# Synthesis and Application of Magnesium-based Nanoparticles for Photocatalytic Degradation of Methylene Blue in Aqueous Solution: Optimization and Kinetic Modelling

A Presentation by

**Eng. Khumbolake Faith Ngulube**

Environmental Engineering Department, Egypt-Japan University of Science and Technology (E-JUST), Alexandria, 21934, Egypt

khumbolake.ngulube@ejust.edu.eg

# Introduction

- Methylene blue dye (MB) is one of the most commonly utilised colorants in the textile industry. Unfortunately, exposure to high concentrations of MB has displayed negative impacts not only on the aesthetic appearance of water bodies they are discharged into, but also on both human and aquatic life.
- In humans it could cause complications such as respiratory issues, abdominal disorders, blindness and mental disorders, amongst others [1].
- On aquatic life, the presence of MB in the marine environment limits light penetration into the marine environment, slowing down photosynthetic processes of aquatic plants, leading to low dissolved oxygen levels [2].
- This is lethal for marine life and leads to disturbances in the marine ecosystems

# Introduction

- It is therefore, important that MB is effectively treated from textile wastewaters and prevented from entering the environment.
- In this regard, several conventional treatment techniques such as adsorption, coagulation/flocculation, phytoremediation and more have been applied.
- However, these techniques are not very effective for treatment of dyes such as MB and have displayed other shortfalls such as production of large amounts of sludge, they require large land areas and they also require long retention times.
- Therefore, more advanced treatment methods such as advanced oxidation processes (AOPs) have become a popular topic because they have displayed the ability to limit the shortfalls presented by conventional techniques and work more effectively.

