

RESEARCH PAPER

Photocatalytic Degradation of Brilliant Green Dye by Using ZnO-Cds/Pd Nanocomposite

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ABSTRACT

In this study, the photocatalytic degradation of textile dyes using ZnO-Cds/Pd nanocomposites synthesized via a hydrothermal approach was investigated. The nanocomposite was characterized using X-ray diffraction, FESEM, TGA, and TEM, and its photocatalytic activity was evaluated through degradation of brilliant green dye under exposure to solar light. The results showed that the optimum mass of Pd/ZnO-Cds nanocomposite for efficient photodegradation was 0.4 g/L, with a degradation efficiency of 86.6%. Scavenging experiments revealed that hydroxyl and superoxide radicals played a significant role in the degradation of brilliant green dye. Additionally, the study summarized some of the fundamental chemical and physical features of H_2O/O_2^- , H_2O_2 , and OH radicals, as well as how nanoparticles interact with nanocomposites and metal ions. The findings suggest that ZnO-Cds/Pd nanocomposite has the potential to be used for the removal of organic contaminants from textile waste due to their improved photocatalytic activity.

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INTRODUCTION

Environmental contamination caused by industrial waste is one of the biggest challenges facing the world today. This pollution is worsening and negatively impacting our daily lives, and urgent action is needed to find a solution. Industrial waste poses a significant threat to the ecosystem, particularly water, due to the vast amounts of industrial water discharged every day [1-4]. Textile factories, laundry and clothing dyeing, the oil industry, pharmaceuticals, iron and steel, paper, food, and power plants are some of the major sources of pollutants that are released into rivers and seas, causing harm to aquatic life and the food chain [5-8].

However, it has been found that using energy to eliminate these pollution sources has led to an increase in carbon dioxide emissions, contributing to global warming. Therefore, while we cannot stop technological and industrial progress, it is essential to develop new substances that do not harm the environment [9-11]. The photocatalysis process is crucial in this regard, as it aims to use renewable energy sources like sunlight to return environmental conditions to their normal state [12].

The photocatalysis process involves using light as an activator for a substance to increase the rate of a chemical reaction without taking part in the reaction itself. This process can be

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used for water treatment and purification, as well as the decomposition of toxic nitrogen oxides in the air, and air purification in homes, workplaces, and other settings [13-16]. Zinc oxide and cadmium sulfide have several applications as semiconductors, including catalysis, electronic devices, and energy conversion. CdS is a flexible and effective material that is resistant to corrosion, affordable, and can react under normal conditions in the form of raw or functionalized powder or thin film [17-20].

Research has extensively studied the development of the photocatalytic process. To dispose of organic pollutants using zinc oxide and cadmium sulfide and produce a material that can be utilized commercially in various applications, it is ideal for the photo catalysis process to be carried out in visible light rather than being limited to infrared or ultraviolet light [21-23].

MATERIALS AND METHODS

The chemical compounds used in this study were obtained from commercial sources and used without purification. Highly pure reagents, including cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), methanol (CH_3OH), sodium sulfide (Na_2S), and palladium chloride (PdCl_2), were purchased from Sigma-Aldrich.

Preparation of ZnO- CdS\Pd nanocomposite

The nanocomposite was prepared in two steps. Firstly, a hydrothermal system was used to prepare the ZnO-CdS nanocomposite by using oxalic acid (8 g), zinc (5 g), cadmium (2 g), and sodium sulfide (1 g). The mixture was thoroughly blended for 30

minutes and then poured into a Teflon cup, which was closed and placed into an electric furnace held at 160 °C for 24 hours. The resulting mixture was washed with water at least four times and dried overnight in a 60°C oven.

Secondly, to prepare the ternary nanocomposite, a deposition process was conducted. 0.5 g of yellow nano-powder ZnO-CdS and 0.05% PdCl_2 were placed in a quartz cell with 100 ml of methanol/deionized water (v/v 1%). The mixture was exposed to nitrogen gas for 10 minutes while continuously magnetic stirring, then sonicated before being irradiated. The resulting powder was washed several times with deionized water using an ultrasonic device and dried at 65°C for 24 hours.

