing the temperature above 30°C, a slight increase in the efficiency occurs.
Figure (4.9): Effect of temperature on photo-degradation of neutral 100 mL of phenazopyridine using 0.12 g ZnO/AC (containing 0.1 g pure ZnO) under solar simulator (0.01 W/cm²). The reaction temperature was thermostated at: a) 10°C  b) 20°C  c) 30°C  d) 40°C.

### 4.3.4.4 Effect of pH:

Phenazopyridine degradation reaction using AC/ZnO system was investigated in solutions with different pH values. The catalytic efficiency did not vary with value of pH in the range 4-10. At higher pH value the reaction rate was slightly lower as shown in Figure (4.10). T.N. values calculated after 20 minutes at different pH values (3.3, 6.4, 8, 11.4) were: (0.00424, 0.00797, 0.0096 and 0.00752), respectively. The results show that the photo-degradation process is more favored around the normal pH 7 value.
Figure (4.10): Effect of pH on photo-degradation of 300 mL solution of phenazopyridine (25 ppm) using 0.12 g ZnO/AC (with 0.1 g net ZnO) at room temperature under direct solar light (0.0134 W/cm²). The solution pH values were: a) 3.3  b) 6.4  c) 8  d) 11.4

4.3.4.5 Catalyst recovery and reuse

The catalyst AC/ZnO was recovered from the phenazopyridine degradation reaction and reused for three successive times. A pronounced efficiency loss occurred in the third recovery catalyst system as shown in Figure (4.11). T.N. values calculated after 40 minutes for the fresh, first, second and third recovery samples were: (0.003, 0.00183, 0.00154, 0.00127), respectively. About 16% and 30% efficiency loss occurred in the second and the third recovery respectively compared to the first recovery.
Figure (4.11): Reaction profiles showing photo-degradation of phenazopyridine in 100 mL neutral solutions (with initial concentration for the fresh sample 30 ppm) at room temperature under Xe lamp (0.01 W/cm²) using  

- a) 0.1 g fresh AC/ZnO catalyst (containing 0.083 g ZnO) ,  
- b) First recovery,  
- c) Second recovery and  
- d) Third recovery.

4.3.4.6 Effect of AC/ZnO calcination

Phenazopyridine degradation reaction using calcinated AC/ZnO and non-calcinated AC/ZnO systems was investigated. The degradation rate using calcinated AC/ZnO system (at 450°C) was higher than the non-calcinated system as shown in Figure (4.12). T.N. values calculated after 40 minutes for the calcinated ZnO/AC and non-calcinated ZnO/AC systems were: (0.00433, 0.00324), respectively. The efficiency of degradation was increased by 25% by calcinations.
Figure (4.12): Comparison between 450°C calcinated ZnO/AC and non-calcinated ZnO/AC systems using 100 mL phenazopyridine neutral solution (35 ppm) at room temperature using Xe lamp (Radiation intensity: 0.01 W/cm²). Catalyst ZnO/AC amount was 0.12 g (containing 0.1 g ZnO). a) ZnO/AC calcinated b) ZnO/AC non-calcinated.

4.3.4.7 Effect of calcination on the reused catalyst efficiency:

The calcinated catalyst AC/ZnO was recovered from the phenzopyridine degradation reaction and reused for three successive times. Calcination did not affect efficiency of reused catalyst. This result is shown in Figure (4.13). The efficiency loss was about 30% on first recovery of calcinated system, compared to the fresh calcinated sample. T.N. values calculated after 60 minutes for the fresh, first, second and third recovery samples were: (0.002378, 0.001668, 0.001635, 0.00134), respectively.
Figure (4.13): Reaction profiles showing photo-degradation of phenazopyridine in 100 ml neutral solutions at room temperature under Xe solar simulator lamp radiation (intensity 0.01 W/cm²) using ZnO/AC catalyst. Net weights of ZnO were: (a) 0.166 g  (b) 0.1 g  
(c) 0.096 g and  (d) 0.085 g
Figure (4.14): UV Visible spectra of phenazopyridine on irradiation in the presence of ZnO (0.2 g). 300 mL of phenazopyridine (25 ppm) at neutral pH.
5.1. INTRODUCTION:

Exposure of aqueous solutions, of methyl orange and phenazopyridine, having different pH values, to direct solar light, in the presence of ZnO particles, caused complete decolorization of the methyl orange and phenazopyridine solutions in reasonably short times. In control experiments conducted in the dark, under otherwise same conditions, no decolorization was observed. Exposure of the methyl orange and phenazopyridine to solar light with no ZnO did not cause any noticeable decolorization. The methyl orange and phenazopyridine solutions, with ZnO suspended, did not exhibit any noticeable decolorization under solar simulator light when a cut-off filter (eliminating 400 nm and shorter wavelengths) was used. This indicates that the decolorization is due to the UV tail available in the solar light, not the visible light itself. The decolorization is a direct indication of photo-degradation of methyl orange and phenazopyridine contaminants. Literature indicated that methyl orange undergoes complete mineralization under PEC conditions [11-12, 16-18]. Therefore, the degraded methyl orange is assumed to be completely mineralized. When a semiconductor is illuminated with photons of energy higher than or equal to its band gap energy, electron-hole pairs are created. In a fluid reaction medium, the photo-generated electrons could reduce the contaminant or react with electron acceptors such as O₂ adsorbed on the catalyst surface or dissolved in water reducing it to super oxide radical anion O₂⁻. The photo-generated holes
can oxidize the organic molecules to form $R^+$, or react with $\text{OH}^-$ or $\text{H}_2\text{O}$ oxidizing them to OH\(^{-}\) Radicals. The relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed as follows [11].

\[
\text{ZnO} + \text{hv(UV)} \rightarrow \text{ZnO(e}^{-}\text{CB} + \text{h}^{+}\text{VB}) \tag{1}
\]

\[
\text{ZnO(h}^{+}\text{VB}) + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}^{+} + \text{OH}^{-} \tag{2}
\]

\[
\text{ZnO (h}^{+}\text{VB}) + \text{OH}^{-} \rightarrow \text{ZnO} + \text{OH}^{-} \tag{3}
\]

\[
\text{ZnO(e}^{-}\text{CB}) + \text{O}_2 \rightarrow \text{ZnO} + \text{O}_2^{-} \tag{4}
\]

\[
\text{O}_2^{-} + \text{H}^{+} \rightarrow \text{HO}_2^{-} \tag{5}
\]

\[
\text{Dye} + \text{OH}^{-} \rightarrow \text{Degradation products} \tag{6}
\]

The ability of ZnO to degrade methyl orange and phenazopyridine under direct solar light is the focal issue here. Effects of catalyst type, pH, temperature, catalyst nominal concentration and contaminant concentration were all studied. Effect of CdS, as a sensitizer for ZnO, was also studied. Moreover, the effect of supporting ZnO onto AC is discussed.
5. 2 Non-supported ZnO Catalyst System:

5.2.1 Effect of added CdS dye:

Naked ZnO showed high efficiency of methyl orange photo-degradation under direct solar light. The active solar light was the UV tail rather than the visible region. This was manifested by the fact that using a cut-off filter (eliminating 400 nm or shorter wavelengths) prevented degradation.

The ability of CdS to enhance efficiency of ZnO in degradation reaction, by sensitization, was assessed here. The ZnO/CdS system showed lower efficiency, under direct solar light, than the naked system. Figure (3.2) shows that the degradation reaction rate was slightly lowered by using small CdS uptakes. With higher CdS uptakes, the inhibition effect was more pronounced, as shown in the Figure. The same behavior was observed from values of quantum yield measured for different reaction runs (a) 0.01276, (b) 0.01137, (c) 0.01082 and (d) 0.002.

Since no noticeable enhancement was observed, even with low CdS uptakes, the CdS dye must be avoided in case of ZnO catalyst. With higher concentrations, the CdS system caused almost complete inhibition for the degradation reaction. The inhibition is attributed to the screening of the UV radiations away from the ZnO particle surfaces. This parallels other reports, where CdS screened UV light away from SC catalyst particles and lowered the efficiency in the UV [38]. Mixing ZnO with other catalysts like TiO₂, SnO₂ also decreased the efficiency of ZnO [49].
Some reports stated that ZnO/CdS (0.2% CdS by mass) enhances efficiency of ZnO in methyl orange degradation by 500 W medium pressure mercury lamp [39], while other reports stated that naked ZnO showed higher efficiency in degrading contaminants under UV light [49]. To verify this matter, special experiments were conducted here. Naked ZnO and ZnO/CdS (with different CdS percent uptakes) were used in methyl orange degradation using direct solar light, with no UV tail (using a cut-off filter eliminating 400 nm and shorter UV) and with UV tail. The results indicated that CdS inhibited the reaction rate under direct solar light (with UV), as shown in Figure (3.2). In case of a filter, with no allowed UV, the naked ZnO did not function, but the ZnO/CdS systems caused less than 15% degradation of methyl orange after one hour as shown in Figure (3.3). With CdS, only very little sensitization occurred in the only-visible light, whereas in the direct solar light (with UV tail) CdS screened UV and inhibited the reaction. The inhibition (in direct solar light) is more profound than the sensitization effect (in only-visible light). Moreover, ZnO/CdS systems used in direct solar light showed another disadvantage. When left under PEC conditions for enough time the CdS was completely degraded and washed away, and the remaining ZnO system showed enhanced efficiency. The formation of an elemental sulfur layer on the surface of the CdS particles caused by photo anodic corrosion may affect significantly the photo-catalysis reaction according to equation (1).

$$\text{CdS}_{(s)} + 2 \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{(g)} + \text{Cd}^{2+}_{(aq)} + \text{S}_{(s)} + 2\text{OH}^-_{(aq)} \quad (1)$$

[50]
These results suggest the incompetence and limitations of CdS as sensitizer for the ZnO particles used here. Its ability to sensitize ZnO particles with smaller sizes (nano-scale) can not be ruled out, as literature suggested [39].