# Introduction

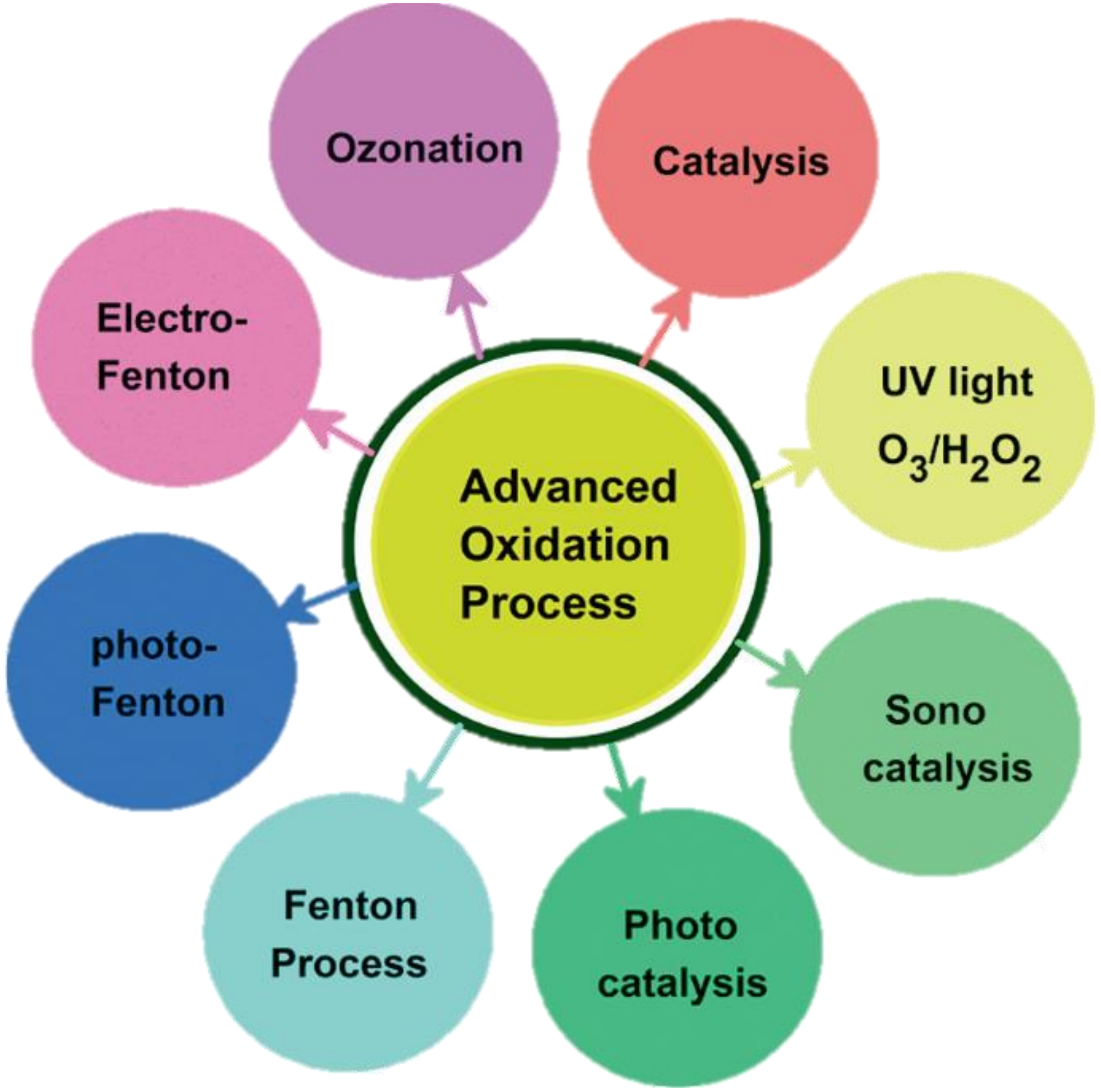



**Figure 1: Advanced Oxidation Processes**

# Introduction

- Heterogeneous photocatalysis is one such AOP which involved the use of a catalyst material (usually a semi conductor material) that is in a different phase than the substance to be treated.
- It is a very efficient treatment technique which can degrade MB by generation of reactive oxygen species (ROS) such as hydroxyl radicals (•OH) which interact with the MB in a repeated cascade of reactions, breaking it down into less harmful intermediated and finally into simple compounds such as $CO_2$ and $H_2O$.
- Many different semiconductor materials such as ZnO, TiO and MgO have been explored for use in heterogeneous photocatalytic processes and have displayed reasonable efficiencies. However, there is still need to explore more materials for more efficient photocatalytic activity.

# Introduction

- In this study, we synthesized a ZnO@MgO core-shell nanocomposite material and applied it for photocatalytic degradation of a MB.

