

## ECO-FRIENDLY GREEN SYNTHESIS AND PHOTOCATALYST ACTIVITY OF Ag- ZnO NANOCOMPOSITE<sup>†</sup>

 Noorullah Mohammed Nemma,  Zainab Sabeeh Sadeq\*

*Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq*

*\*Corresponding Author e-mail: zainab.sadeq@sc.uobaghdad.edu.iq*

Received June 21, 2023; revised July 8, 2023; accepted July 11, 2023

The study successfully synthesized Ag NPs, ZnO NPs, and Ag/ZnO nanocomposites using an easy, cost effect and sustainable green synthetic approach. The purpose of synthesizing Ag/ZnO nanocomposites using two different plant extracts was to study their photo-degradation activity on Methylene Blue (MB) dye. (XRD) diffraction analysis confirmed the presence of Ag crystalline size and the wurtzite hexagonal structure of ZnO. (FE-SEM) results indicated spherical, nanorods and there is Clustering of NPs with an irregular shape. The resulting metal/semiconductor oxide nanocomposites possessed unique photo degradation characteristics that were absent in the individual Ag NPs and ZnO NPs.

**Keywords:** *Nanoparticles; Nanocomposite; Wastewater treatment; Catalyst*

**PACS:** 61.82.Fk, 81.07.Bc, 81.07.De, 81.16.Be, 81.16.Hc

### 1. INTRODUCTION

In recent decades, the disposal of harmful and toxic contaminants, such as organic dyes and heavy metal ions, has led to water pollution, which has become a significant environmental issue. Industrial effluent streams are the primary sources through which heavy metals and dyes enter the ecological system, posing substantial risks to human health [1]. Dyes have diverse applications across various fields in industries such as textiles, cosmetics, printing, and pharmaceuticals. Furthermore, these dyes are known to be environmentally stable and resistant to biodegradation unless a catalyst is present [2]. Effluents containing dyes are typically treated using chemical, physicochemical, or biological methods [3]. However, the utilization of these methods may prove to be both expensive and time-intensive. As a result, it is crucial to explore highly efficient and environmentally friendly approaches to degrade these pollutants in the environment.

Among the different methods proposed for wastewater treatment [4-6], the photocatalytic process utilizing nano-sized materials has emerged as a reliable and environmentally safe technique. This process offers complete mineralization of dyes on the surface of these materials and is known for its high sensitivity, reasonable costs, and effectiveness [7-16].

Photo catalysis process is a technique that uses ultraviolet or visible light to break down organic dirt on surfaces [17-20]. A typical photo-catalysis process has a high photocatalytic activity under ultraviolet or visible light for the degradation of Methylene blue. A semiconductor photo catalyst absorbs photons to generate charge separation and activate the oxidation process. Light capturing, electron-hole pair formation and separation, and catalytic reaction have all been recognized as key processes in photo catalysis in latest years [21]. While numerous nanomaterials are used for wastewater treatment, many of them exhibit limitations such as low catalytic activity, limited adsorption capacity, constraints on photocatalytic efficiency, light absorption, and expensive production costs. [22, 23]

Researchers have dedicated significant attention to studying metal nanoparticles (MNPs) during the past few decades [24-27]. Noble metal NPs have garnered greater interest compared to other metal nanoparticles because of their small size and high surface-to-volume ratio [28], the utilization of MNPs as heterogeneous catalysts offers notable advantages. [26, 29-33]. However, one challenge that arises is the tendency of MNPs to aggregate. To address this issue and minimize the aggregation of nanoparticles (NPs), we require a support ideal material. Various inorganic compounds, including TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>3</sub>, CuO, NiO, Cr<sub>2</sub>O<sub>3</sub>, RuO<sub>2</sub>, etc.), transition metal oxides with wide band gaps and stability can play an important role on the photocatalytic to remove organic [34]. Between of the different heterogeneous photo catalysts, zinc oxide, silver and gold NPs appeared as a more attractive alternative for controlling the pollution-related environmental issues [35-38].

The combination of metal nanoparticles (NPs) with metal oxide semiconductor nanocomposites has garnered significant attention from researchers worldwide. This is primarily due to their remarkable optical, electrical, and chemical properties, as well as their promising potential in various applications [39-41].

Nanoparticles (NPs) are commonly produced through various methods, including solvothermal processes, chemical reduction methods, and sol-gel techniques [42-47]. However, these methods are often highly cost and require the utilization of harmful chemicals. These chemicals are pose potential risks to the environment and biological systems [42-47].

Recently, there has been a development of biosynthetic approaches for the synthesis of MNPs. These methods make use of solvents that are comparatively less toxic, such as water, biological extracts, biological systems, and microwave technology [48-51].

Utilizing plant extracts for various applications offers several advantages, including their widespread availability, ease of handling, and possessing a diverse range of metabolites, although plant extracts contain a variety of secondary

<sup>†</sup> **Cite as:** N.M. Nemma, Z.S. Sadeq, East Eur. J. Phys. 3, 271 (2023), <https://doi.org/10.26565/2312-4334-2023-3-24>

© N.M. Nemma, Z.S. Sadeq, 2023

metabolites with notable reducing potential, they can be effectively utilized as both reducing and stabilizing agents in the production of environmentally friendly nanoparticles (NPs) [52]. These characteristics make plant extracts a favorable option when compared to other biosynthetic approaches [53].

The aim of the present work is synthesis Ag- ZnO Nanocomposite by eco-green approach in ambient conditions using the extract of plant which work as both reducing and stabilizing agents and study their Photo catalysis activity.

## 2. EXPERIMENTAL

### 2.1 Materials

Silver nitrate ( $\text{AgNO}_3$ ), zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), sodium hydroxide ( $\text{NaOH}$ ), and methylene blue were obtained from Carlo Erba and Himedia chemical companies in highly pure form and used without further purification. The aloe vera plant and Hibiscus sabdariffa leaves were acquired from nearby markets. All glassware used in the experiment underwent thorough cleaning, including washing twice with distilled water (DW) and ethanol, followed by drying in the oven prior to use.