Experiments involving photocatalysis

Photocatalytic degradation was carried out in an experimental setup consist of a home-made photoreactor and Irradiation source is Philips mercury lamp UVT (A), and Thorlabs.

Photocatalytic activity of the prepared photocatalyst has been tested by Brilliant green (BG) dye under solar light irradiation. A common approach involves adding 0.4 g of nanocomposite at the same optimum conditions. The photocatalytic mixture was agitated for 10 minutes while being kept in a dark area to achieve equilibrium (adsorption vs desorption). The solution was then irradiate for 60 minutes.

$$\text{Degradation efficiency (\%)} = (1 - C/C_0) \times 100\% \text{ [24].}$$

Where C_0 is the initial concentration of BG, and C is the concentration after irradiation.



Fig. 1. Real image of photos demonstrate the effectiveness of the photocatalytic process.

The real image appear in Fig. 1 demonstrate the effectiveness of the photocatalytic process as the removal rate was attained utilizing the overlaid brilliant green dye after 60 min, which has an optimum weight of 0.4 g of the catalyst at and an optimum concentration of the dye (50 mg/L) for and the intensity of 1.27mW/cm².

RESULTS AND DISCUSSION

Characterization of nanocomposite

X-ray diffraction (XRD) has been a crucial experimental technique for addressing various aspects related to the crystal structure of solids, including lattice constants, geometry, and identification of unidentified materials, for an extended period of time. Fig. 2a-b illustrates the powder X-ray diffraction patterns of a pure ZnO-CdS nanoparticle and a ZnO-Cds/Pd nanocomposite. The lower crystallinity of CdS compared to ZnONPs and the presence of crystalline ZnO NPs contribute to this difference. In the Pd-doped ZnO-CdS nanocomposite, only the binary ZnO-CdS crystalline structures match the diffraction peaks, and a clear Pd peak is absent, likely due to the low intensity and content of Pd. Pd doping causes the peaks to widen and shift to higher positions, indicating a decrease in particle size[25].

TEM analysis was conducted to examine the morphology of the ZnO-CdS powders. As shown in Fig. 3a, the undoped powder consisted mainly of nanoflake and polygon-like structures. Fig. 3a revealed a regular hexagonal arrangement, whereas Fig. 3b indicated that the CdS particles

in ZnO-CdS were notably larger than the average size of Pd-doped ZnO-CdS nanocomposites. However, purification produced homogeneous and crystalline ZnO-CdS nanoparticles with constant particle sizes. The uniformly dispersed doped ZnO-CdS nanostructure had a size of 100 nm. Several research results have supported the optical effective mass approximation model, which suggests that the particle size is affected by the amount of doping present, and it decreases as the degree of doping increases. TEM images revealed the poor crystallinity of Pd-doped ZnO-CdS nanocomposites. Our findings demonstrated that the Pd ion was effectively deposited onto the ZnO-CdS surface and the binary ZnO-CdS was successfully assembled [26, 27].

Additionally, the binary composite ZnO-CdS was characterized both before and after doping with palladium using FE-SEM. The surface of ZnO-CdS binary nanocomposites (shown in Fig. 4a) appeared as spherical pallets with highly distributed surface. However, some agglomerated surface areas were also observed, especially in pallets with a size of 500 nm. The FESEM image of ZnO-CdS binary nanocomposites' surfaces (Fig. 4b) showed widely scattered platforms and a bumpy surface. A stretcher with a size of 500 nm was used to observe it. A Pd-doped ZnO-CdS nanocomposite that revealed a new column of nanostructures with a spherical appearance. The figure showed the palladium ion in the ZnO-CdS lattice, and this conformation is controllable [28]. By comparing Fig. 4a, we noticed that the