# Experimental Methods

- **PHOTOCATALYST SYNTHESIS**

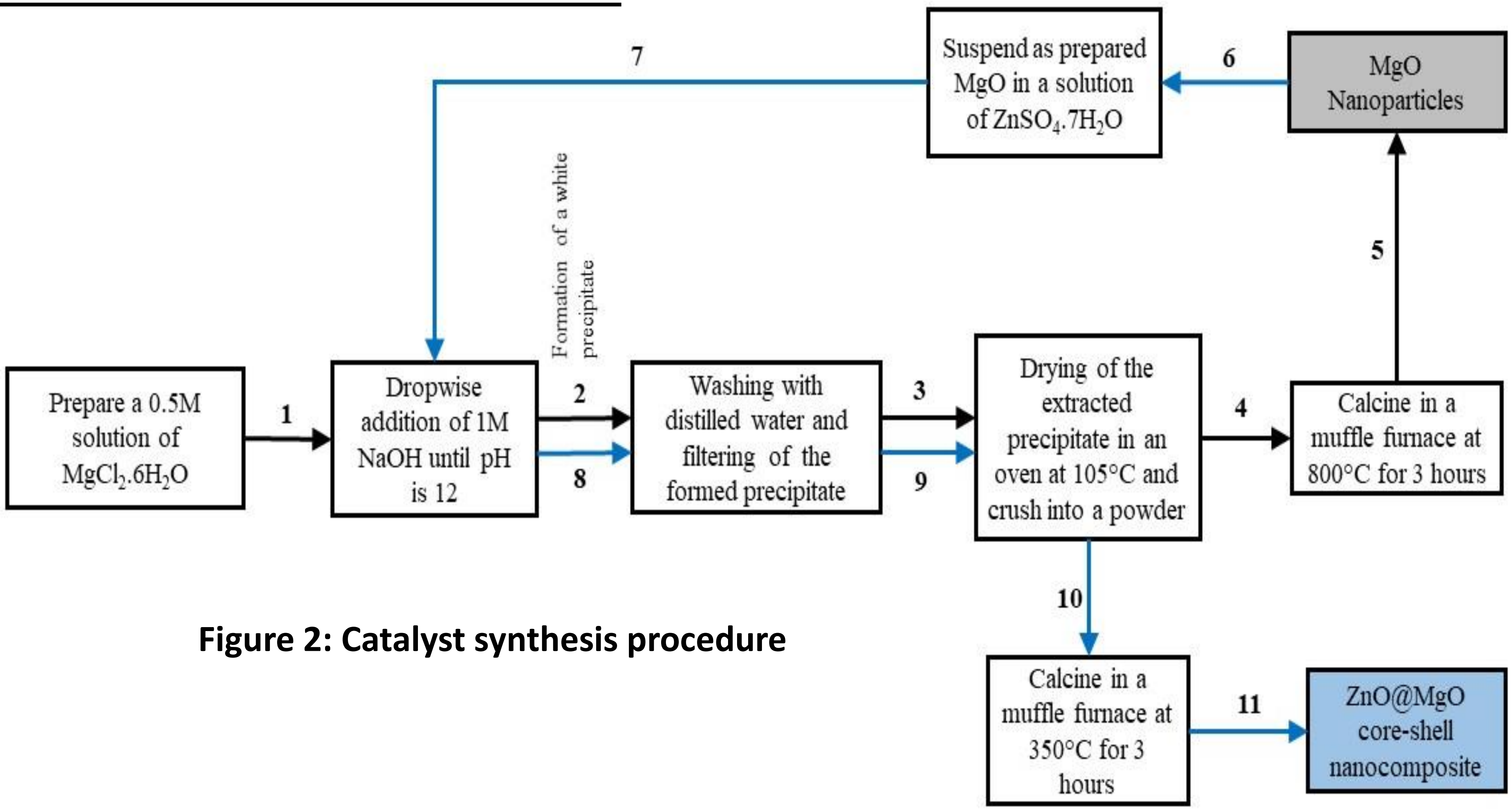



**Figure 2: Catalyst synthesis procedure**

# Experimental Methods

- **STATISTICAL ANALYSIS**
- The experimental design and optimization of parameters was done in design expert 13 software using a box-behnken design (BBD).
- The BBD was used to study the effects of four independent variables i.e.; A (dye concentration), B (catalyst dose), C (pH) & D (time) on MB dye removal.

| Variable name | Symbol | Units | Low | Mid | High |
|---|---|---|---|---|---|
| | | | Coded | | |
| | | | -1 | 0 | 1 |
| | | | Actual | | |
| Dye Concentration | A | mg/L | 10 | 55 | 100 |
| Catalyst Dose | B | mg/L | 100 | 550 | 1000 |
| pH | C | - | 3 | 6.5 | 10 |
| Time | D | minutes | 60 | 120 | 180 |

# Experimental Methods

- To verify the adequacy of the generated model and each of the independent variables, analysis of variables (ANOVA) was done, and the significance of each parameter was denoted by a p-value less than 0.05. The model significance was also verified using the coefficient of determination (R2) values. Once the model was verified, optimization of parameters was done using numerical optimization and the degradation kinetics were studied.