### 2.2 Preparation of Ag NPs, ZnO NPs and Ag-ZnO nanocomposite via Aloe vera plant extract

Initially, we produced the aloe vera extract by washing and cutting the leaves, extracting the gel, and blending it with a mixer. We took 100 grams of the gel and mixed it with 300 milliliters of distilled water, before placing it on a magnetic stirrer for 30 minutes. Subsequently, once it had cooled down we centrifuged the solution at 4000 rotations per minute for approximately 10 minutes. Then to get the Ag NPs, we prepared 0.1M of  $\text{AgNO}_3$  solution, the solution was stirred for 30 min at  $60^\circ\text{C}$  on the magnetic stirrer and then we added 50 ml of the aloe vera extract to 100 ml of  $\text{AgNO}_3$ . On the other hand, we prepared other solution from mixing 20 ml of aloe vera gel which was diluted with 150 ml of deionized water. After filtered and purified, 2 g of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was dissolved in 150 ml of the plant extract with stirring using the magnetic stirrer for 1 h at an  $80^\circ\text{C}$ . Leave the zinc solution overnight. Separately, 4 g of Sodium hydroxide ( $\text{NaOH}$ ) is dissolved in 35 ml of deionized water. Then 12 ml of  $\text{NaOH}$  solution was added to the precursor solution with the extract. Following the formation of a white precipitate, the Ag/ZnO nanocomposite is produced by gradually adding 100 milliliters of Ag nanoparticles to 100 milliliters of ZnO nanoparticles at 60 degrees Celsius, while continuously stirring to ensure thorough mixing. Final indicate was Ag/ZnO nanocomposite. Then all solutions were deposit on slides for further work.

### 2.3 Preparation of Ag NPs, ZnO NPs and Ag-ZnO nanocomposite via Hibiscus sabdariffa plant extract

Similar method was adapted to prepare Ag/ZnO nano-campsite via Hibiscus sabdariffa. First, we take the Hibiscus flowers then washed thoroughly with DW. Then they were sun dried and grinded into small pieces we mixed 2 gr with 100 ml of DW then placed on a magnetic stirrer at  $60^\circ\text{C}$  for 30 min. The red extract was filtered twice with cotton wool balls. After the completion of the extraction process, we take 50 ml of aqueous extract and repeat the same operation to prepare the Ag NPs. Then to prepare ZnO NPs, 4g of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was dissolved in 150 ml of the plant extract with stirring using the magnetic stirrer for 1 h at an  $80^\circ\text{C}$ . Leave the solution overnight. Separately, 4 g of Sodium hydroxide ( $\text{NaOH}$ ) is dissolved in 35 ml of deionized water. Then 20 ml of  $\text{NaOH}$  solution was added to the precursor solution with the extract. After the formation of a white precipitate, the Ag/ZnO nanocomposite is also produced by gradually adding 100 milliliters of Ag nanoparticles to 100 milliliters of ZnO nanoparticles at 60 degrees Celsius, while continuously stirring to ensure thorough mixing. Then we deposit all the solutions on slides for further experiments.

### 2.4 Photocatalytic activity

The procedure was conducted in according to previous work [54, 55]. The efficiency of the synthesized photocatalyst samples were assessed by monitoring the degradation of MB dye as a model pollutant. To control the photo-catalytic degradation process, the optical absorption peak of MB dye at 664.5 nm was determined. We prepared solution of MB dye by dissolving 10 mg in 1000 ml of distilled water and stirring it on a magnetic stirrer for two hours. The solution was left overnight to ensure complete dissolution of the MB dye before using it. Approximately 30 mg of nanomaterial (Samples) was adding, 50 ml of MB (10 mg/ml), the solution was stirred in a dark room for one hour to ensure adsorption equilibrium between Methylene Blue (MB) and the catalyst surfaces. Subsequently, the solution was exposed to UV light from a 6W lamp with a wavelength of 254 nm serving as the irradiation source. At equal intervals of time (15 minutes), samples were collected, filtered, and monitored for MB degradation using UV-visible spectroscopy (Shimadzu 1900i-Japan). Using the following equation [56] to calculate the degradation efficiency.

$$\text{Efficiency} = \frac{(C_0 - C)}{C_0} \times 100\% = \frac{(A_0 - A)}{A_0} \times 100\% \quad (1)$$

$C_0$ ,  $C$ ,  $A_0$ , and  $A$  refer to the concentration and absorbance of methylene blue (MB) before and after exposure to UV light, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 X-ray diffraction (XRD) analysis

First, analysis of Ag NPs via A. vera leaves and H. sabdariffa flower extracts. (Figure 1.a) shows XRD pattern and the crystalline size of the synthesized Ag NPs with diffraction peaks at  $2\theta = 35.2^\circ$ ,  $43^\circ$ ,  $67^\circ$ , and  $74.8^\circ$  for the Aloe vera, and

diffraction peaks with  $2\theta = 35^\circ, 46.4^\circ, 65^\circ,$  and  $72.2^\circ$  for Hibiscus sabdariffa respectively. Which both can be corresponded to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) Bragg's planes. Also, the X-ray diffraction powder pattern in the two extract also had small peaks. This could be formed because of the organic ingredients of the leaves and flower extracts and because of the small residual amounts of  $\text{AgNO}_3$  that it is did not diminished. It is notable that the peak was associated with the (111) plane is the highest and most intense of the peaks. The Ag NPs produced in the present process are naturally crystalline with an FCC structure and the determined patterns of XRD matched closely with the standard (JCPDS: 01-1164) [57].

On the other hand, the diffraction pattern of the ZnO NPs samples that prepared via Aloe vera and Hibiscus sabdariffa plants extract fig (Figure 1.b) shows diffraction peaks at  $2\theta = 31.96^\circ, 34.6^\circ,$  and  $36.52^\circ$ , corresponding to Bragg's planes of (100), (002), and (101), respectively, while the other peaks at  $2\theta = 47.68^\circ, 56.8^\circ, 63.16^\circ, 66.36^\circ, 68.16^\circ,$  and  $69.4^\circ$ , corresponding to lattice planes of (102), (110), (103), (200), (112), and (201), respectively. It has been that all the major peaks characteristic of hexagonal wurtzite structure of ZnO and determined patterns of XRD matched closely with the standard (JCPDS: 36-1451) [58].

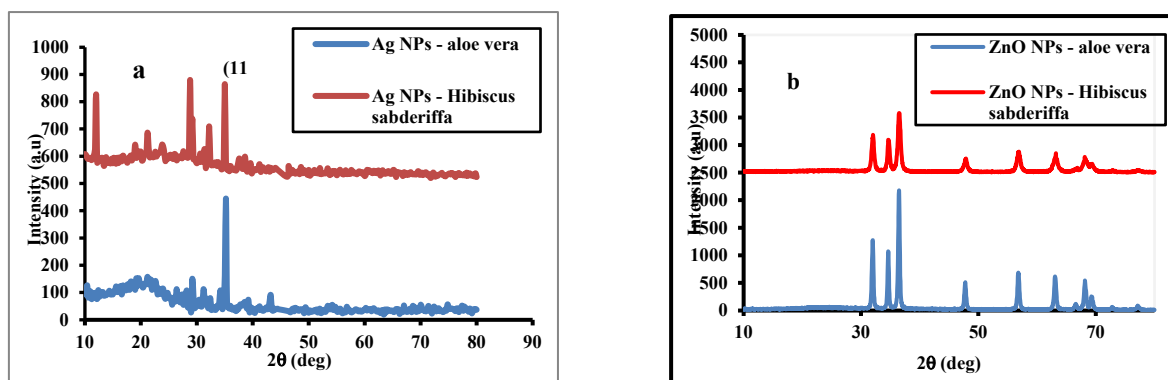


Figure 1. XRD of (a) Ag NPs, (b) of ZnO NPs via Aloe vera and Hibiscus sabdariffa.