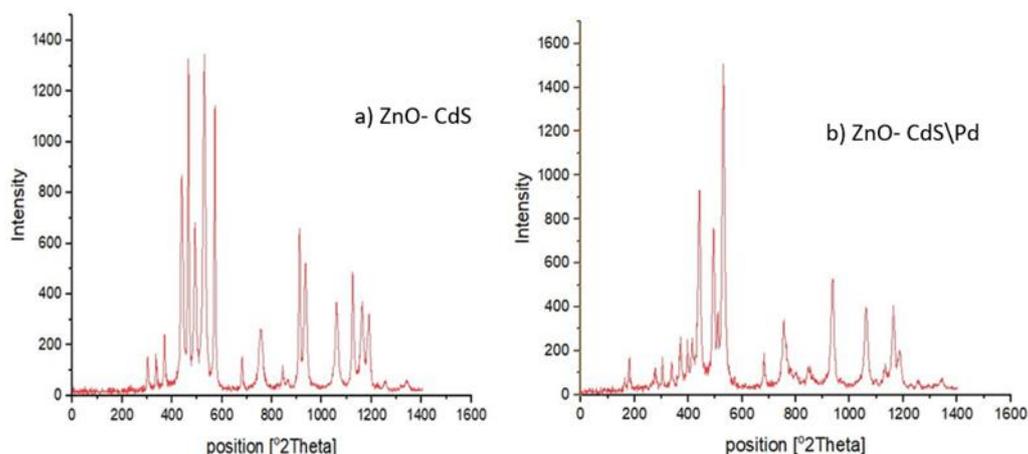


Fig. 2. X-ray diffraction patterns of (a) ZnO-CdS and (b) ZnO-CdS /pd.

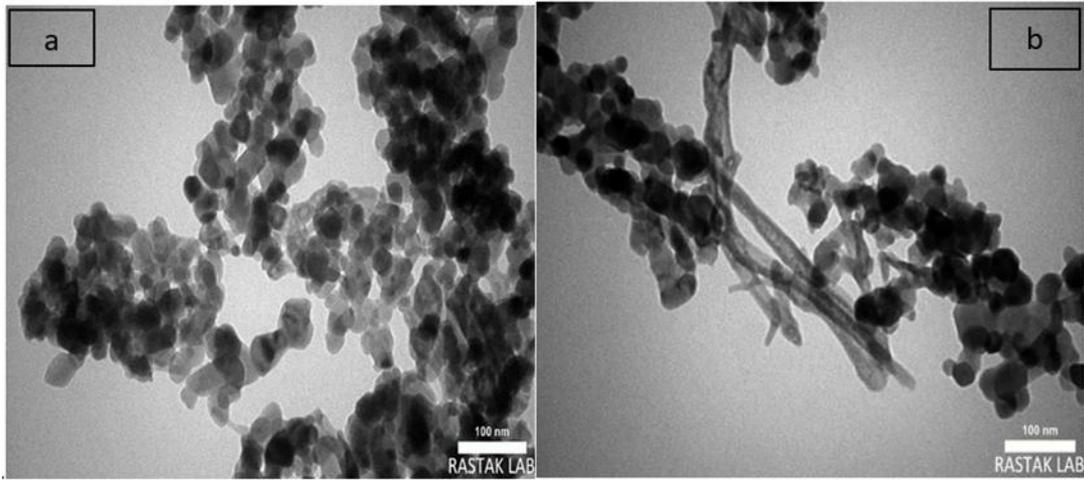


Fig. 3. TEM image of (a) ZnO-Cds nanoparticles, (b) ZnO-Cds/Pd nanocomposite.