In CdS-sensitized TiO$_2$ particles, CdS showed high sensitization power to visible light that surpassed its screening effect, and the TiO$_2$/CdS showed higher efficiency than the naked TiO$_2$ under solar simulators [51]. In case of ZnO systems the CdS failed to behave similarly. This, together with the hazardous nature of CdS to leach out toxic Cd$^{2+}$ ions into solution, are compelling evidence against using CdS as sensitizer here [44]. The ability of ZnO to catalyze decomposition in direct solar light puts an end to many costly and difficult sensitization-based techniques. This alone makes naked ZnO an excellent candidate for catalytic photo-degradation processes.

5.2.2 Effect of pH

Waste water from textile industries usually has wide range of pH values. Experiments conducted at different pH values showed that the rate of the reaction was reasonably fast and not much affected with the value of pH. The change of pH of the solution causes positive or negative charging of crystal particles, consequently, a change in the rate of adsorption of the compound being degraded occurs [52]. Figures (3.4) and (3.5) show effect of using different acidities on the rate of methyl orange degradation. T.N. values calculated after 15 minutes at different pH values (4.7, 7, 9, 11) were: (0.00529, 0.00536, 0.00538, 0.00496), respectively. Figure (4.2) shows effect of using different acidities on the rate of phenazopyridine
degradation. T.N. values calculated after 30 minutes at different pH values (3.3, 6.4, 8, 11.4) were: (0.00597, 0.00797, 0.00978, 0.00752), respectively. Based on T.N. values, pH did not show significant effect on reaction rates. Therefore, methyl orange or phenazopyridine experiments were conducted using neutral solutions, unless otherwise stated.

At higher basicity (pH more than 11), a slightly different behavior occurred. The reaction demanded an induction period. At the beginning, it did not start efficiently, but after a few minutes the reaction progress was more clearly noticed, Figures (3.2)-(3.3). In a strongly alkaline environment ZnO can undergo dissolution, as shown in equation (2).

Therefore the photo catalytic activity of ZnO is reduced

$$\text{ZnO}_{(s)} + \text{H}_2\text{O}_{(l)} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-}_{(aq)}$$  \hspace{1cm} (2)

ZnO powder exhibit tendency to dissolve with decreasing the pH \[37, 52\] as shown in equation (3):

$$\text{ZnO}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{H}_2\text{O}_{(l)}$$  \hspace{1cm} (3)

These behaviors explain the decrease in the rate of photo-degradation at low pH as shown in Figure (4.3). Such behaviors should not be counted against ZnO catalyst systems, because the natural working conditions for water purification involve pH ranges closer to the pH 7. Its ability to completely degrade MO or phenazopyridine in less than 30 min under pH conditions in range 4.7-9, is an outstanding characteristic for ZnO system.
5.2.3 Effect of temperature:

Temperature showed no significant effect on catalyst efficiency. Figures (3.6) and (4.3) show that the reaction rate did not increase with higher temperature, and that the value for activation energy was negligible. For better control of reaction mixture a Xe lamp solar simulator was used instead of direct solar light. This is contrary to thermally induced catalytic reactions where the rate increases with higher temperature. Photochemical degradation reactions, using high band gap SC catalysts, normally have rates that are known to be independent of temperature [7, 53]. What matters here is the value of the photon energy which is in the order 3.2 eV or higher. Thermal energy gained by heating at ambient temperatures (less than 100°C) is far less than 3.0 eV, viz. heat energy lies within the IR region only not UV. Moreover, higher temperatures encourage the dissolved oxygen, present in the reaction mixture, to escape. Therefore, OH’ radical formation, necessary for contaminant oxidation, will be prevented by the lack of dissolved oxygen.

5.2.4 Effect of catalyst concentration:

The effect of ZnO nominal concentration on photo-degradation of MO has been examined by varying its initial amount from 100 to 1200 mg/300 mL of the MO solution, Figure (3.7). When using lower catalyst concentration (100-600) mg, the rate of reaction increased with increasing catalytic amount. This can be attributed to the fact that more light is
transmitted through the reactor and the transmitted light is not utilized in the photo-catalytic reaction. Increasing the catalytic amount leads to a higher surface area of the catalyst that is available for adsorption and degradation. At higher concentrations the rate was independent of catalyst concentration as shown in Figure (3.8). This is a common behavior among semiconductor catalytic systems in photo-degradation processes. This is understandable, because at higher catalyst concentrations, large proportions of the catalyst sites are screened away from incident light, and the efficiency is expected to decrease. T.N. values (mole reacted MO per mole ZnO after 30 min) relatively decreased with higher catalyst nominal concentrations. For lower catalyst amounts (0.6 g/300 mL) the value was 0.00224, whereas for higher catalyst amount (1.2 g/300 mL) it was 0.00111 only.