### 3.2 Field emission scanning electron microscopy (FE-SEM)

The FE-SEM images in Figure (2) illustrate the morphology of Ag NPs, ZnO NPs and Ag/ZnO NCPs synthesized via a green method using plant extracts like Aloe vera and Hibiscus sabdariffa respectively.

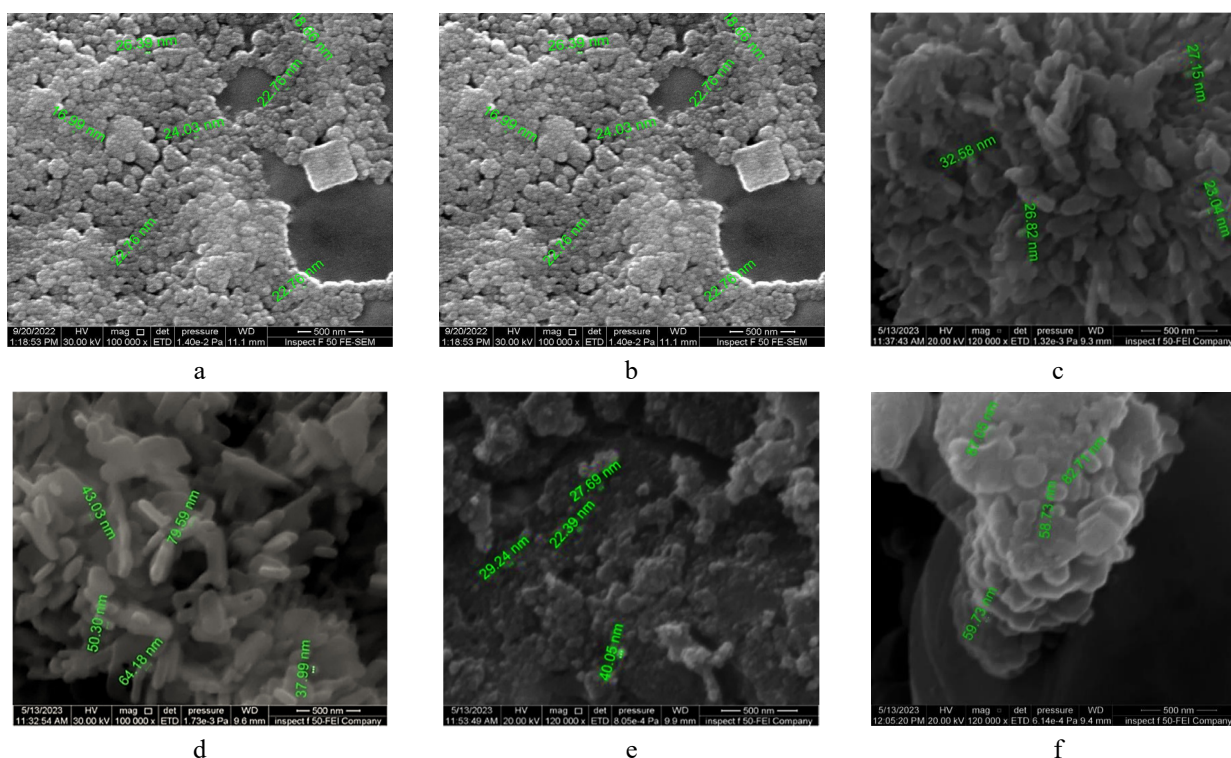


Figure 2. FE- SEM of Ag NPs formed via (a) aloe vera, (b) hibiscus sabdariffa, FE- SEM of ZnO NPs formed via (c) aloe vera, (d) hibiscus sabdariffa, FE- SEM of Ag/ZnO nanocomposite formed via (e) aloe vera, (f) hibiscus sabdariffa.

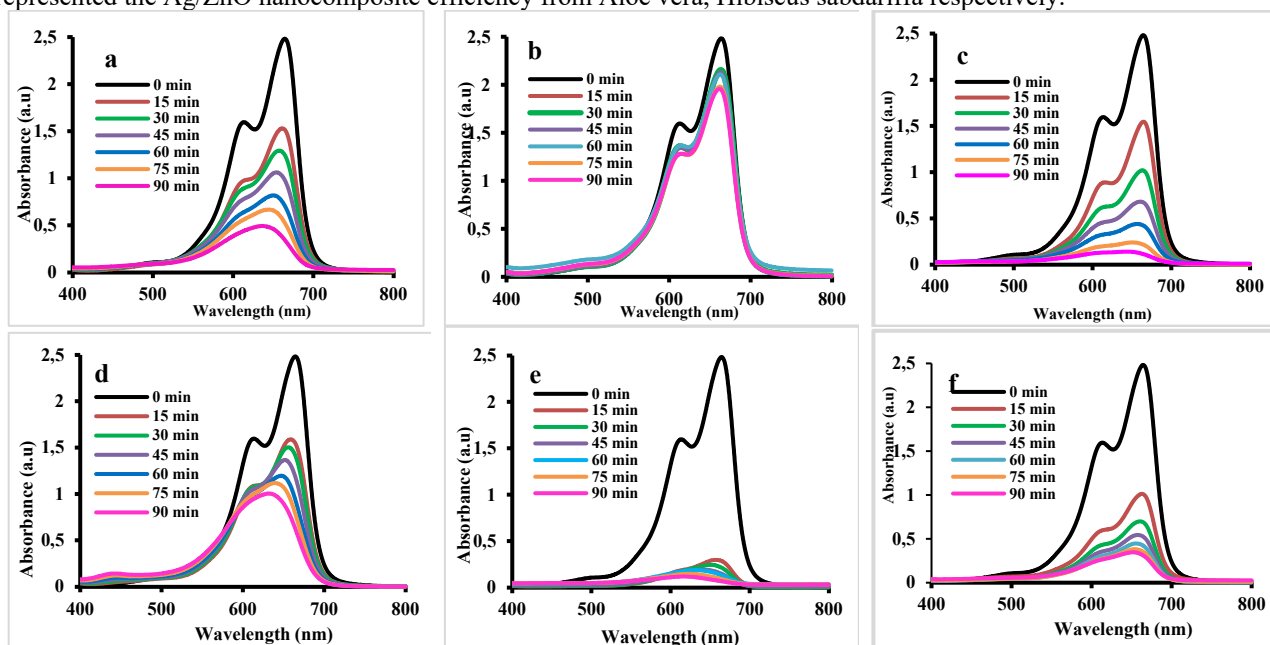
These images exhibit a spherical shape of Ag NPs, with particle sizes ranging from (16.99 -26.39) nm and (13.11 - 29.50) nm using Aloe vera and Hibiscus sabdariffa respectively as shown in Fig. 2 (a & b), while Fig. 2 (c & d)