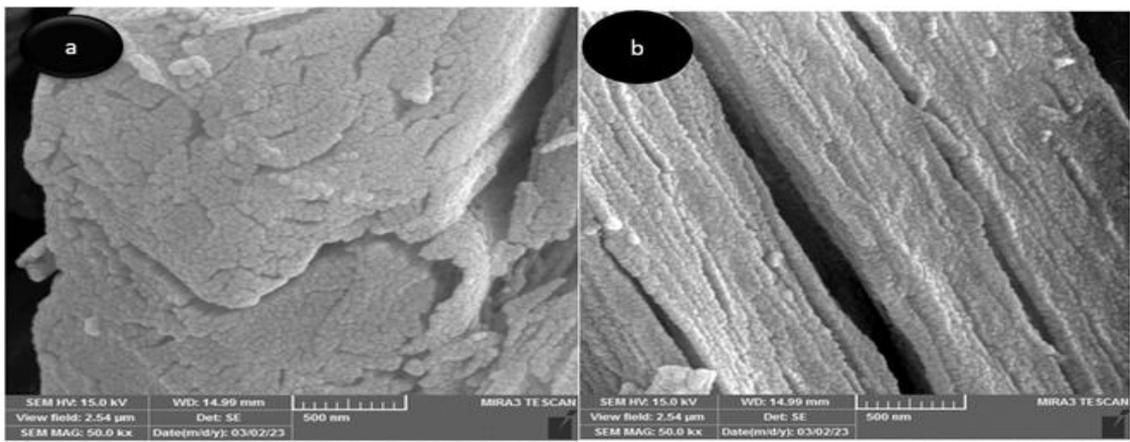


Fig. 4. FESEM images of ZnO-cds binary composites a), Pd doped ZnO-Cds nanocomposites b).

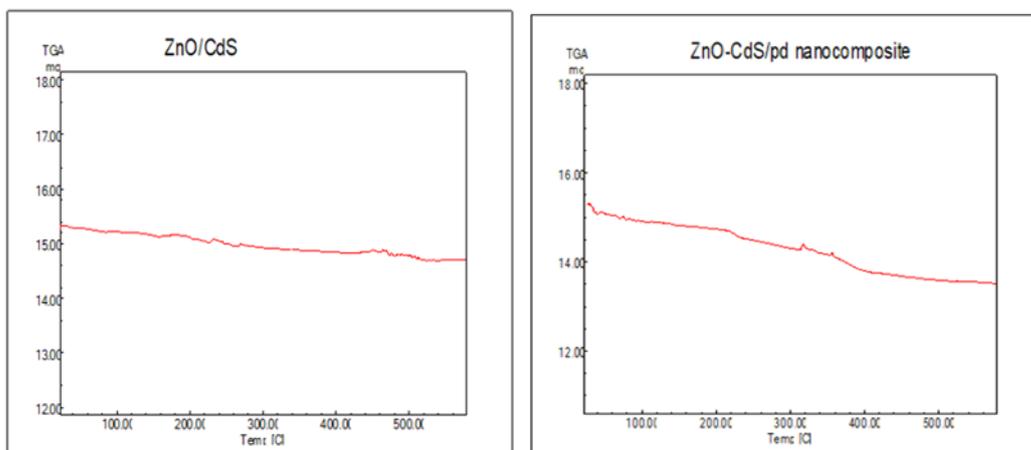


Fig. 5. TGA analysis images of ZnO-Cds Cds , a) ZnO- CdS / Pd nanocomposites.

ZnO-CdS superimposed dopant Pd displayed uniform size and high porosity, making it a distinctive and optimum surface for absorbing brilliant green dye. Fig. 4b demonstrated that the addition of palladium to the original binary nanocomposite surface changed the compounds' shape, displaying nanoparticles as an indistinct agglomerated surface. The irregular agglomerated surface showed a larger particle size due to the added amount of dopant Pd in ZnO-CdS binary nanocomposites [29].

A thermogravimetric analysis was conducted on the sample obtained from the binary composite and the nanocomposite after palladium doping (Fig. 5). The analysis revealed no significant weight

loss, indicating the excellent thermal stability of the prepared composite [30].

Treatment of dye pollution from aqueous solution

The study presents a method for treating water pollution caused by toxic textile dyes using a nanocomposite, specifically the ZnO-CdS/Pd nanocomposite. A laboratory sample of a 100 ml mixture containing various toxic textile dyes such as brilliant green dye BG, Congo red (CR), methyl violet (MV), crystal violet (CV), methylene blue (MB), brilliant blue (BB), and others, was used for the treatment. The solution was subjected to a photocatalytic degradation system for different periods using solar light. The effectiveness of the

