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# RESEARCH ARTICLE

# HIGHLY EFFICIENT VISIBLE-LIGHT-DRIVEN AgI/ZnO/\alpha-Fe_2O_3 TERNARY NANOCOMPOSITE FOR PHOTOCATALYTIC DEGRADATION OF MALACHITE GREEN DYE

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## ABSTRACT

This study reports the facile synthesis and enhanced phototocatalytic performance of a novel ternary AgI/ZnO/α-Fe2O3 nanocomposite. The catalyst was prepared through cost effective hydrothermal and doping method. The photocatalyst was designed to overcome the limitation of pure ZnO ( limited visible light absorption) and the recombination rate of charge carriers. The efficiency was evaluated through the degradation of malachite green (MG), a toxic water pollutant, under visible light irradiation. The presence of non-degradable organic dyes, such as malachite green ( MG), in industrial waste water poses a significant threat to aquatic ecosystem and human health. Furthermore the degradation efficiency of the prepared AgI/ZnO/α-Fe2O3 was systematically investigated under optimized condition such as pH, light intensity, dose of catalyst, concentration of dye.

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# INTRODUCTION

Polluted water is global issue as a consequence of expeditious industrialization and urbanization. Organic compound which are generated from various industries produce problematic pollutant in water. Recently doped metal oxides based semiconductor stands out as a promising methods for diverse toxic and organic pollutants. Zinc oxide(ZnO) is a cheap, abundant, biocompatible, and wide band gap semicounductor material with easy tunable morphologies and properties, makes it one of the mostly studied metal oxide in the area of material science, physics, chemistry, biochemistry, and soild state electronics. its versatility, easy band gap engineering with transitional and rare earth metals, as well as the diverse nanomorphology empower ZnO as a promising photocatalyst.[1] Iron (III) oxide hematite(α-$Fe_2O_3$) is an inexpensive, environmentally friendly and corrosion resistant compound,which is therefore a desirable material for different application.[2] the construction of heterojunction between ZnO and other narrow bandgap semiconductor with appropriate energy level can not only increase the light absorption region but also facilitate the sepration and transfer of photogenerated charge carrier, ultimately contributing to better photoelectrochemical performaces[3]. Various strategies have been implanted to enhance the photoelectric conversion of metal oxide, semiconductor materials coupled with narrow semiconductor resulting in different photoelectrochemical behavior[4] .

Abdi et al[5] AgI doped ZIF-8 photocatalyst, as a green catalytic technology, can degrade and remove large numbers of organic pollutants without selection. Studies show that more than 3000 kinds of organic compounds which can't degrade easily successfully degraded by the help of most promising photocatalyst $_2$. In recent years, interest in photocatalysis has focused on the use of semiconductor materials as photocatalysts for the removal of ambient concentrations of organic and inorganic species from aqueous or gas phase systems. This redox process can clean environment treat drinking water and also used in industrial and health applications.
Hasija et al [6] reportes that Ag/AgI/$WO_3$ heterojunction anchored P and S co- doped graphitic carbon nitride as dual Z scheme photoocatlytic degradation of organic pollutants is a promising technology due to its advantage of degradation on pollutants instead of their transformation under ambient conditions. Bae-ho-sub et al [7] palladium metal oxide/ hydroxide clustered cobalt co-loading on acid treated $TiO_2$ nanorods for degradation of organic pollutants and salmonella typhimurium inactivation under simulated solar light The process is capable of removing a wide range of organic pollutants such as pesticides, herbicides, and even micro pollutants such as endocrine disrupting compounds. An important advantage of photocatlytic process is that this can be carried out at low or ambient temperature and usually leads to the complete mineralization of pollutants.[8]

Malachite green (MG) dye is a hazardous chromatic compound predominantly utilized as a textile dye, exhibiting a strong affinity for the substrate to which it is applied[9] . Now a days Fe based tricomposite[10], $TiO_2$ biogenic nanopartcles[11] and silver mangnanese oxide nanoparticles (Ag-Mn NPs) were synthesized and employed as degradation of Malachite green under sunlight irradiation[12]. The objectives of this study are multifaceted. Firstly, it aims to devlop a cost-effective and efficient photocatalyst for the degradation of Malachite green. Second, the research delves into parameters that influence degradation efficiency under optimizing parameters including pH, photocatalytic dosage, dye concentration, light intensity.

# EXPERIMENTAL

# MATERIALS AND METHODS

Chemical compound which were used in the experimental work, such as[$Zn(NO_3)_2.6\ H_2O$],[ $Fe(NO_3)_2.9\ H_2O$], $AgNO_3$,KI were of analytical grade and purchased from Merck and co. and used as received without further purification. All the aqueous solution of reagent and dyes were made up in double distilled water.