demonstrate the formation of agglomerate ZnO NPs with hexagonal nanorod shape, with particle sizes ranging from (23.04 – 32.58) nm and (37.99 - 79.59) nm, the metallic silver nanospheres are evenly dispersed on the surface of ZnO NPs, loose agglomerations of NPs have grown larger and formed clusters, resulting in the formation of nanorod-like Ag/ZnO NCPs with particle sizes ranging from (22.39 - 40.05) nm and (59.73 -87.05) nm as in Fig. 2 (e & f). It is evident that the agglomerations of Ag/ZnO NCPs were significantly larger in size compared to pure Ag NPs and ZnO NPs.

In this process, silver nanoparticles form an outer layer coating on the surface of ZnO particles. In one possible method, that the silver nanoparticles introduced to a solution containing ZnO particles and allowed to bond with the ZnO surface due to attractive electrostatic forces or chemical interactions. The silver nanoparticles can then continue to accumulate on the surface of the ZnO particles, forming a layer. This can be facilitated by agitation or heating of the solution. Our results agree with the results of other work [59-61].

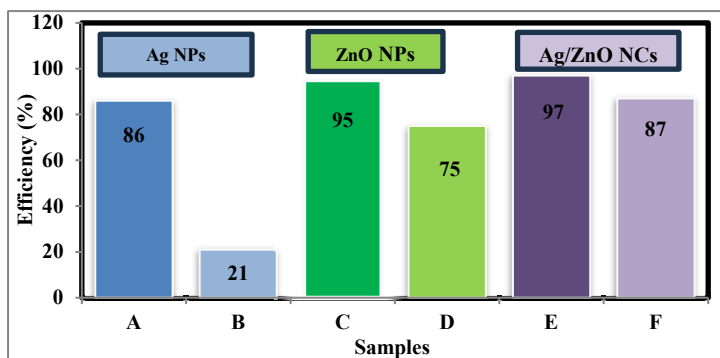
### 3.3 Dye degradation activity

The photocatalytic effectiveness of Ag nanoparticles, ZnO nanoparticles, and Ag/ZnO nanocomposite powder, the degradation rate of Methylene Blue dye in a solution was measured under UV light. Samples of the degraded dye solutions were collected at different time intervals, and their absorbance was determined using a UV-Visible Spectrophotometer to quantify the dye degradation rate using the equation (1) above. Figure 3 showed UV-visible absorption spectra of the 6 samples, where Fig. 3 (a & b) represent the Ag NPs efficiency from Aloe vera, Hibiscus sabdariffa respectively. Fig. 3 (c & d) represented the ZnO NPs efficiency from Aloe vera, Hibiscus sabdariffa respectively. And Fig. 3 (e & f) represented the Ag/ZnO nanocomposite efficiency from Aloe vera, Hibiscus sabdariffa respectively.



**Figure 3.** UV-Vis absorption spectra of Ag NPs via (a) aloe vera, (b) hibiscus sabdariffa, UV-Vis absorption spectra of ZnO NPs via (c) aloe vera, (d) hibiscus sabdariffa, UV-Vis absorption spectra of Ag/ZnO NCs via (e) aloe vera, (f) hibiscus sabdariffa of photo degradation samples against MB.

The above results indicate that the Ag/ZnO nano composite had the highest photo degradation activity as shown in Figure 4, with a degradation rate of 97% for Aloe vera and 87% for Hibiscus sabdariffa.



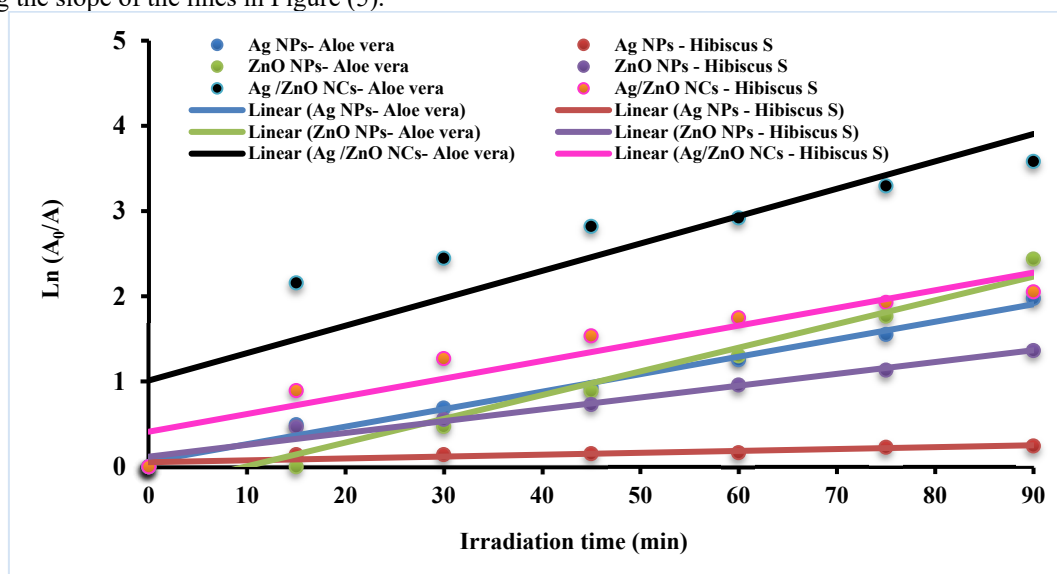
**Figure 4.** The efficiency of Ag NPs, ZnO NPs and Ag/ZnO NCs against MB dye.

The ZnO NPs also showed a high level of photo degradation activity, with degradation rates of 95% and 75% for Aloe vera and Hibiscus sabdariffa, respectively, while the Ag NPs had lower levels of activity, with degradation rates of



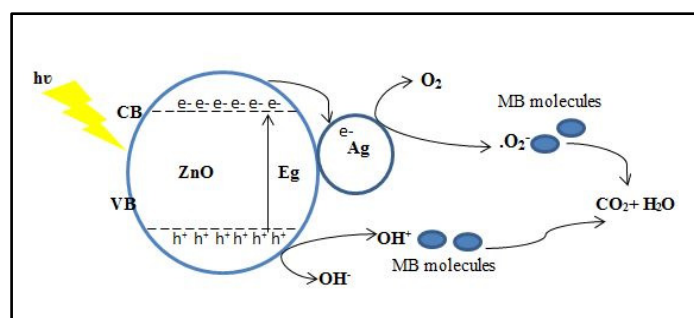
86% and 21% for Aloe vera and Hibiscus sabdariffa, respectively. These results suggest that the Ag/ZnO nano composite could be a promising material for photocatalytic applications.