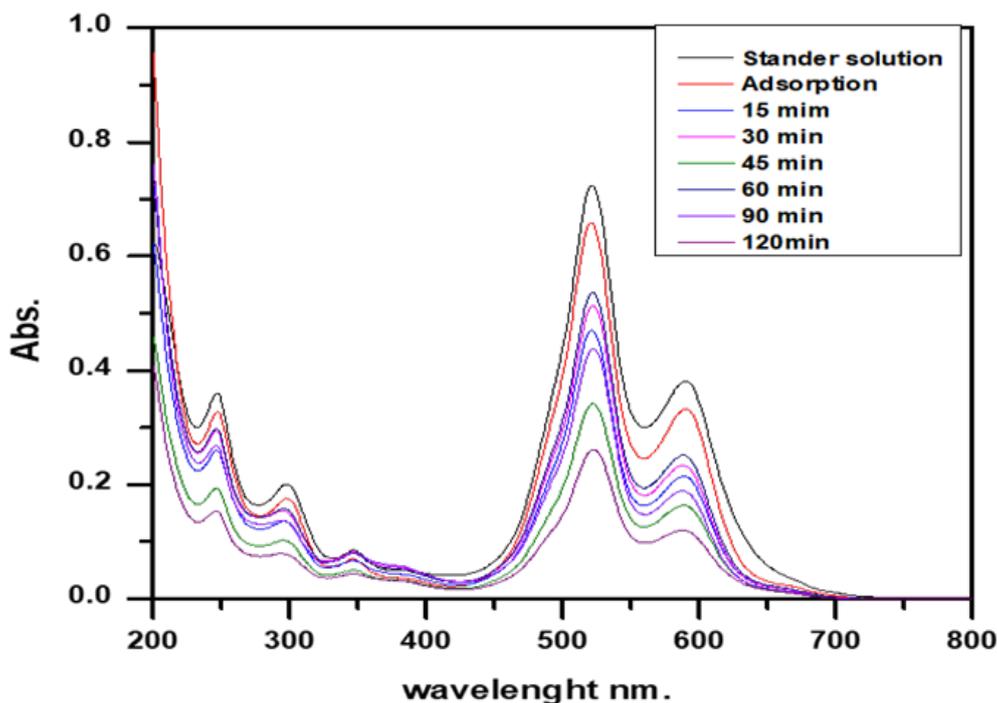


Fig. 6. Removing the mixture of pollutants under test conditions

Table 1. Roles of reactive oxygen species (ROS)

compound	Scavenger type	Reactions	Percentage of contribution (%)
H ₂ O ₂	O ₂ • ⁻	H ₂ O ₂ → e ⁻ +OH+O ₂ ⁻	99%
Methanol	OH	CH ₃ OH + HO• → (CH ₂ OH•)+H ₂ O	84.4%

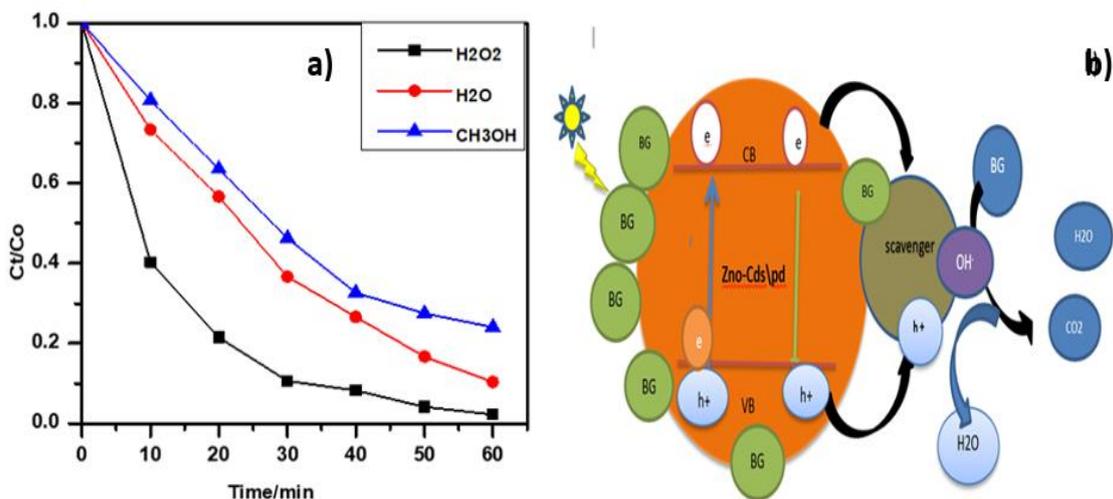


Fig. 7. a) Roles of reactive oxygen species (ROS), b) mechanism Scavenger-assisted photodegradation of BG on ZnO-Cds/Pd nanocomposite.

treatment was evaluated by examining the surface of the solution with a UVA meter and measuring the remaining concentration using a UV-Visible spectrophotometer [31-35]. Fig. 6 presents the results, which indicate that photocatalytic degradation of at least 80% was achieved using 0.4 g of the ZnO-Cds/Pd nanocomposite.