**Synthesis of photocatalyst:** In the typical experimental procedure, AgI/ZnO/ α-$Fe_2O_3$ was synthesized from [$Zn(NO_3)_2.6\ H_2O$],[ $Fe(NO_3)_2.9\ H_2O$], $AgNO_3$,KI as starting materials.

**Firstly prepare Binary intermediate (ZnO/α- $Fe_2O_3$) :** Prepare a aqueous solution containing stoichiometric amount of [$Zn(NO_3)_2.6\ H_2O$], [ $Fe(NO_3)_2.9\ H_2O$] and slowly add 1.0 M NaOH solution dropwise for pH adjustment this precipitates the metal hydroxide [$Zn(OH)_2$ and $Fe(OH)_3$]. Transfer the resulting suspension to a sealed Teflon-lined autoclave and heat it at controlled tempreture for several hours. This process facilitates the crystallization of ZnO and the conversion of $Fe(OH)_3$ to α- $Fe_2O_3$ . Collect the precipitate via filtration wash with water and ethanol, and dry the final powder.

**Deposition of AgI and formation of the AgI/ZnO/ α-$Fe_2O_3$ ternary composite:** Disperse a calculated mass of the dry ZnO/ α-$Fe_2O_3$powder into a beaker containing DD water and stir vigorously to form a stable suspension.

Slowly add calculated volume of Silver Nitrate ( $AgNO_3$ ) solution to the suspension while stirring in the dark. Now introduce the Potassium iodide ( KI ) dropwise into the mixed solution. The immediate formation of bright yellow precipitate of AgI on the surface of the binary composite will be observed :

$$AgNO_3\,(aq.) + KI\,(aq.) \longrightarrow AgI\,(s) + KNO_3(aq.)$$

Allow the suspension to age under stirring for a defined period to ensure complete deposition and collect the final powder via filtration.

**Degradation experiment:** The degradation of aqueous malachite green under visible light in the presence of AgI/ZnO/ α-$Fe_2O_3$ ternary composite was carried out. The irradiation was carried out by the experimental reaction mixture deferment to a 200W tungsten lamp. Its light intensity is measured by solarimeter (70.0mW $cm^2$). A stock solution of malachite green dye $1.0 \times 10^{-3}$M standard solution was prepared. This standard solution is diluted and achieved the desirable concentration of the solution. The maximum absorbance of malachite green dye solution was determined with the help of a UV-Vis spectrophotometer giving $\lambda_{max}$ is at 617 nm.

The progression of the reaction was investigated by measuring the absorbance of malachite green dye and AgI/ZnO/α-$Fe_2O_3$ Containing reaction mixture at standard time intervals during exposure. A decrease in absorbance of the malachite green experimental reaction solution was observed with increasing time of exposure. A plot between (1+logA) and time found linear for our photocatalyst which indicates the pseudo-first order kinetics followed by photodegradation of malachite green using AgI/ZnO/α-$Fe_2O_3$ was measured with the help of reaction: k=2.303×slope, which is $k = 2.30 \times 10^{-4}\ s^{-1}$.

**Active species:** The photocatalytic degradation rate dropped most significantly upon the addition of TBA (quencher for ·OH) followed by BQ (quencher for $\cdot O_2^-$). This result clearly indentifies the hydroxyl radical ·OH as the dominant active species responsible for the degradation of malachite green. Band alignment prevents recombination and favors radical generation. Hydroxyl radical (·OH) : The valence band holes ($h^+$), which are highly oxidizing , react with water or surface hydroxyl ions.

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \quad (1)$$

$$h^+ + OH^- \rightarrow \cdot OH \quad (2)$$

Superoxide radical ($\cdot O_2^-$ ) : The conduction band electrons react with dissolved oxygen ($O_2$)

$$e^- + O_2 \rightarrow \cdot O_2^- \quad (3)$$

The superior photocatalytic activity of AgI/ZnO/α-$Fe_2O_3$ nanocomposite stems from the synergistic band heterojunction. The alignment effectively separates the photogenerated carriers, increasing the life time of holes ($h^+$) and electrons( $e^-$). The increased availability of $h^+$on the catalyst surface leads to a higher yield of ·OH radicals, which are the primary oxidizing agents for malachite green degradation.