To determine the rate of photocatalytic reactions, the pseudo-first order rate constant ( $k \text{ min}^{-1}$ ) can be calculated by estimating the slope of the lines in Figure (5).



**Figure 5.** First-order kinetics of MB dye degradation against Ag NPs, ZnO NPs, Ag/ZnO NCs using different plant extracts with irradiation time.

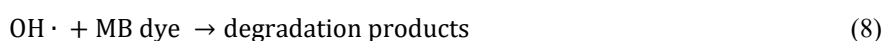
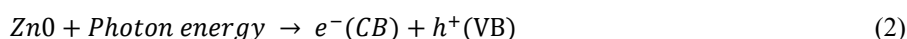
These lines are plotted between  $\ln(A_0/A)$  and irradiation time, and the results indicate an increase in the value of  $k$  for samples prepared from Aloe vera extract. Table (1) presents the efficiency values and  $k$  for each sample. Figure (6) demonstrates a possible mechanism of the Ag/ZnO NCs photocatalyst.



**Figure 6.** A possible mechanism of Ag/ZnO NCs photocatalyst.

When exposed to UV light, electrons in the Ag/ZnO NCs can absorb photon energy and move to the conduction band (CB), generating an equal number of holes in the valence band (VB). Since the conduction band CB energy level of ZnO is higher than the Fermi level of Ag-ZnO, the electrons can transfer from ZnO to Ag. Consequently, the photogenerated electrons can be trapped by Ag, preventing their recombination with holes. This leads to an accumulation of more electrons and holes at the Ag/ZnO interface, ultimately enhancing the photocatalytic activity of the Ag/ZnO NCs.

The conduction band (CB) electrons may subsequently generate superoxide anion radicals ( $O_2^-$ ), while the valence band (VB) holes may react with  $H_2O$  to create hydroxyl radicals ( $\cdot OH$ ). These hydroxyl radicals can facilitate the degradation of MB. The reactions can be summarized as follows [62 - 64].



**Table 1.** The efficiency values and pseudo-first-order rate constant (k) for each sample.

Prepared samples	Degradation efficiency	K (min <sup>-1</sup> )
Ag NPs via A. vera	86	0.020507143
Ag NPs via H. sabdariffa	21	0.00220619
ZnO NPs via A. vera	95	0.033383333
ZnO NPs via H. sabdariffa	75	0.01387381
Ag/ZnO NCPs via A. vera	97	0.032133333
Ag/ZnO NCPs via H. sabdariffa	87	0.020735714

#### 4. CONCLUSION

In summary, Ag/ZnO NPs, Ag NPs, ZnO NPs were successfully prepared via nontoxic, fast, low cost, eco-friendly and simple green method using two kind of plant extracts that is having comparable functional groups that could potentially aid in the production of NCPs and ultimately be transformed into valuable nanomaterial. XRD and FE-SEM analyses were utilized to check structural properties. Ag/ZnO NCs showed powerful photocatalytic activity compared with Pure Ag NPs and Pure ZnO NPs, against MB which totally decolorized as a wastewater pollutant. The novelty of the investigated results of Ag/ZnO NCs which utilizes leave and fruit extract as a cost effect and eco-friendly additive that have a significant effect in the enhancement of wastewater treatment.

#### ORCID

 Noorullah Mohammed Nemma, <https://orcid.org/0000-0002-7697-2143>

 Zainab Sabeeh Sadeq, <https://orcid.org/0000-0003-1450-785X>

#### REFERENCES

- [1] C. Forstner, T.G. Orton, P. Wang, M.P. Kopittke, and P.G. Dennis, "Wastewater treatment processing of silver nanoparticles strongly influences their effects on soil microbial diversity", *Environmental Science and Technology*, **54** (21), 13538-13547 (2020). <https://doi.org/10.1021/acs.est.0c01312>
- [2] R. Dai, J. Chen, J. Lin, S. Xiao, S. Chen, and Y. Deng, "Reduction of nitro phenols using nitroreductase from *E. coli* in the presence of NADH", *J. Hazard. Mater.*, **170**(1), 141-143 (2009). <https://doi.org/10.1016/j.jhazmat.2009.04.122>
- [3] C.A. Martínez-Huitle, and E. Brillas, "Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review," *Appl. Catal. B: Environ.* **87**(3-4), 105-145 (2009). <https://doi.org/10.1016/j.apcatb.2008.09.017>
- [4] W. Sami, and Z.S. Sadeq, "MgFe<sub>2</sub>O<sub>4</sub>@ZnFe<sub>2</sub>O<sub>4</sub> nanocomposite as a magnetic catalyst: Synthesis and oil spill removal from water," *Journal of Physics: Conference Series*, **2437**, 020054 (2022). <https://doi.org/10.1063/5.0094019>
- [5] C.K. Mbamba, D.J. Batstone, X.F. Alsina, and S.A. Tait, "Generalised chemical precipitation modelling approach in wastewater treatment applied to calcite," *Water Res.* **68**, 342-353 (2015). <https://doi.org/10.1016/j.watres.2014.10.011>
- [6] M.L. Christensen, K. Keiding, P.H. Nielsen, M.K. Jorgensen, "Dewatering in biological wastewater treatment: a review," *Water Res.* **82**, 14-24 (2015). <https://doi.org/10.1016/j.watres.2015.04.019>
- [7] K.Y. Kumar, H.B. Muralidhara, Y.A. Nayaka, J. Balasubramanyam, and H. Hanumanthappa, "Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution," *Powder Tech.* **246**, 125-136 (2013). <https://doi.org/10.1016/j.powtec.2013.05.017>
- [8] H. Zangeneh, A.A.L. Zinatizadeh, M. Habibi, M. Akia, and M.H. Isa, "Photocatalytic oxidation of organic dyes and pollutants in wastewater using diferent modified titanium dioxides: a comparative review," *J. Ind. Eng. Chem.* **26**, 1-36 (2015). <https://doi.org/10.1016/j.jiec.2014.10.043>
- [9] L. Mingxin, et al. "Photocatalytic performance and mechanism research of Ag/HSTiO<sub>2</sub> on degradation of methyl orange," *ACS Omega*, **5**, 21451-21457 (2020). <https://doi.org/10.1021/acsomega.0c01832>
- [10] M. Li, R. Guan, J. Li, Z. Zhao, J. Zhang, Y. Qi, H. Zhai, and L. Wang, "Effects of Ag doping content and dispersion on the photocatalytic and antibacterial properties in ZnO nanoparticles," *Chem. Res. Chin. Univ.* **35**, 271-276 (2019). <https://doi.org/10.1021/acsomega.0c01832>
- [11] L. Jiayi, G. Renquan, Z. Junkai, Z. Zhao, Z. Hongju, S. Dewu, and Q. Yunfeng, "Preparation and photocatalytic performance of dumbbell Ag<sub>2</sub>CO<sub>3</sub>-ZnO heterojunctions", *ACS Omega*, **5**, 570-577, 2020.
- [12] J. Liu, Y. Yue, L. Ge, P. Chen, F. Tan, W. Wang, X. Wang, "Facile fabrication of magnesium peroxide with diferent morphologies via the isomorphic transformation of magnesium oxide for Fenton-like degradation of methylene blue," *Colloids Surf. A Physicochem. Eng. Aspects*, **607**, 125499 (2020). <https://doi.org/10.1016/j.colsurfa.2020.125499>
- [13] J. Liu, Y. Yue, W. Wang, F. Tan, H. Xia, X. Wang, X. Qiao, "Facile one-step synthesis of 3D hierarchical flower-like magnesium peroxide for efficient and fast removal of tetracycline from aqueous solution", *J. Hazard. Mater.* **397**, 122877 (2020). <https://doi.org/10.1016/j.jhazmat.2020.122877>
- [14] P. Chen, F. Sun, W. Wang, F. Tan, X. Wang, and X. Qiao, "Facile one-pot fabrication of ZnO particles for the efcient Fenton-like degradation of tetracycline," *J. Alloys Compd.* **834**, 155220 (2020). <https://doi.org/10.1016/j.jallcom.2020.155220>
- [15] Y. Yue, P. Zhang, W. Wang, Y. Cai, F. Tan, X. Wang, and X. Qiao, et al., "Enhanced dark adsorption and visible-light-driven photocatalytic properties of narrower-band-gap Cu<sub>2</sub>S decorated Cu<sub>2</sub>O nanocomposites for efcient removal of organic pollutants," *J. Hazard. Mater.* **384**, 121302 (2020). <https://doi.org/10.1016/j.jhazmat.2019.121302>
- [16] D. Wu, Y. Bai, W. Wang, H. Xia, F. Tan, S. Zhang, B. Su, et al., "Highly pure MgO<sub>2</sub> nanoparticles as robust solid oxidant for enhanced Fenton-like degradation of organic contaminants," *J. Hazard. Mater.* **374**, 319-328 (2019). <https://doi.org/10.1016/j.jhazmat.2019.04.058>
- [17] H.A. Alrubaie, and B.M. Alshabander, "The effect of ZnO nanoparticles on the self-cleaning of ZnO/epoxy composites", *AIP Conference Proceedings*, **2437**, 020184 (2022). <https://doi.org/10.1063/5.0094219>