Roles of reactive oxygen species (ROS)

In order to investigate the critical role played by active species in the degradation of reactive dyes under solar light exposure, a quenching experiment was carried out. Fig. 7 displays the experimental data on radical trapping, where various ROS were utilized to evaluate their effects on the relative photonic efficiencies of BG dye. This approach aimed to distinguish the contribution of surface reactions involving (OH•, O₂•⁻, h⁺) species. To provide a summary of the scavengers and their interactions with free radicals [36], as show in Table 1.

The degradation of BG occurs through a reaction pathway that involves the formation of radicals from photo-generated electron-hole pairs (e⁻ CB; h⁺ VB). Hydroxyl radicals and electrons and holes (e⁻ CB; h⁺ VB) have an impact on the photocatalytic degradation process. The total quantum efficiency of photocatalysis is determined by the interfacial electron-transfer rate and the photogenerated electron and hole recombination lifetime. To increase quantum efficiency, the recombination

of photogenerated holes and electrons is typically delayed. This can be achieved by filling the valence band holes with electrons from a reductant for up to 60 minutes to confirm photocatalytic activity [37-39]. To scavenge superoxide radicals, hydrogen peroxide was used, and methanol was used to scavenge hydroxyl radicals. These two specific quenchers were selected because superoxide and hydroxyl radicals play a crucial role in the degradation of organic contaminants under visible light irradiation.

Fig. 7 shows the degradation efficiency between H₂O₂ and Methanol, and the photo catalytic degradation changed and decreased, showing that OH• can be essential in the photo catalytic.

CONCLUSION

In conclusion, we have successfully created Pd-doped ZnO-CdS nanocomposites through hydrothermal chemical synthesis, which have shown good photocatalytic efficiency with a degradation rate of 86.66% within 60 minutes. Our scavenging activity experiments have also revealed that the presence of primary active species, such as O₂ radical, is crucial for the degradation, while the photocatalytic degradation decreased with the absence of OH•. Furthermore, the TGA analysis confirmed the composite's stability with no significant weight loss. These results contribute to our understanding of photocatalytic material synthesis and their potential for organic pollutant