# RESULT AND DISCUSSION

**Influence of pH:** The pH of the solution is one of the most significant operating parameter in heterogenous photocatalysis, as it dictates three critical factor: Catalyst surface charge, Dye adsorption efficiency, Generation of reactive species **(** ·OH **).** The photolytic degradation of malachite green dye solution may be affected by the pH of the medium. The rate of photocatalytic decomposition of dye was studied within pH ranges 2 to 10. The reaction mixture shows tge highest degradatrion at pH 8. In the protonated condition dye molecule repluse from the surface of catalyst. Due to this at low pH , the rate of degradation becomes slow. Once a corresponding value obtained if pH increases it will decrease the rate of degradation process. At higher pH due to absorption of $OH^-$ ions on the semiconductor surface, the electron rich dye molecule will electrostatically be repelled to each other and the rate will be decreased.fig 2. Successfully interpreted the effect of pH.

**Influence of malachite green concentration:** The photolytic degradation rate is affected by the starting concentration of dye typically, the degradation efficiency decreases as the initial dye concentration increases. In fig 3. the role of malachite green dye concentration was illustrated in the concentration limits from$5.5 \times 10^{-5}$ to $8.5 \times 10^{-5}$ M. as the MG concentration increases from $5.5 \times 10^{-5}$ up to $7.0 \times 10^{-5}$(optimum point) the reaction rate increases from $1.75 \times 10^{-4}\ sec^{-1}$ to a maximum of about $2.3 \times 10^{-4}\ sec^{-1}$. The maximum rate is observed at an MG concentration of approximately **7.0** x $10^{-5}$. This is the optimum concentration for our AgI/ZnO/α-$Fe_2O_3$ photocatalyst. The observed non- linear trend is characteristic of a surface – mediated catalytic reaction and is explained at two competing factor:

- Rate increase (up to $7.0 \times 10^{-5}$) – In the lower concentration range, the number of a MG molecules is low. As MG concentration increases, more dye molecules are absorbed onto the available active sites ( $h^+$and ·OH generation sites) on the catalyst surface. The increased adsorption leads to a higher probability of reaction between the MG molecules and the photogenerated reactive species, hence increasing the degradation rate(k).
- Rate decreases (beyond $7.0 \times 10^{-5}$) – when the MG concentration exceeds the optimum value, the available active site on the AgI/ZnO/α-$Fe_2O_3$ surface become fully saturated. The rate of active species generation( $h^+$and ·OH) remains constant, but the number of dye molecules increases. Thus, the rate cannot increases further,and the overall percentage degradation efficiency drop.