The decrease in efficiency of degradation at higher catalyst concentrations may also be attributed to deactivation caused by collision of activated molecules with ground state molecules [15].

\[
\text{ZnO}^* + \text{ZnO} \rightarrow \text{ZnO}^# + \text{ZnO}
\]

Where \( \text{ZnO}^* \) is the ZnO with active species absorbed on its surface and \( \text{ZnO}^# \) the deactivated form of ZnO.

The effect of ZnO loading on photo-degradation of phenazopyridine has been examined by varying the amount of ZnO from (90-250) mg/100 mL solution of phenazopyridine using Xe lamp. Increasing the ZnO amount more than 150 mg/100 mL phenazopyridine exhibited no effect on the rate of reaction as shown in Figure (4.4). T.N. values calculated after 60
minutes at different catalyst amounts (0.09, 0.15, 0.2 and 0.25) were: (0.00125, 0.00135, 0.000758 and 0.000613), respectively. This support the idea of radiation screening away from catalyst active sites while using higher catalyst amounts.

5.2.5 Effect of contaminant concentration:
The effect of initial concentration of the MO on the rate of MO degradation was performed by varying the initial dye concentration from (1.52X10^-5 to 6.1X10^-5) mole/L (5-20) ppm. With constant catalyst loading 0.1 g/300 mL. The degradation rate was higher with higher contaminant concentration as shown in Figure (3.9). T.N. values calculated after 20 minutes at different concentrations of MO (5, 10, 15, 20 ppm) were: (0.004345, 0.00721, 0.008557, 0.00912), respectively. These T.N. values indicate that the rate of photo-degradation increases as the initial contaminant concentration increases. Plots of ln(initial rate) vs. ln(initial conc.) showed linear relation and the calculated reaction order was 0.7 with respect to the methyl orange concentration. In case of phenazopyridine degradation, using the same concentrations of MO described above, (5-20) ppm, the results in Figure (4.5) reveal that the initial dye concentration influences the rate of degradation of the dye. The rate of degradation was higher with higher dye concentrations. This trend was supported by T.N. values calculated after 20 minutes at different phenazopyridine concentrations (10, 15, 20 ppm) that were: (0.00755, 0.00941, 0.01), respectively. Plots of ln(initial rate) vs. ln(initial concentration) showed linear relation and the calculated reaction order was 0.4 with respect to the phenazopyridine concentration.
It is generally noted that the degradation rate increases with increasing dye concentration to a certain limit. Further increase leads to a lowering in the dye degradation rate. A possible explanation for such lowering is that as the initial concentration of the dye increases, the allowed path length of photons entering the solution decreases. In other words, the contaminant molecules exhibit screening of radiation away from ZnO. At low concentrations, the reverse effect is observed, thereby, increasing the number of photon absorption by the catalyst in lower concentration [12, 15, 23, 24, 54].

5.2.6 Catalyst recovery and reuse

Naked ZnO catalyst samples were recovered for reuse in MO and phenazopyridine photo-degradation. Figure (3.10) showed that the first and second recovery samples showed almost similar activity as fresh samples. Quantum yield values for the first and second recovered system in MO degradation showed quantum yields (0.0237) comparable to that for the fresh sample (0.0246), with up to 4% loss of activity. The third recovery catalyst lost up to 35 % of its activity compared to the fresh sample. Its quantum yield was 0.0159. In case of phenazopyridine degradation, Figure (4.6) showed loss of catalyst efficiency on first and second recoveries by 13% and 21%, respectively, compared to the fresh sample. In third recovery, the loss of efficiency occurred to a higher extent (63%). Quantum yields for fresh, first, second and third recovery samples were: (0.00582, 0.00501, 0.00455, 0.00215), respectively.
A possible explanation is that coagulation of ZnO powder caused by interaction by MO molecules or their intermediates resulting in a reduction of the surface area of ZnO particles. Nano scale inorganic oxides have a high tendency to aggregate [55]. However, researchers discovered that during the photo-degradation process, interaction by certain pollutant molecules or their intermediates could cause the TiO$_2$ powder to coagulate, thereby reducing the amount of UV radiation from reaching the TiO$_2$ active centers (due to reduction of its surface area) and thus reducing its catalytic effectiveness [56]. Another explanation for efficiency loss is due to poisoning sulfur chemicals deposited onto ZnO surface.

Loss of efficiency on recovery and reuse should not count against the ZnO systems. Literature reports [14, 51] showed more efficiency loss in recovered semiconductor catalysts. The technical difficulty in recovering ZnO powder out of the reaction mixture may count against ZnO system. However, this difficulty is not associated only with ZnO systems. Normally, micro-scale and nano-scale catalyst systems exhibit technical difficulty in recovery. One possible technique to facilitate ZnO catalyst recovery is by using solid AC support as will be discussed below.