- [18] X. Zhang, A. Fujishima, M. Jin, A.V. Emeline, and T. Murakami, "Double-layered TiO<sub>2</sub>- SiO<sub>2</sub> nanostructured films with self-cleaning and antireflective properties", *J. Phys. Chem. B.* **110**(50), 25142-25148 (2006). <https://doi.org/10.1021/jp064442u>
- [19] S. Tek, D. Yucel, and G. Celiker, "High Optical Efficiency of ZnO Nanoparticles", in: *Conference on Lasers and Electro-Optics/Pacific Rim 2007*, (Optica Publishing Group, 2007), paper WF3\_7. [https://opg.optica.org/abstract.cfm?URI=CLEOPR-2007-WF3\\_7](https://opg.optica.org/abstract.cfm?URI=CLEOPR-2007-WF3_7)
- [20] S.N. Zailan, A. Bouaissi, N. Mahmed, M. Mustafa, A. AlBakri, "Influence of ZnO nanoparticles on mechanical properties and photocatalytic activity of self-cleaning ZnO-based geopolymer Paste", *J. Inorg. Organomet. Polym. Mater.* **30**, 2007-2016 (2020). <https://doi.org/10.1007/s10904-019-01399-3>
- [21] Y. Li, C. Gao, R. Long, and Y. Xiong, "Photocatalyst design based on two-dimensional materials," *Mater. Today Chem.* **11**, 197 (2019). <https://doi.org/10.1016/j.mtchem.2018.11.002>
- [22] V.K. Gupta, R. Kumar, A. Nayak, T.A. Saleh, and M.A. Barakat, "Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review," *Adv. Colloid Interface Sci.* **193**, 24-34 (2013). <https://doi.org/10.1016/j.cis.2013.03.003>
- [23] W. Konicki, M. Aleksandrak, D. Moszynski, and E. Mijowska, "Adsorption of anionic azo dyes from aqueous solutions onto graphene oxide: equilibrium, kinetic and thermodynamic studies", *J. Colloid Interface Sci.* **496**, 188-200 (2017). <https://doi.org/10.1016/j.jcis.2017.02.031>
- [24] W. Sami, and Z.S. Sadeq, "Role of Glycine-to-Nitrate Ratio in Physical and Magnetic Properties of Zn- Ferrite Powder," *Iraqi Journal of Science*, **63**, 170-181 (2022). <https://doi.org/10.24996/ij.s.2022.63.1.18>
- [25] X. Lu, X. Bian, G. Nie, C. Zhang, C. Wang, and Y. Wei, "Encapsulating conducting polypyrrole into electrospun TiO<sub>2</sub> nanofibers: a new kind of nanoreactor for in situ loading Pd nanocatalysts towards p-nitrophenol hydrogenation," *J. Mater. Chem.* **22**, 12723-12730 (2012). <https://doi.org/10.1039/C2JM16559G>
- [26] M. Nasrollahzadeh, M. Atarod, and S.M. Sajadi, "Green synthesis of the Cu/Fe<sub>3</sub>O<sub>4</sub> nanoparticles using Morinda morindoides leaf aqueous extract: a highly efficient magnetically separable catalyst for the reduction of organic dyes in aqueous medium at room temperature," *Appl. Surf. Sci.* **364**, 636-644 (2016). <https://doi.org/10.1016/J.APSUSC.2015.12.209>
- [27] S. Wei, Z. Dong, Z. Ma, J. Sun, and J. Ma, "Palladium supported on magnetic nanoparticles as recoverable catalyst for one-pot reductive amination of aldehydes with nitroarenes under ambient conditions," *Catal. Commun.* **30**, 40-44 (2013). <https://doi.org/10.1016/j.catcom.2012.10.024>
- [28] P. Dauthal, and M. Mukhopadhyay, "Noble metal nanoparticles: plant-mediated synthesis, mechanistic aspects of synthesis, and applications," *Ind. Eng. Chem. Res.* **55**(36), 9557-9577 (2016). <https://doi.org/10.1021/acs.iecr.6b00861>
- [29] M. Bordbar, and N. Mortazavimanesh, "Green synthesis of Pd/walnut shell nanocomposite using Equisetum arvense L. leaf extract and its application for the reduction of 4-nitrophenol and organic dyes in a very short time," *Environ. Sci. Pollut. Res.* **24**, 4093-4104 (2017). <https://doi.org/10.1007/s11356-016-8183-y>
- [30] J. Lee, J. Chung, S.M. Byun, B.M. Kim, and C. Lee, "Direct catalytic C-H arylation of imidazo[1,2-a] pyridine with aryl bromides using magnetically recyclable PdFe<sub>3</sub>O<sub>4</sub> nanoparticles," *Tetrahedron.* **69**, 5660-5664 (2013). <https://doi.org/10.1016/j.tet.2013.04.031>
- [31] G.K. Naik, P.M. Mishra, and K. Parida, "Green synthesis of Au/TiO<sub>2</sub> for effective dye degradation in aqueous system," *Chem. Eng. J.* **229**, 492-497 (2013). <https://doi.org/10.1016/j.cej.2013.06.053>
- [32] A. Hatamifard, M. Nasrollahzadeh, and S.M. Sajadi, "Biosynthesis, characterization and catalytic activity of an Ag/zeolite nanocomposite for base- and ligand-free oxidative hydroxylation of phenylboronic acid and reduction of a variety of dyes at room temperature," *New J. Chem.* **40**, 2501-2513 (2016). <https://doi.org/10.1039/C5NJ02909K>
- [33] M. Bordbar, Z. Sharifi-Zarchi, and B. Khodadadi, "Green synthesis of copper oxide nanoparticles/clinoptilolite using Rheum palmatum L. root extract: high catalytic activity for reduction of 4-nitro phenol, rhodamine B, and methylene blue," *J. Sol-Gel Sci. Technol.* **81**, 724-733 (2017). <https://doi.org/10.1007/s10971-016-4239-1>
- [34] M.S.S. Danish, L.L. Estrella, I.M.A. Alemaida, A. Lisin, N. Moiseev, M. Ahmadi, M. Nazari, *et al.*, Metals, "Photocatalytic applications of metal oxides for sustainable environmental remediation", *J. Metals*, **11**, 80 (2021). <https://doi.org/10.3390/met11010080>
- [35] V. Prasad, S.G. Gnanamani, E.M. Ansha, N. Jayaprakash, "Microwave Assisted Synthesis, Characterization and Photo-catalytic Study of Cu/ZnO Nanocomposite," *Rasayan J. Chem.* **12**, 860 (2019). <http://dx.doi.org/10.31788/RJC.2019.1225226>
- [36] K.M. Lee, C.W. Lai, K.S. Ngai, and J.C. Juan, "Recent Developments of Zinc Oxide Based Photocatalyst in Water Treatment Technology", *Water Res.* **88**, 428 (2016). <https://doi.org/10.1016/j.watres.2015.09.045>
- [37] E. Murugan, and P. Shanmugam, "Surface Grafted Hyper-Branched Polyglycerol Stabilized Ag and AuNPs Heterogeneous Catalysts for Efficient Reduction of Congo Red," *J. Nanosci. Nanotechnol.* **16**, 426 (2016). <https://doi.org/10.1166/jnn.2016.10655>
- [38] E. Murugan, and J.N. Jebaranjitham, "Environmentally benign heterogeneous nano-particle catalysts: synthesis, characterization and catalytic activity of 4-nitrophenol," *J. Biomed. Nanotechnol.* **7**, 158 (2011). <https://doi.org/10.1166/jbn.2011.1248>
- [39] F.H. Dowlatabadi, G. Amiri, and S.M. Mohammadi, "Investigation of the antimicrobial effect of silver doped Zinc Oxide nanoparticles," *Nanomedicine Journal*, **4**, 50-54 (2017). <https://doi.org/10.22038/nmj.2017.8053>
- [40] B. Baruwati, and R.S. Varma, "High Value Products from Waste: Grape Pomace Extract - A Three -in -One Package for the Synthesis of Meta Nanoparticles", *Chem. Sus. Chem.* **2**, 1041-1044 (2009). <https://doi.org/10.1002/cssc.200900220>
- [41] R. Sahay, V.J. Reddy, and S. Ramakrishna, "Synthesis and applications of multifunctional composite nanomaterials," **9**, 25 (2014). <https://doi.org/10.1186/s40712-014-0025-4>
- [42] Z.S. Sadeq, Z.F. Mahdi, and A.M. Hamza, "Low cost, Fast and Powerful Performance Interfacial Charge Transfer Nanostructured Al<sub>2</sub>O<sub>3</sub> Capturing of Light Photocatalyst Eco-Friendly System using Hydrothermal Method," *Materials Letters*, 120-124 (2019). <https://doi.org/10.1016/j.matlet.2019.07.050>
- [43] E.C.H. Sykes, F.J. Williams, and M.S. Tikhov, "Nucleation, growth, sintering, mobility, and adsorption properties of small gold particles on polycrystalline titania," *J. Phys. Chem. B.* **106**(21), 5390-5394 (2002). <https://doi.org/10.1021/jp014562w>
- [44] X.Z. Li, and F.B. Li, "Study of Au/Au<sup>3+</sup>-TiO<sub>2</sub> photocatalysts towards visible photooxidation for water and wastewater treatment," *Environ. Sci. Technol.* **35**(11), 2381-2387 (2001). <https://doi.org/10.1021/es001752w>
- [45] X. Wang, D.R.G. Mitchell, and K. Prince, "Gold nanoparticle incorporation into porous titania networks using an agarose gel templating technique for photocatalytic applications," *Chem. Mater.* **20**(12), 3917-3926 (2008). <https://doi.org/10.1021/cm703509f>