breakdown in wastewater treatment.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Sekar A, Yadav R. Green fabrication of zinc oxide supported carbon dots for visible light-responsive photocatalytic decolorization of Malachite Green dye: Optimization and kinetic studies. *Optik*. 2021;242:167311.
2. Arunraja L, Thirumorthy P, Karthik A, Subramanian R, Rajendran V. Investigation and characterization of ZnO/CdS nanocomposites using chemical precipitation method for gas sensing applications. *Journal of Materials Science: Materials in Electronics*. 2017;28(23):18113-18120.
3. Thame A, Mohamed S. Characterization of undoped and doped CdS nano-thin films by ZnO for photocatalytic application. *Chalcogenide Letters*. 2023:847-856.
4. Aljeboree AM, Abdulrazzak FH, Saleh ZM, Abbas HA, Alkaim AF. Eco-Friendly Adsorption of Cationic (Methylene Blue) and Anionic (Congo Red) Dyes from Aqueous Solutions Using Sawdust. *RAiSE-2023*; 2024/01/24: MDPI; 2024. p. 213.
5. Jamble SN, Ghoderao KP, Kale RB. Effect of temperature on structural and optical properties of solvothermal assisted CdS nanowires with enhanced photocatalytic degradation under natural sunlight irradiation. *Res Chem Intermed*. 2018;45(3):1381-1399.
6. Ritika, Kaur M, Umar A, Mehta SK, Kansal SK, Khan MA, et al. Enhanced solar light-mediated photocatalytic degradation of brilliant green dye in aqueous phase using BiPO₄ nanospindles and MoS₂/BiPO₄ nanorods. *Journal of Materials Science: Materials in Electronics*. 2019;30(23):20741-20750.
7. Aljeboree AM, Al-Baitai AY, Abdalhadi SM, Alkaim AF. Investigation Study of Removing Methyl Violet Dye From Aqueous Solutions Using Corn-Cob as A Source of Activated Carbon. *Egyptian Journal of Chemistry*. 2021;0(0):0-0.
8. Removal of Pharmaceutical Amoxicillin drug by using (CNT) decorated Clay/ Fe₂O₃ Micro/Nanocomposite as effective adsorbent: Process optimization for ultrasound-assisted adsorption. *International Journal of Pharmaceutical Research*. 2019;11(4).
9. Aljeboree AM, Noor Alshirifi A. Oxidative coupling of Amoxicillin using 4-Aminoantipyrine: Stability and higher sensitivity. *Journal of Physics: Conference Series*. 2019;1294(5):052001.
10. Jia Y, Wang Z, Qiao X-Q, Huang L, Gan S, Hou D, et al. A synergistic effect between S-scheme heterojunction and Noble-metal free cocatalyst to promote the hydrogen evolution of ZnO/CdS/MoS₂ photocatalyst. *Chem Eng J*. 2021;424:130368.
11. Alkadir OKA, Taifi A, Aljeboree AM, Bayaa ALA, Abed SA, Alkaim AF. Environmental Removal of some Dyes from Aqueous Solution by using highly adsorbent surface derived from Malva parviflora plant leaves: multifactors Studies. *IOP Conference Series: Earth and Environmental Science*. 2022;1029(1):012022.
12. Khanchandani S, Kundu S, Patra A, Ganguli AK. Shell Thickness Dependent Photocatalytic Properties of ZnO/CdS Core-Shell Nanorods. *The Journal of Physical Chemistry C*. 2012;116(44):23653-23662.
13. Lu H, Liu Y, Zhang S, Wan J, Wang X, Deng L, et al. Clustered tubular S-scheme ZnO/CdS heterojunctions for enhanced photocatalytic hydrogen production. *Materials Science and Engineering: B*. 2023;289:116282.
14. Mezher MJ, Kudhier MA, Dakhil OAA. Using ZnO-CdS Composite Nanofibers in the Photolytic Activity Under Sunlight Irradiation. *Elsevier BV*; 2023.
15. Midya L, Patra AS, Banerjee C, Panda AB, Pal S. Novel nanocomposite derived from ZnO/CdS QDs embedded crosslinked chitosan: An efficient photocatalyst and effective antibacterial agent. *J Hazard Mater*. 2019;369:398-407.
16. Nithya R, Ragupathy S, Sakthi D, Arun V, Kannadasan N. Photocatalytic efficiency of brilliant green dye on ZnO loaded on cotton stalk activated carbon. *Materials Research Express*. 2020;7(7):075002.
17. Qi C, Guo X, Lu B, Ruan B, Li P. Enhanced Photocatalytic Performance of a ZnO/CdS Heterostructure for Hydrogen Production and Mixed Dye Degradation. *ChemistrySelect*. 2023;8(1).
18. Ragupathy S, Priyadharsan A, AlSalhi MS, Devanesan S, Guganathan L, Santhamoorthy M, et al. Effect of doping and loading Parameters on photocatalytic degradation of brilliant green using Sn doped ZnO loaded CSAC. *Environ Res*. 2022;210:112833.
19. Thirumala Rao G, Babu B, Joyce Stella R, Pushpa Manjari V, Venkata Reddy C, Shim J, et al. Synthesis and characterization of VO₂⁺ doped ZnO-CdS composite nanopowder. *J Mol Struct*. 2015;1081:254-259.
20. Revathi M, Pricilla jeyakumari A, Saravanan SP. Design and Fabrication of ZnO/CdS heterostructured nanocomposites for enhanced hydrogen evolution from solar water splitting. *Inorg Chem Commun*. 2021;134:109056.
21. S. Malghe Y, B. Lavand A. Synthesis Of C/ZnO/CdS Nanocomposite With Enhanced Visible Light Photocatalytic Activity *Advanced Materials Letters*. 2016;7(3):239-245.
22. Sadhasivam S, Sadhasivam T, Oh TH. Electrochemically synthesized Cd doped ZnO nanorods and integrated atomic Cd-S bridged Cd:ZnO/CdS heterostructure photoanode for enhanced visible light responsive water oxidation applications. *J Electroanal Chem*. 2023;934:117289.
23. Yashaswini M, Naik KG. Solvothermal synthesis of ZnO/CdS nanocomposite and its structural and optical properties. *AIP Conference Proceedings: AIP Publishing*; 2019. p. 140022.
24. Yadav R, Chundawat TS, Surolia PK, Vaya D. Photocatalytic degradation of textile dyes using β-CD-CuO/ZnO nanocomposite. *Journal of Physics and Chemistry of Solids*. 2022;165:110691.
25. Matinise N, Fuku XG, Kaviyarasu K, Mayedwa N, Maaza M. ZnO nanoparticles via Moringa oleifera green synthesis: Physical properties and mechanism of formation. *Appl Surf Sci*. 2017;406:339-347.
26. Hashim FS, Alkaim AF, Salim SJ, Alkhayatt AHO. Effect of (Ag, Pd) doping on structural, and optical properties of ZnO nanoparticles: As a model of photocatalytic activity for water pollution treatment. *Chem Phys Lett*. 2019;737:136828.
27. Hashim FS, Alkaim AF, Mahdi SM, Omran Alkhayatt AH. Photocatalytic degradation of GRL dye from aqueous