5.3 AC-Supported ZnO system:

The AC/ZnO system is a dark-color solid, with 83% (or higher in some cases) ZnO and the remaining was AC. The AC/ZnO is hydrophilic in nature as readily mixes with water without difficulty. It was also easy to isolate from water by simple filtration. This alone makes up for any other
shortcoming that could possibly be associated with using AC support. The efficiency of AC/ZnO system has been investigated using different parameters, keeping an eye on its credibility to use commercially in the future.

5.3.1 Effect of catalyst amount

The methyl orange degradation reaction was studied using different AC/ZnO nominal amounts, as shown in Figure (3.11). Unlike naked ZnO catalyst systems, the AC/ZnO system exhibited relatively high adsorption onto the AC surface which accounted for about 10 ppm of contaminant concentration adsorption on the AC surface (0.02 g). For this reason, relatively high contaminant concentrations were used in the AC/ZnO systems. The catalyst and contaminant mixture was allowed to stand for prolonged time intervals before irradiation started. This was to ensure AC surface was saturated with contaminant molecules. Any contaminant loss after that was due to degradation.

Figure (3.11) shows that measured initial contaminant concentration values did not match nominal used concentrations. Moreover, the initial rate calculations could not be accurately measured for the AC/ZnO systems. Therefore, efficiency comparisons were performed based on quantum yields only.

Quantum yields calculated for MO photo-degradation after 15 minutes using different catalytic amounts of ZnO/AC (0.6 g, 0.72 g, 0.84 g) were:
(0.05928, 0.08928, 0.0872), respectively. The quantum yield values indicate that the best catalytic AC/ZnO amount is 0.72 g (net ZnO 0.6 g) per 300 mL of MO solution. Using higher catalyst amount caused some light screening. Further the addition of surplus catalyst also results in the deactivation of activated molecules by collision with ground state molecules, Therefore the efficiency of photo-degradation decreased [57]. It should be noted that only surface sites of ZnO system are catalytically active sites, and the majority of the ZnO active sites are inaccessible bulk type. This shows the competitiveness of the ZnO system in methyl orange degradation.

In case of phenazopyridine photo-degradation, Figure (4.7), quantum yield values calculated after 10 minutes, using different AC/ZnO catalytic amounts (0.84 g, 0.96 g, 1.08 g and 1.2 g) were: (0.05, 0.0575, 0.0575, 0.0478), respectively. The quantum yield values indicate that using more than net 0.8 g ZnO/400 mL phenazopyridine solution is useless. As mentioned before light screening is responsible for the decrease in the efficiency of photo-degradation with higher catalyst amounts.

5.3.2 Effect of contaminant concentration:

The effect of contaminant concentration on the AC/ZnO catalyzed reaction was studied. Due to contaminant adsorption it was not possible to measure or compare initial reaction rates, Figure (3.12). T.N. values obtained after 30 minutes at (30, 40, 50, 100 ppm) for MO degradation were: (0.002,
0.007224, 0.009385, 0.006426), respectively. This indicated that the reaction was faster with higher contaminant concentration up to 50 ppm. An explanation for this, is as the initial concentration of the dye increases, more dye molecules are adsorbed onto the surface of ZnO/AC. But the adsorbed dye molecules are not degraded immediately because the intensity of light and the catalyst amount is constant and also the light penetration is less. Still at higher concentration of the dye, the path length will be reduced and the reaction rate slows down [57, 58]. The results thus indicate the ability of AC/ZnO to effectively function in the degradation reactions of relatively methyl orange high concentration, 100 ppm or higher. In case of phenazopyridine degradation, the reaction was faster up to initial concentration of 30 ppm, above that the reaction slowed dawn as shown, Figure (4.8). T.N. values measured after 20 minutes using 20 ppm, 25 ppm, 30 ppm and 35 ppm concentrations were: (0.00495, 0.00862, 0.008944, 0.00828), respectively.

5.3.3 Effect of temperature:

A systematic effect, for temperature on reaction rate was been observed for the AC/ZnO catalyzed methyl orange degradation. Figure (3.13) shows reaction profiles with time for different experiments conducted at different temperatures. Contaminant adsorbs onto the AC surface, being more as the temperature decreased, causing inconsistency between measured contaminant concentrations and nominal counterparts. T.N. values, calculated after 40 min, for MO degradation at 19°C, 29°C , 38°C, were:
The efficiency of photo-degradation increased as the temperature decreased. This is presumably related to contaminant adsorption onto the AC surface which increases as the temperature decreases. This in turn enhances the reactivity of photo-degradation. In case of phenazopyridine photo-degradation, T.N. values calculated after 60 minutes at temperatures 10, 20, 30 and 40°C were: (0.00264, 0.00233, 0.00182, 0.00212), respectively. These T.N. values showed also a systematic effect as mentioned above for MO, up to temperature 30°C. Figure (4.9) illustrated this result. T.N. value at temperature 40°C is higher than that at temperature 30°C. This behavior can be explained as follow: at temperatures 30°C, 40°C, the adsorption difference is so little, so adsorption is not the limiting factor that determines the efficiency of photo-degradation. Instead temperature becomes the factor which affects the efficiency of photo-degradation at temperatures above 30°C. Increasing the temperature above 30°C cause a slight increase in the efficiency of photo-degradation.