- [46] M. Bordbar, T. Alimohammadi, and B. Khoshnevisan, "Preparation of MWCNT/TiO<sub>2</sub>-Co nanocomposite electrode by electrophoretic deposition and electrochemical study of hydrogen storage," *Int. J. Hydrog. Energy*, **40**, (31), 9613-9620 (2015). <https://doi.org/10.1016/j.ijhydene.2015.05.138>
- [47] B. Khodadadi, M. Bordbar, and A. Yeganeh-Faal, "Optical, structural, and photocatalytic properties of Cd-doped ZnO powders prepared via sol-gel method," *J. Sol-Gel Sci. Technol.* **77**(3), 521-527 (2016). <https://doi.org/10.1007/s10971-015-3877-z>
- [48] E.S. Abdel-Halim, M.H. El-Rafie, and S.S. Al-Deyab, "Polyacrylamide/guar gum graft copolymer for preparation of silver nanoparticles," *Carbohydr. Polym.* **85**(3), 692-697 (2011). <https://doi.org/10.1016/j.carbpol.2011.03.039>
- [49] S.P. Dubey, M. Lahtinen, and M. Sillanpää, "Tansy fruit mediated greener synthesis of silver and gold nanoparticle," *Process Biochem.* **45**(7), 1065-1071 (2010). <https://doi.org/10.1016/j.procbio.2010.03.024>
- [50] G. Zhan, J. Huang, and M. Du, "Green synthesis of Au-Pd bimetallic nanoparticles: single-step bioreduction method with plant extract," *Mater. Lett.* **65**(19-20), 2989-2991 (2011). <https://doi.org/10.1016/j.matlet.2011.06.079>
- [51] X. Huang, H. Wu, and S. Pu, "One-step room-temperature synthesis of Au@Pd core-shell nanoparticles with tunable structure using plant tannin as reductant and stabilizer," *Green Chem.* **13**, 950-957 (2011). <https://doi.org/10.1039/C0GC00724B>
- [52] S. Jain, and M.S. Mehata, "Medicinal plant leaf extract and pure flavonoid mediated green synthesis of silver nanoparticles and their enhanced antibacterial property", *Scientific Reports*, **7**(1), 15867 (2017). <https://doi.org/10.1038/s41598-017-15724-8>
- [53] S. Matussin, M.H. Harunsani, A. Tan, and L.M. Khan, "Plant-extract-mediated SnO<sub>2</sub> nanoparticles: synthesis and applications," *ACS Sustainable Chemistry and Engineering*, **8**(8), 3040-3054 (2020). <https://doi.org/10.1021/acssuschemeng.9b06398>
- [54] R.S. Sabry, W.J. Aziz, and M.I. Rahmah, "Enhanced photocatalytic activity of Ag and Fe<sub>2</sub>O<sub>3</sub> co-doped ZnO nanostructure under visible light irradiation," *Materials Technology*, **35**(6), 326-334 (2020). <https://doi.org/10.1080/10667857.2019.1681717>
- [55] M.I. Rahmah, H.S. Majidi, W.K. Al-Azzawi, M.J. Rasn, H.H. Jasim, M.S. Jabir, R.A.S.A. Al Kareem, and T.M. Rashid, "Synthesis of ZnO/Ag-doped C/N heterostructure for photocatalytic application", *International Journal of Modern Physics B*, **235**-239 (2023). <https://doi.org/10.1142/S0217979223502399>
- [56] N.C. Joshi, A. Gaur, and A. Singh, "Synthesis, Characterisations, Adsorptive Performances and Photo-catalytic Activity of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> Based Nanosorbent (Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> BN)," *Journal of Inorganic and Organometallic Polymers and Materials*, **30**, 4416-4425 (2020). <https://doi.org/10.1007/s10904-020-01622-6>
- [57] Y. Jhuang, and W. Cheng, "Fabrication and characterization of silver/titanium dioxide composite nanoparticles in ethylene glycol with alkaline solution through sonochemical process," *Ultrasonics Sonochemistry*, **28**, 327-333 (2016). <https://doi.org/10.1016/j.ultsonch.2015.08.011>
- [58] G. Madhumitha, J. Fowsiya, N. Gupta, A. Kumar, and M. Singh, "Graphical abstract SC," *J. Phys. Chem. Solids*, **127**, 43-51 (2019). <https://doi.org/10.1016/j.jpccs.2018.12.005>
- [59] N.M. Nemma, and Z.S. Sadeq, "Green Route of Synthesis Ag NPs Using Reductant and Stabilizer Agent from Plants Extract as an Efficient Antibacterial and Antifungal Activity," *Chemical methodologies*, **7**(4), 325-334 (2023). <https://doi.org/10.22034/chemm.2023.381408.1646>
- [60] R. Viswanatha, Y.A. Nayaka, C.C. Vidyasagar, and T.G. Venkatesh, "Structural and optical properties of Mg doped ZnO nanoparticles," *J. Chem. Pharm. Res.* **4**, 1983-1989 (2012).
- [61] J. Iqbal, N. Safdar, T. Jan, M. Ismail, S.S. Hussain, A. Mahmood, S. Shahzad, and Q. Mansoor, "Facile Synthesis as well as Structural, Raman, Dielectric and Antibacterial Characteristics of Cu Doped ZnO Nanoparticles," *J. Mater. Sci. Technol.* **31**, 300-304 (2015). <https://doi.org/10.1016/j.jmst.2014.06.013>
- [62] M. Samadi, M. Zirak, A. Naseri, E. Khorashadizade, and A.Z. Moshfegh, "Recent progress on doped ZnO nanostructures for visible-light photocatalysis," *Thin Solid Films*, **605**, 2-19 (2016). <http://dx.doi.org/10.1016%2Fj.tsf.2015.12.064>
- [63] C.B. Ong, L.Y. Ng, and A.W. Mohammad, "A review of ZnO nanoparticles as solar photocatalysts: synthesis, mechanisms and applications," *Renew. Sustain. Energy Rev.* **81**, 536-551 (2018). <https://doi.org/10.1016/j.rser.2017.08.020>
- [64] F. Kayaci, S. Vempati, I. Donmez, N. Biyikliab, and T. Uyar, "Role of zinc interstitials and oxygen vacancies of ZnO in photocatalysis: a bottom-up approach to control defect density," *Nanoscale*, **6**(17), 10224-10234 (2014). <https://doi.org/10.1039/C4NR01887G>