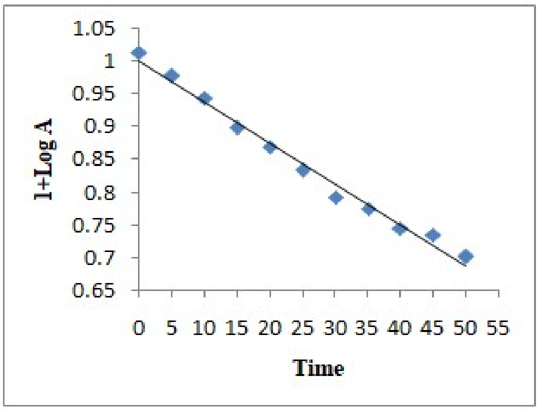


**Fig. 1 A typical run**

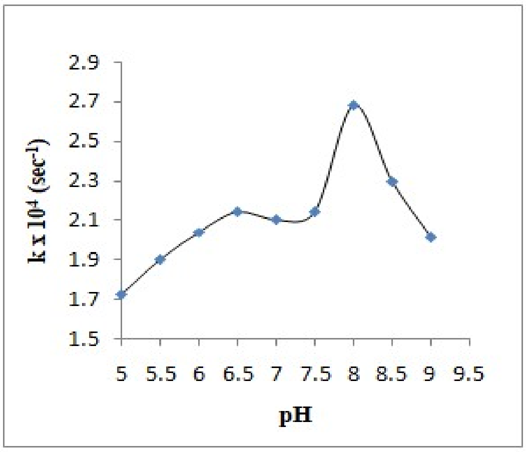


**Fig. 2 Influence of pH**

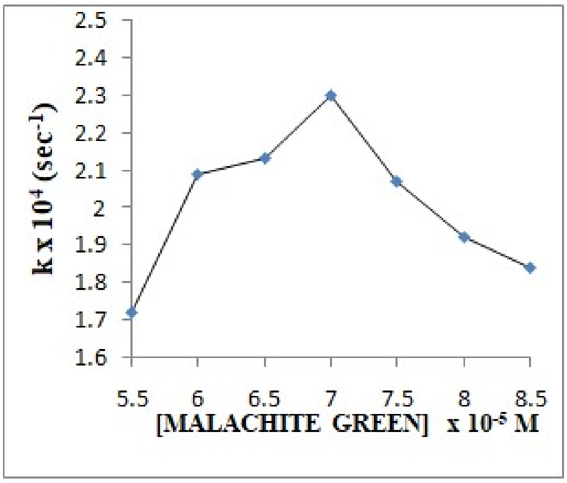


**Fig. 3 Influence of MG concentration**

**Influence of amount of catalyst:** The amount of photocatalyst may also effect the photocatalytic degradation of malachite green may also affect the photocatalytic degradation. In fig 4. As the catalyst amount increases from 0.06g up to approximately 0.14g, the reaction rate increases linearly. The rate constant peak at about 2.3 x 10-4 sec -1. The maximum reaction rate is achieved at a catalyst mass of approximately 0.14 g. this is the optimal catalyst loading for the specific volume of dye solution used in the experiment. Beyond the optimal amount (0.14g) the reaction rate decreases sharply.

**Influence of light intensity:** The consequences of varying light intensity on the growth of the rate of dye degradation was analyzed in

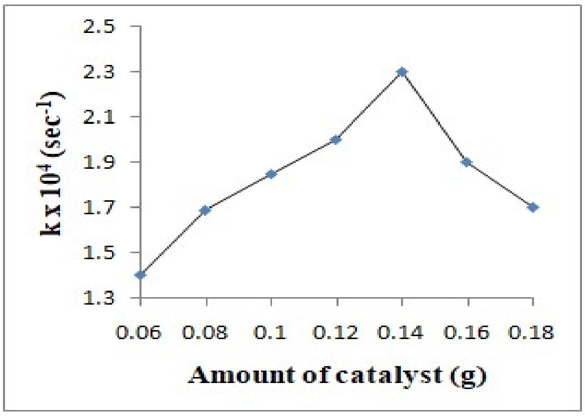


**Fig. 4 Influence of amount of catalyst**

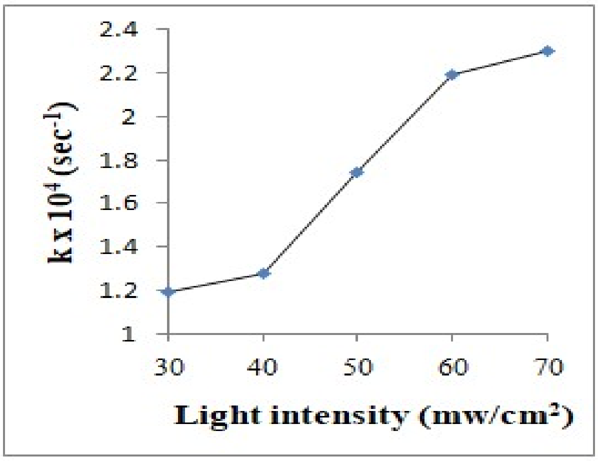


**Fig. 5 Influence of light intensity**

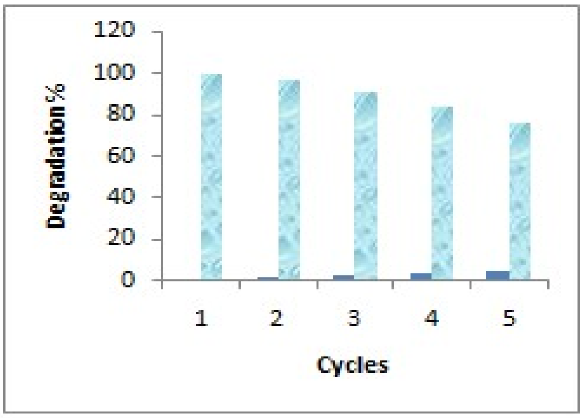


**Fig. 6 Stability and Reusability**

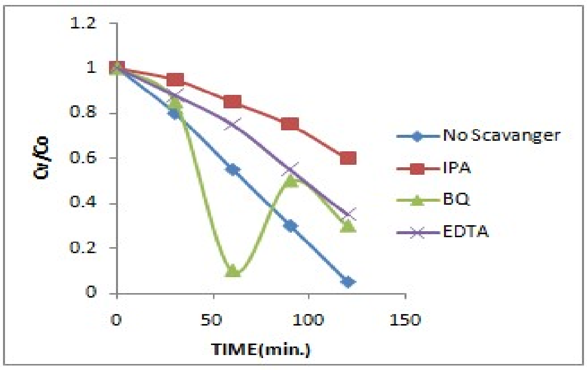


**Fig. 7 Influcence of various scavenger on malachite green**

the range from 30.0 to 70.0 $mW/cm^2$ .In Fig 5 it was observed that the rate of degradation increases with an increase in the light intensity, but after attaining ultimate limits of intensity, more increment of light radiation was found to falling off the rate of photodegradation. An increment in photoactivity may be due to a boost of several photons collisions per unit area per unit time. After the maximum favorable light intensity (70 $mW/cm^2$) higher intensity of light was avoided because it will perform the thermal and some kind of side reactions.