5.3.4 Effect of pH:

AC/ZnO-catalyzed methyl orange degradation reaction was investigated in solutions with different pH values. Figure (3.14) shows that the catalyst values of efficiency and turnover number did not vary with value of pH in the range 4-10. At pH 12, the reaction rate was slightly lower after 30 min. T.N. values calculated after 40 minutes at pH values (4.2, 8.4, 10, 12) for methyl orange degradation were (0.0114, 0.0122, 0.0123, 0.0107),
respectively. N. Sobana et al. studied the effect of pH in the range (3-11) on the photo-degradation of Direct Blue 53 using ZnO/AC as a catalyst. They observed that the removal rate increases with increase in pH up to 9 and then it is almost constant [58].

In case of phenazopyridine, Figure (4.10) shows that the rate was slightly different at low pH. T.N. values calculated after 20 minutes at different pH values (3.3, 6.4, 8, 11.4) were: (0.00424, 0.00797, 0.0096, 0.00752), respectively. Based on turnover number values, the lowering in the rate at pH 3.3 is attributed to the amphoteric behaviour of ZnO. ZnO powder tends to dissolve at lower pH [37].

\[ \text{ZnO}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{H}_2\text{O}_{(l)} \]

The results indicate the ability of the ZnO system to effectively function under different pH values, almost indifferently. The technique would thus be suitable to purify natural waters, which have pH values closer to 7. This reflects the applicability of AC/ZnO system in future natural water purification technologies.

**5.3.5 Catalyst recovery and reuse:**

Recovery of AC/ZnO from the methyl orange degradation reaction mixture after reaction cessation was achieved effectively and simply by filtration. This shows the importance of using the AC support. The catalyst was recovered and reused for three successive times. Quantum yield values for
the fresh, first, second and third recovery samples in MO degradation were: (0.03515, 0.04606, 0.03661, 0.03865), respectively. The quantum yield values showed that a slight efficiency loss on recovery was observed. The efficiency loss in the second and third recovery was about 14% compared to the first recovery. The slightly increase in the quantum yields in the first and third recovered systems compared to the fresh sample is related to the initial concentration effect, since in this range the rate of degradation increases as the initial concentration of MO increases. The results are shown in Figure (3.15).

In case of phenazopyridine degradation, Figure (4.11), the T.N. values calculated after 60 minutes for the fresh, first, second, and third recovery samples were: (0.002, 0.00183, 0.00154, 0.00127), respectively. Part of the difference in T.N. values between fresh sample and the first recovery is due to initial concentrations. In the discussion on the effect of initial concentration of phenazopyridine on the rate of degradation using ZnO/AC catalyst, the T.N. values at 6.67 ppm and 13.28 ppm were: (0.00495, 0.00862), respectively. About 9%, 23% and 37% efficiency loss occurred in the first, second and third recoveries, respectively, compared to the fresh sample.

It is worthwhile to compare between recovered naked ZnO systems and AC/ZnO systems in terms of efficiency loss on recovery. In case of MO photo-degradation using AC/ZnO systems, a slight efficiency loss on recovery was observed for the all recoveries if the effect of concentration is
ignored. In case of ZnO systems, first and second recoveries showed negligible loss of activity (up to 4%) while the third recovery showed up to 35% loss of activity compared to the fresh catalyst sample. In case of photo-degradation of phenazopyridine, using ZnO/AC systems the third recovery showed loss of activity up to 37% compared to the fresh sample, while ZnO systems showed loss of activity up to 63% in the third recovery compared to the fresh one. This is presumably due to degradation of ZnO catalyst itself under PEC conditions, being higher in the naked system than in the supported one. Tendency of ZnO to degrade into Zn$^{2+}$ ions is discussed below.

5.3.6 Effect of calcination

The effect of calcination on the AC/ZnO catalyzed reaction was studied. Compared to non-annealed AC/ZnO system, the efficiency of photo-degradation of MO was increased by 30% as shown in Figure (3.16). T.N. values calculated after 60 minutes for calcinated and non-calcinated AC/ZnO systems were: (0.00242, 0.001631), respectively. This indicates a higher efficiency for the calcinated system. In case of phenazopyridine photo-degradation, the same result was obtained as shown in Figure (4.12). The 25% higher efficiency of calcinated ZnO/AC system over non-calcinated system was confirmed by calculating T.N. values after 60 minutes which were: (0.00433, 0.00324) for calcinated and non-calcinated systems, respectively. An explanation for the high efficiency caused by calcination is due to ZnO agglomerations in the AC pores. This enhances
ZnO and carbon interactions, leading to synergistic effect and high photocatalytic ability. Gianluca et al. reported that calcination at 450°C caused the titania agglomerations in the AC pores to enhance metal oxide interactions with carbon [56].