- **<u>DEGRADATION EXPERIMENTS</u>**
- The photocatalytic degradation experiments involved the dilution of an MB stock solution to the desired concentration and adjusting the pH by adding NaOH or H2SO4 until the desired pH was achieved.

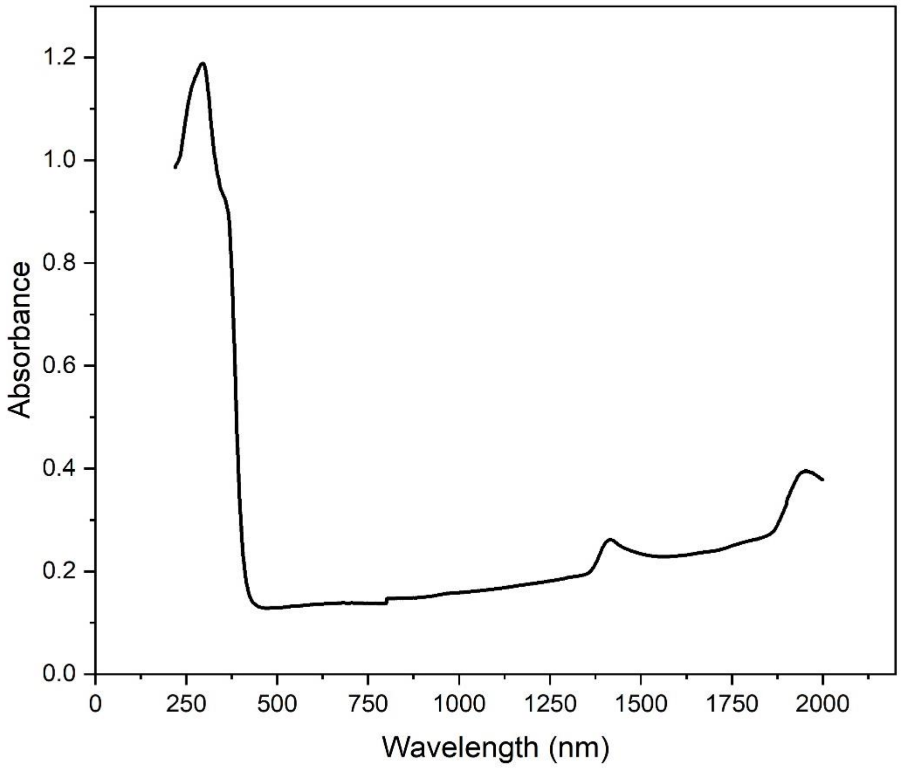
# Experimental Methods

- The catalyst was then added into the MB solution and placed in the reactor under constant stirring in the dark for 1 hour to allow for adsorption-desorption equilibrium.
- After adsorption-desorption equilibrium was achieved, a 2 ml sample was extracted and centrifuged to separate the catalyst from the solution and the concentration, $C_o$ was measured.
- The light in the reactor was switched on and photocatalytic degradation was allowed to proceed for the desired amount of time, t, after which, another 2 ml sample was extracted and the final MB concentration, $C_t$ was measured.
- MB removal, R%, was calculated using the formula given by;