**Stability and reusability:** The stability of AgI/ZnO/α-$Fe_2O_3$ photocatalyst is a critical factor in large scale technology application. To evaluate the stability of the AgI/ZnO/α-$Fe_2O_3$ photocatalyst, recycling experiments were conducted on the catalyst for the degradation of malachite green under visible light irradiation. The photocatalyst was collected by simple centrifugation and then washed using distilled water and ethanol. Thereafter, it was dried in an oven at 60°C overnight. The sample was reused by subsequent degradation. The photocatalyst maintained a very high photocatalytic activity and the removal rate was 76% after 5 cycles. Fig 6 shows the marginal decrease is not typically due to total collapse of material's structure. Instead, the gradual decline is attributed to physical loss which is a minor loss of catalyst particle during the recovery procedure( washing, centrifugation, drying) and active side blocking which is irreversible adsorption of some complex degradation intermediate or by product that block a small fraction of active sites.

**Scavenger test:** To further investigate the responsible radical for malachite green dye degradation radical trapping experiment were performed. In this study, different scavangers i.e. ethylenediaminetetraacetate (EDTA -2Na) for valence band hole ( $h^+$) , isopropyl alcohol (IPA) for ·OH and p-benzoquinone (BQ) for superoxide anion $\cdot O_2^-$ were used.

It is evident with fig. 7 that all scavenger were capable of decreasing the degradation of malachite green to some extent. The degradation of malachite green reduced from 70%, 65%, 40% in the presence of BQ , EDTA and IPA respectively.

**Plausible Mechanism:** The manner of photocatalytic degradation of malachite green using AgI/ZnO/α-$Fe_2O_3$ was based on the above observation. An experimental mechanism is proposed for the malachite green molecules. A light of suitable wavelength was absorbed by the malachite green dye and it gets excited to its excited singlet state. This first excited state of the malachite green dye undergoes intersystem crossing (ISC) and gets converted to its triplet state. AgI/ZnO/α-$Fe_2O_3$ also absorbs the incident light energy and excites its electron from the valence band to the conduction band leaving a hole in the valence band.

$$^1MG_0 + h\nu \rightarrow {}^1MG_1 \quad (4)$$

$$^1MG_1 + ISC \rightarrow {}^3MG_1 \quad (5)$$

$$AgI/ZnO/\alpha\text{-}Fe_2O_3 + h\nu \rightarrow AgI/ZnO/\alpha\text{-}Fe_2O_3\,[h^+(VB) + e^-(CB)] \quad (6)$$

$$h^+ + OH^- \rightarrow {}^{\cdot}OH \quad (7)$$

$$e^- + O_2 \rightarrow \cdot O_2 \quad (8)$$

$$^3MG_1 + \cdot O_2^- \rightarrow Leuco\ MG \quad (9)$$

$$Leuco\ MG \rightarrow Mineralization\ product \quad (10)$$

On the other hand AgI/ZnO/α-$Fe_2O_3$ photocatalyst also utilizes the incident light to excite its electron from valence band to conduction band ; thus, leaving behind a hole. The hole react with hydroxyl ion (aqueous solution) which generates hydroxyl radicals. The electron reacts with oxygen (aqueous solution) which generates electrophilic oxygen radical anions. The oxygen radical anions will oxidize the MG dye to its leuco form.

# CONCLUSION

AgI/ZnO/α-$Fe_2O_3$ was prepared and investigated for the application of photolytic degradation of malachite green dye. The contemplation showed that cmalachite green dye could be degraded successfully by using AgI/ZnO/α-$Fe_2O_3$ photocatalyst under visible light.

The optimum reaction condition were obtained as : pH = 8.0 , [malachite green] =7.0 x $10^{-5}$ ,amount of AgI/ZnO/α-$Fe_2O_3$ = 0.14 g, light intensity = 70 $mW/cm^2$.This AgI/ZnO/α-$Fe_2O_3$ could be reused 5 times without any significant loss in its photoactivity which is essential in practical environment protection.

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