#### ЕКОЛОГІЧНО ЧИСТИЙ ЗЕЛЕНИЙ СИНТЕЗ, ТА ФОТОКАТАЛІЗАТОРНА АКТИВНІСТЬ НАНОКОМПЗИТУ Ag-ZnO Нуруллах Мохаммед Немма, Зейнаб Сабіх Садек

*Факультет фізики, Науковий коледж, Багдадський університет, Багдад, Ірак*

Дослідження успішно синтезувало наночастинки Ag, наночастинки ZnO та нанокмпозити Ag/ZnO, використовуючи простий, економічний та стійкий екологічний синтетичний підхід. Мета синтезу нанокмпозитів Ag/ZnO з використанням двох різних рослинних екстрактів полягала у дослідженні їх фотодеградаційної активності на барвнику метиленового синього (MB). (XRD) дифракційний аналіз підтвердив наявність розміру кристалів Ag і гексагональної структури вюрцити ZnO. Результати (FE-SEM) показали сферичність, нанострижні та наявність кластеризації НЧ неправильної форми. Отримані нанокмпозити метал/напівпровідник оксид володіли унікальними характеристиками фотодеградації, які були відсутні в окремих наночастинках Ag і наночастинках ZnO.

**Ключові слова:** наночастинки; нанокмпозит; очищення стічних вод; каталізатор