$$R\% = [(C_o - C_t)/C_o] \times 100$$

# Results and Discussion

- <u>**UV-vis DRS**</u>



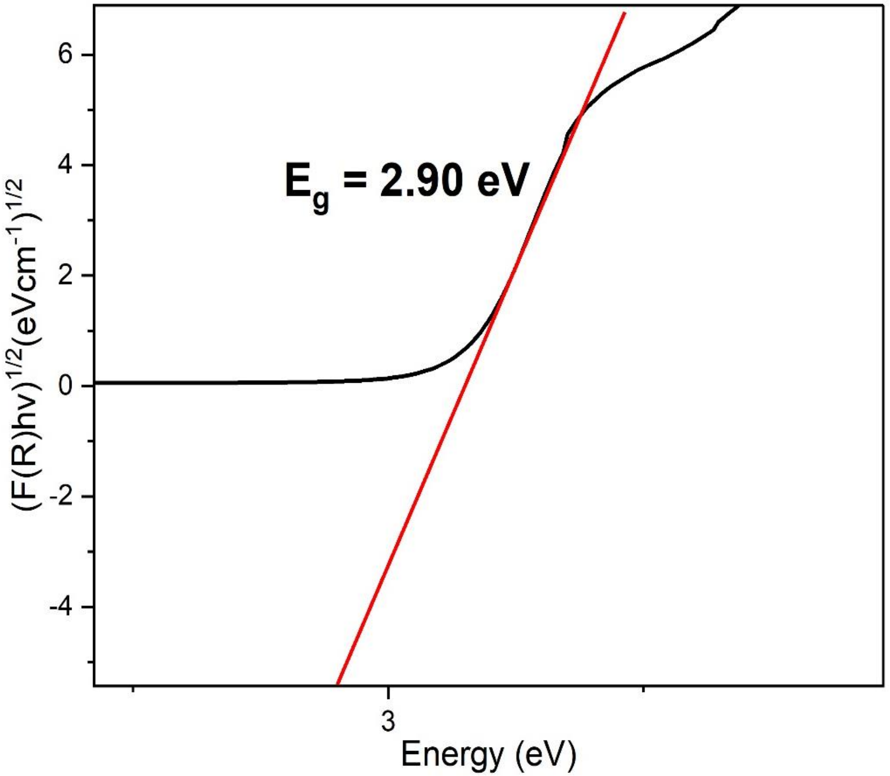




**Figure 3: Absorbance spectrum and Indirect tauc plot of ZnO@MgO**

# Results and Discussion

- The theoretical band gap energy of pure ZnO has been identified in literature to be around 3.33 eV [3] whereas that of pure MgO has been identified as 4.8 eV [4].
- The reduction in the energy band gap of the nanocomposite shows successful band gap narrowing by the core-shell combination of the two materials which can facilitate better electron excitation within the visible light irradiation range (400 – 800 nm) compared with the pure ZnO and MgO separately

- **<u>OPTIMIZATION VALIDATION AND KINETICS</u>**

$$R\% = 9.56 - 29.84A + 2.84B + 13.18C + 2.71D - 1.99AB - 14.05AC - 2AD + 6.05BC + 1.37BD + 8.72CD + 19.56A2 + 1.43B2 - 1.40C2 + 1.01D2$$

# Results and Discussion

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Model | 16927.30 | 14 | 1209.09 | 324.54 | < 0.0001 | significant |
| A-Dye Conc. | 10687.08 | 1 | 10687.08 | 2868.62 | < 0.0001 | |
| B-Catalyst Dose | 96.65 | 1 | 96.65 | 25.94 | 0.0002 | |
| C-pH | 2084.83 | 1 | 2084.83 | 559.61 | < 0.0001 | |
| D-Time | 88.13 | 1 | 88.13 | 23.65 | 0.0003 | |
| AB | 15.77 | 1 | 15.77 | 4.23 | 0.0587 | |
| AC | 789.96 | 1 | 789.96 | 212.04 | < 0.0001 | |
| AD | 15.99 | 1 | 15.99 | 4.29 | 0.0572 | |
| BC | 146.57 | 1 | 146.57 | 39.34 | < 0.0001 | |
| BD | 7.49 | 1 | 7.49 | 2.01 | 0.1780 | |
| CD | 304.33 | 1 | 304.33 | 81.69 | < 0.0001 | |
| $A^2$ | 2480.93 | 1 | 2480.93 | 665.93 | < 0.0001 | |
| $B^2$ | 13.31 | 1 | 13.31 | 3.57 | 0.0796 | |
| $C^2$ | 12.77 | 1 | 12.77 | 3.43 | 0.0853 | |
| $D^2$ | 6.66 | 1 | 6.66 | 1.79 | 0.2025 | |
| $R^2$ | 0.9969 | | | | | |
| Adjusted $R^2$ | 0.9939 | | | | | |
| Predicted $R^2$ | 0.9826 | | | | | |