5.3.7 Effect of calcinations on catalyst recovery and reuse

The calcinated AC/ZnO catalyst was recovered and reused for three successive times. As shown in Figure (4.13), calcination has no effect on the activity of the recovered catalyst.

A 30% efficiency loss in the first recovered system, compared to fresh sample, was observed. T.N. values calculated after 60 minutes for phenazopyridine degradation by fresh samples, first, second and third recoveries were: (0.002378, 0.001668, 0.001635, 0.00134), respectively. The T.N. values indicated that considerable loss of activity occurred, parallel to the non-calcinated ZnO/AC system. The T.N. values indicate that calcinations did not reduce leaching out of Zn$^{2+}$ ions into the solution.

5.3.8 Catalyst stability under PEC conditions:

Under PEC conditions, the ZnO in the AC/ZnO systems underwent leaching to form aqueous Zn$^{2+}$ ions. This was confirmed by polarographic analysis of the catalytic reaction mixture with time. Such leaching tendency was more obvious in acidic conditions than in basic conditions. At pH 12, only 3.3% of the supported ZnO degraded into solution phase Zn$^{2+}$. At pH 3.2, up to 6.3 %
degradation occurred. At higher values (pH 12) precipitation of Zn(OH)$_2$ is possible [15]. This accounts for low Zn$^{2+}$ tendency to leaching out.

Naked ZnO systems also showed some leaching out tendency. Under neutral or slightly basic conditions, 3.3% of originally used naked ZnO leached out under PEC conditions. However, efficiency lowering was not highly prominent and it did not undermine the major advantage of the supported system, in making recovery more feasible. Moreover, the Zn$^{2+}$ is not considered as a highly hazardous ion [59, 60]. Thus leaching out of Zn$^{2+}$ ions should not be counted against using AC/ZnO systems. Despite this, work is underway here to develop techniques that would minimize ZnO degradation processes under PEC conditions.
**Conclusions:**

1- Both ZnO and AC/ZnO systems were catalytically active when used in photo-degradation of methyl orange or phenazopyridine with solar light.

2- The CdS-sensitized ZnO system showed lower efficiency under direct solar light, than naked ZnO system. Tendency of CdS to leach the toxic Cd$^{2+}$ ions is a good reason to avoid using it as sensitizer.

3- Temperature did not significantly affect catalyst efficiency in methyl orange or phenazopyridine photo-degradations using either AC/ZnO or naked systems.

4- Both ZnO and ZnO/AC systems were recoverable and reusable, showing the future value of the ZnO catalyst system in water purification strategies.

5- Calcinated ZnO/AC system showed higher catalytic activity than the non-calcinated ZnO/AC system in photo-degradation of MO or phenazopyridine using Xe lamp.

6- ZnO/AC system showed higher catalytic activity than the naked ZnO system.

7- The rate of photo-degradation was increased as the initial concentration of MO or phenazopyridine increase in both ZnO and ZnO/AC systems to a certain limit then it decreased.

8- The rate of photo-degradation of MO or phenazopyridine was not much affected with the value of pH. In both ZnO and ZnO/AC systems, at high or low basicity a slightly different behaviour occurred due to the amphoteric behaviour of ZnO.
SUGGESTIONS FOR FURTHER WORK:

1- Using lenses to concentrate the solar radiation in photo-degradation of the contaminants by ZnO

2- Regenerate ZnO by heating under air at high temperature before reuse in photo-degradation

3- Replace the magnetic stirring method by other non-destructive method continuous flow reactors, using fixed-bed catalyst technique may be examined. AC/ZnO system may be stabilized onto reaction internal walls as thin films to maximize exposure to radiation.

4- Degrade other wide-spread water contaminants, such as drugs formulation, fertilizers, chlorinated hydrocarbons and other insecticides using ZnO

5- Preparing ZnO onto other insoluble materials, such as clay, sand and glass.
References:


38) S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, "Solar photocatalytic degradation of
ago dye: comparison of photocatalytic efficiency of ZnO and TiO$_2$, 


42) The Book of Photon Tools, Oriel Instruments, Stratford, CT, USA, pp. 44, 50 (Manual)


45) http://en.wikipedia.org/wiki/Methyl orange


50) D. Robert, "Photosensitization of TiO$_2$ by M$_x$O$_x$ and M$_x$S$_x$ nano particles for heterogeneous photo-catalysis applications", *Catal. Today*, **122**(2007) 20-26


60) http://www.healthatoz.com/healthatoz/Atoz/common/standard/transform.jsp?requestURI=/healthatoz/Atoz/ency/mineral_toxicity.jsp
جامعة النجاح الوطنية
كلية الدراسات العليا