**Table 2: ANOVA Table**

# Results and Discussion

- Optimization of parameters gave an MB removal of 95.948% in 115.7 minutes, for dye concentration 10mg/L, catalyst dose of 1000mg/L and pH 10.
- A validation run was carried out at optimum conditions and resulted in an MB removal of 90.858%.
- Kinetic modelling was then carried out to determine the reaction rate constant.
- The reaction was tested with zero order, half order, first order and second order degradation kinetics.
- It was found that the model kinetics were best suited to pseudo first-order degradation kinetics with a reaction rate constant of 0.07593 min-1.

# Results and Discussion

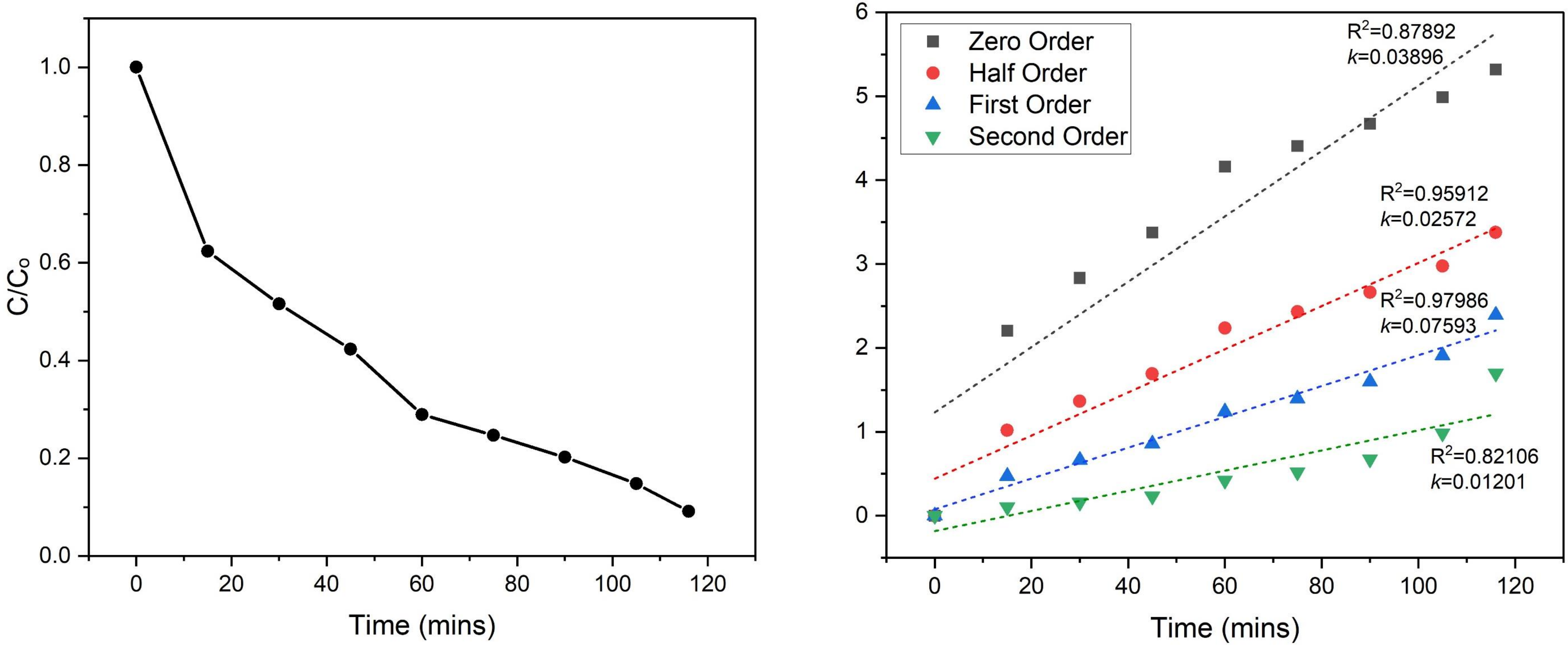
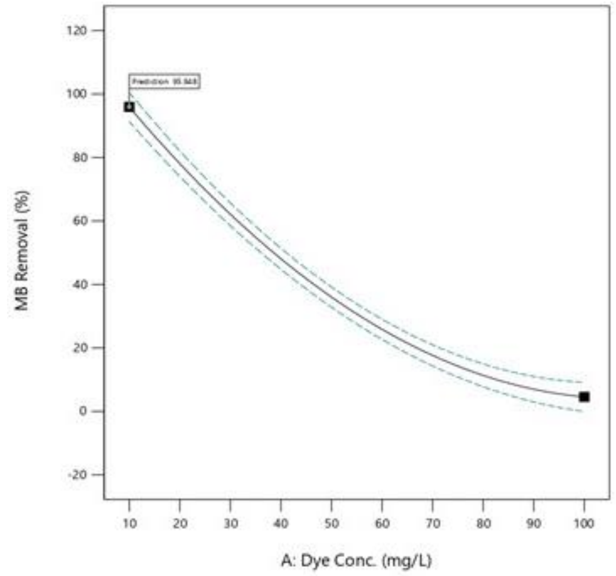
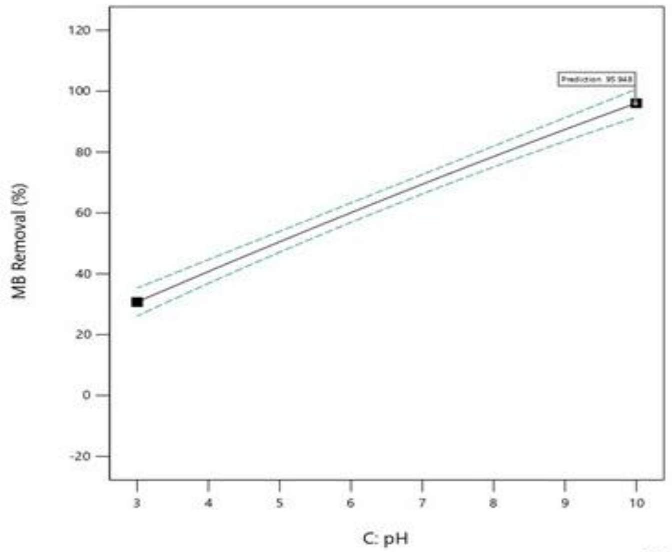


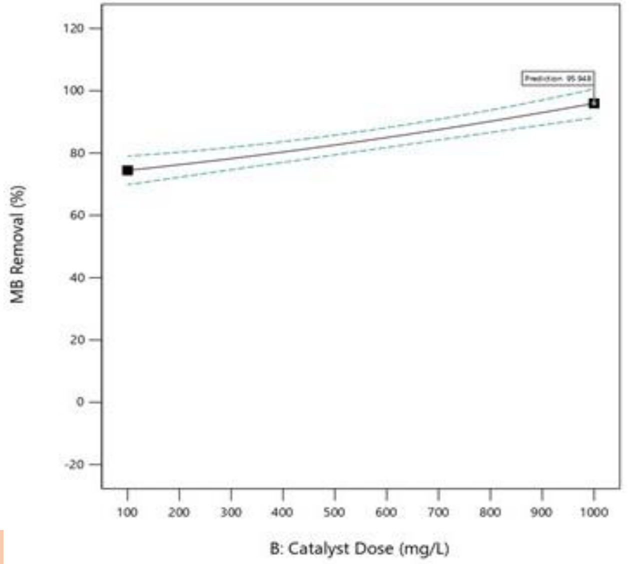

**Figure 4: degradation curve and degradation kinetics**

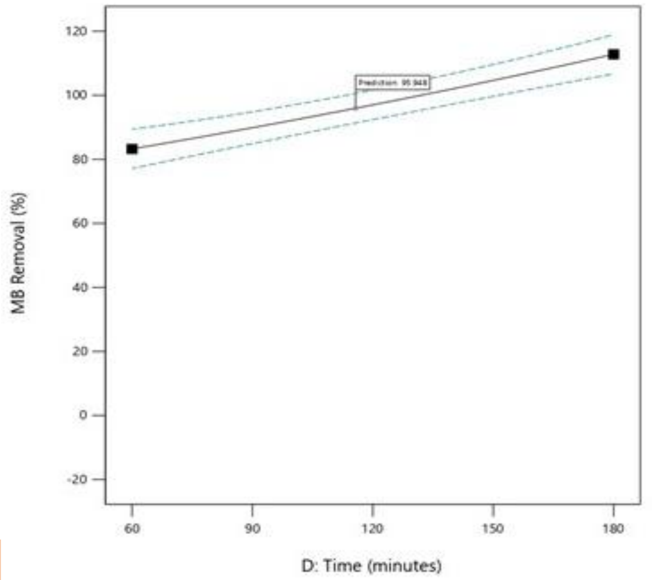
# Results and Discussion

- **EFFECT OF OPERATIONAL PARAMETERS**



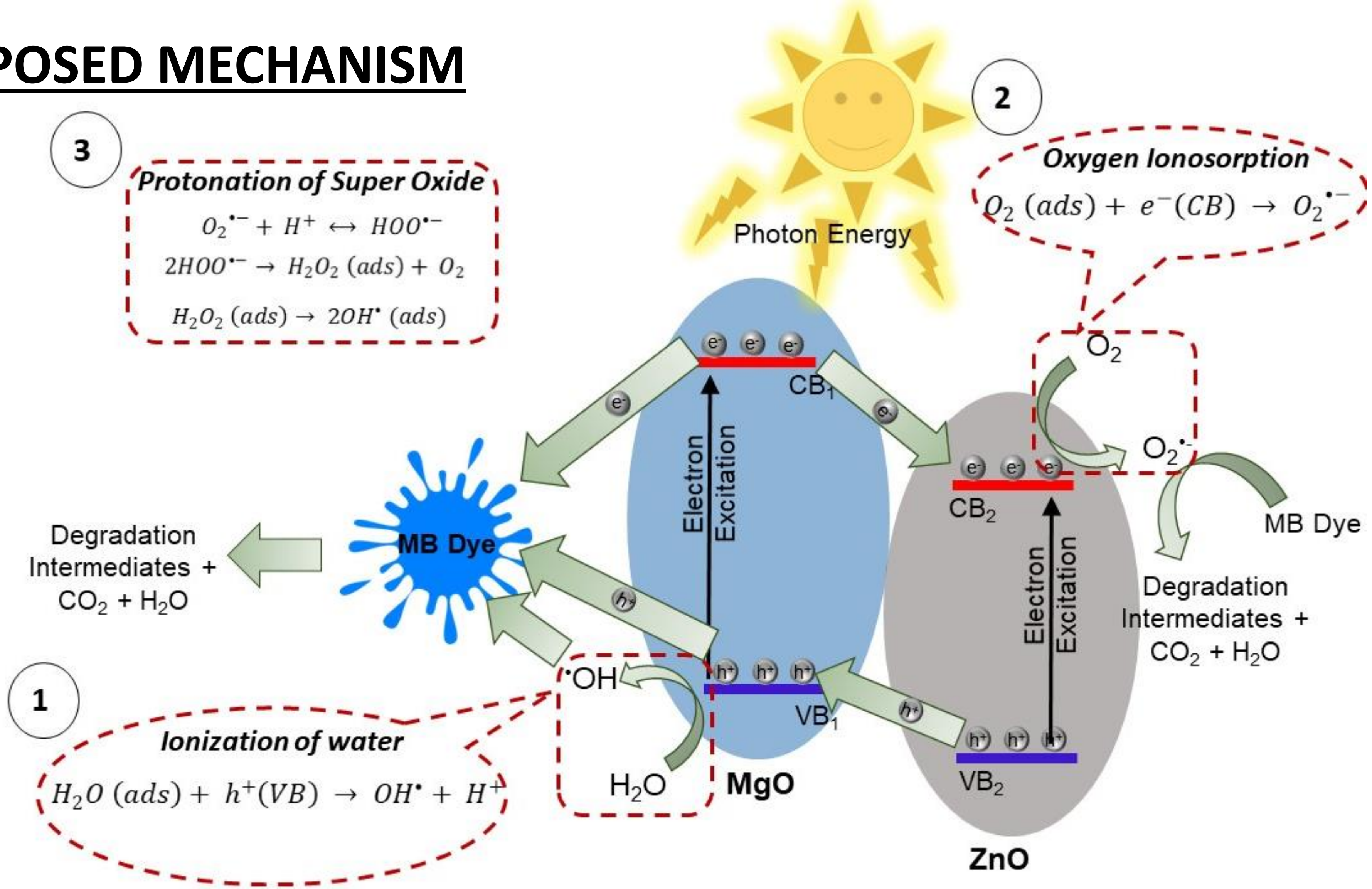



# Results and Discussion

- **PROPOSED MECHANISM**



# Results and Discussion

- **COMPARISON WITH LITERATURE**

| Photocatalyst | Optimum Reaction Conditions | | | | Removal efficiency % | Reference |
|---|---|---|---|---|---|---|
| | MB Concentration (mg/L) | Catalyst Dose (mg/L) | pH | Reaction time (mins) | | |
| ZnO@MgO core-shell nanocomposite | 10 | 1000 | 10 | 115.7 | 90.858 | Present study |
| ZnO/MgO/AC nanoparticle | 3.2 | 1000 | 7 | 20 | 100 | [5] |
| Novel tri-phase CuO–MgO–ZnO nanocomposite | 5 | 400 | 7 | 100 | 88.5 | [6] |
| Hollow MgO-ZnO microspheres | 5 | 300 | 7 | 150 | 100 | [7] |
| CdO–ZnO–MgO nanocomposite | 1 | 25 | 7 | 120 | 91 | [8] |

# Results and Discussion

- **<u>COMPARISON WITH LITERATURE</u>**
- The performance of the core-shell nanocomposite was compared with other photocatalyst materials containing ZnO and MgO for the degradation of MB dye.
- Other photocatalysts have displayed high degradation efficiencies for lower MB concentrations and/or longer degradation times.
- It was also observed that most studies combined ZnO, MgO and a third material in their catalyst materials for enhanced performance. In our study, the photocatalyst material contained ZnO and MgO only and the parameters were optimized to use shorter degradation periods in order to yield higher degradation efficiencies.
- The results obtained show that the ZnO@MgO core-shell nanocomposite could be utilized as an alternative for MB degradation.