التحطيم الضوئي لبعض الملوثات العضوية باستخدام أكسيد الزنك المثبت وغير المثبت على الكربون المنطـث

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قدمت هذه الرسالة استكمالا لمتطلبات الماجستير في الكيمياء بكلية الدراسات العليا
في جامعة النجاح الوطنية في نابلس
التحطيم الضوئي لبعض الملوثات العضوية باستخدام أكسيد الزنك المثبت وغير المثبت على الكربون المنشط

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المخصص
ان أكسيد الزنك من أشباه الموصلات التي تمتلك فجوة طاقة (energy band gap) واسعة، وتحت تنتقل الإلكترونات من حزمة التكافؤ (valence band) إلى حزمة التوصيل (conduction band) فائتها بحاجة إلى ضوء ذات طول موجي قصير. رغم ذلك فإنه من المناسب استخدام الطاقة الشمسية في التحطيم الضوئي لملوثات مختلفة لعدة أسباب، اذ بين

الاعتبار أن جزءاً يسيراً من الإشعاع الشمسي يمتلك أطوال موجية ضمن الأشعة فوق البنفسجية. ان القدرة العالية لأكسيد الزنك على امتصاص الأشعة فوق البنفسجية تجعله فعالاً

للإستخدام في التحطيم الضوئي، علاوة على كونه رخيص الثمن ومتوفراً ولا يتطلب خطورة. لقد تم استخدام أكسيد الزنك المثبت وغير المثبت على الكربون المنشط لتحطيم كل من صبغة (phenazopyridine) الميثيل البرتقالي المعروفة، وعقار الفينازوبيريدين (in the yellow oil) تحت أشعة الشمس المباشرة علاوة على استخدام مصابيح من الزينون (Xe lamp) مماثلة لأشعة الشمس كمصدر للضوء أحياناً.
كان لكلا النظامين (أكسيد الزنك المثبت وغير المثبت على الكربون المنشط) فاعلية عالية في تحطيم الملوثات المستخدمة مع كون أكسيد الزنك المثبت على الكربون ذا فاعلية أكبر.

في كلا النظامين وجد أن سرعة التفاعل تعتقد على تركيز الحفاز، حيث كانت سرعة التفاعل تزداد بزيادة كمية الحفاز حتى تركيز معين. وبعد ذلك التركيز لا يوجد أثر لزيادة التركيز على سرعة التفاعل. كذلك تم دراسة أثر زيادة تركيز الملوثات على سرعة التحليم، حيث وجد أن سرعة التفاعل في كلا النظامين زادت بزيادة تركيز الملوث حتى تركيز معين سواء كان الملوث المستخدم الميثيل البرتقالي أو الفينازوبيريدين. وقد تم أيضاً دراسة أثر درجة الحموضة حيث لم تظهر تأثيراً كبيراً على سرعة التفاعل في المدى (4-10) مع أفضلية بسيطة لدرجة الحموضة قليلة القاعدية، في كلا الملوثين. كذلك تم دراسة ثباتية أكسيد الزنك المثبت أثناء التحليم الضوئي في الوسط الحمضي والوسط القاعدي وتبين أن ثبات أكسيد الزنك في الوسط القاعدي أعلى منها في الوسط الحمضي. هذا وقد تم فصل الحفاز (أكسيد الزنك المثبت على الكربون) واستخدامه لمرات عدة دون أن يؤثر ذلك على فعاليته بشكل ملحوظ في تحطيم الميثيل البرتقالي. وذلك مقارنة مع الحفاز غير المثبت الذي انخفضت فعاليته في تحطيم الميثيل البرتقالي خاصة في الاستخدام الثالث. أما عندما كان الملوث المستخدم الفينازوبيريدين فان إعادة الاستخدام أدت إلى انخفاض فعالية الحفاز وخاصة في إعادة الثلاثة في كلا النظامين المثبت وغير المثبت.

تم في هذه الدراسة محاولة تحسين سطوح أكسيد الزنك بهببات كبريتيد الكادميوم ذات حجوم النانو بطريقة الترسيب الكيميائي، وتبين أن كبريتيد الكادميوم خفض من فعالية التحليم. إن حببات كبريتيد الكادميوم على أسطح أكسيد الزنك حجبت جزءًا من الأشعة فوق البنفسجية وبالتالي انخفضت فعالية التحليم. كذلك وجد أن كبريتيد الكادميوم يتفكك وينفصل عن أسطح أكسيد الزنك مما يحد من استخدامه كمحسن لسطح أكسيد الزنك.

وباختصار تبين هذه الدراسة إمكانية استخدام سطوح أكسيد الزنك المثبت وغير المثبت على الكربون في تنقية المياه باستخدام أشعة الشمس المباشرة دون اللجوء إلى أصباغ صناعية ضارة.