# Results and Discussion

- ECONOMIC FEASIBILITY

| | Unit | Cost |
|---|---|---|
| **TOTAL CAPITAL COSTS** | $ | 2,941,149.22 |
| **TOTAL OPERATING COSTS** | $/year | 182,443.56 |
| **TOTAL REVENUES** | $/year | 1,097,416.73 |

- To estimate the feasibility of the up-scale synthesis and application of the ZnO@MgO core-shell nanocomposite for dye removal, an economic analysis was carried out where the capital costs, operating costs and possible revenues were estimated based on the optimized parameters of the lab experiments.
- The analysis assumes a daily wastewater inflow of 80m3 which is suitable for a roughly medium size treatment plant.

# Results and Discussion

- <u>**ECONOMIC FEASIBILITY**</u>
- The capital costs included the costs of the photocatalytic reactor and all its components, catalyst synthesis apparatus, plant infrastructure construction costs, contractor charges and contingencies. The total capital costs were then estimated to about $2,941,149.22.
- The operational costs were also estimated and comprised expenses such as electricity, cost of chemicals, water bills, statutory obligations such as taxes, workers' salaries as well as equipment repair and maintenance costs.
- The total annual operational costs estimate amounted to $182,443.56 which gave a running cost of $7.6/m3 of influent water.
- The possible revenues identified were the removal of the dye from the water, the sale of the synthesized catalyst material as well as the reuse of the treated effluent for on-site applications.

# Results and Discussion

- **ECONOMIC FEASIBILITY**
- The estimate of the total revenues was $1,097,416.73.
- Finally, the capital costs, operational costs and the revenues were used to derive the payback period and it was estimated at 3.2 years using the formula given as;

$$\text{Payback period} = \frac{\text{total capital costs } (\$)}{\text{total revenues } (\$/\text{year}) - \text{total operating costs} (\$/\text{year})}$$

# References


[1] L. F. Cusioli, H. B. Quesada, A. T. A. Baptista, R. G. Gomes, and R. Bergamasco, “Soybean hulls as a low-cost biosorbent for removal of methylene blue c ontaminant,” *Environ. Prog. Sustain. Energy*, vol. 39, no. 2, p. e13328, 2020, doi: https://doi.org/10.1002/ep.13328.

[2] O. Ebi Ebi, A. Falilat Taiwo, and A. Tunde Folorunsho, “Kinetic Modelling of the Biosorption of Methylene Blue onto Wild Melon (Lagenariasphaerica),” *Am. J. Chem. Eng.*, vol. 6, no. 6, pp. 126–134, 2018, doi: 10.11648/j.ajche.20180606.12.

[3] N. Kamarulzaman, M. F. Kasim, and R. Rusdi, “Band Gap Narrowing and Widening of ZnO Nanostructures and Doped Materials,” *Nanoscale Res. Lett.*, vol. 10, no. 1, p. 346, Aug. 2015, doi: 10.1186/s11671-015-1034-9.

[4] A. Almontasser, A. Parveen, and A. Azam, “Synthesis, Characterization and antibacterial activity of Magnesium Oxide (MgO) nanoparticles.,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 577, p. 012051, Dec. 2019, doi: 10.1088/1757-899X/577/1/012051.

# References

[5] M. A. Karimi, A. Hatefi-Mehrjardi, A. Askarpour kabir, and M. Zaydabadi, “Synthesis, characterization, and application of MgO/ZnO nanocomposite supported on activated carbon for photocatalytic degradation of methylene blue,” *Res. Chem. Intermed.*, vol. 41, Jun. 2014, doi: 10.1007/s11164-014-1729-z.

[6] T. Munawar *et al.*, “Sunlight-induced photocatalytic degradation of various dyes and bacterial inactivation using CuO–MgO–ZnO nanocomposite,” *Environ. Sci. Pollut. Res.*, vol. 28, no. 31, pp. 42243–42260, 2021, doi: 10.1007/s11356-021-13572-8.

[7] S. Vishwanathan and S. Das, “Glucose-mediated one-pot hydrothermal synthesis of hollow magnesium oxide-zinc oxide (MgO-ZnO) microspheres with enhanced natural sunlight photocatalytic activity,” *Environ. Sci. Pollut. Res.*, vol. 30, no. 4, pp. 8512–8525, Jan. 2023, doi: 10.1007/s11356-022-20283-1.

[8] V. Revathi and K. Karthik, “Microwave assisted CdO–ZnO–MgO nanocomposite and its photocatalytic and antibacterial studies,” *J. Mater. Sci. Mater. Electron.*, vol. 29, no. 21, pp. 18519–18530, Nov. 2018, doi: 10.1007/s10854-018-9968-1.