- solutions in the presence of ZnO/Fe₂O₃ nanocomposites. *Composites Communications*. 2019;16:111-116.
28. Sood S, Umar A, Kumar Mehta S, Sinha ASK, Kumar Kansal S. Efficient photocatalytic degradation of brilliant green using Sr-doped TiO₂ nanoparticles. *Ceram Int*. 2015;41(3):3533-3540.
29. Mahdi ZS, Aljeboree AM, Rasen FA, Salman NAA, Alkaim AF. Synthesis, Characterization, and Regeneration of Ag/TiO₂ Nanoparticles: Photocatalytic Removal of Mixed Dye Pollutants. *RAiSE-2023*; 2024/01/26: MDPI; 2024. p. 216.
30. Sharma M, Jeevanandam P. Synthesis, characterization and studies on optical properties of hierarchical ZnO–CdS nanocomposites. *Mater Res Bull*. 2012;47(7):1755-1761.
31. Zou L, Wang H, Jiang X, Yuan G, Wang X. Enhanced photocatalytic efficiency in degrading organic dyes by coupling CdS nanowires with ZnFe₂O₄ nanoparticles. *Solar Energy*. 2020;195:271-277.
32. Zirak M, Akhavan O, Moradlou O, Nien YT, Moshfegh AZ. Vertically aligned ZnO@CdS nanorod heterostructures for visible light photoinactivation of bacteria. *J Alloys Compd*. 2014;590:507-513.
33. Zhang X, Zhang R, Yang A, Wang Q, Kong R, Qu F. Aptamer based photoelectrochemical determination of tetracycline using a spindle-like ZnO-CdS@Au nanocomposite. *Microchimica Acta*. 2017;184(11):4367-4374.
34. Yu Z, Yin B, Qu F, Wu X. Synthesis of self-assembled CdS nanospheres and their photocatalytic activities by photodegradation of organic dye molecules. *Chem Eng J*. 2014;258:203-209.
35. Jonnalagadda M, Prasad VB, Raghu AV. Synthesis of composite nanopowder through Mn doped ZnS-CdS systems and its structural, optical properties. *J Mol Struct*. 2021;1230:129875.
36. He W, Kim H-K, Wamer WG, Melka D, Callahan JH, Yin J-J. Photogenerated Charge Carriers and Reactive Oxygen Species in ZnO/Au Hybrid Nanostructures with Enhanced Photocatalytic and Antibacterial Activity. *Journal of the American Chemical Society*. 2013;136(2):750-757.
37. Titanium Dioxide (P25) Produces Reactive Oxygen Species in Immortalized Brain Microglia (BV2): Implications for Nanoparticle Neurotoxicity. *American Chemical Society (ACS)*.
38. Abebe B, Murthy HCA, Amare E. Enhancing the photocatalytic efficiency of ZnO: Defects, heterojunction, and optimization. *Environmental Nanotechnology, Monitoring and Management*. 2020;14:100336.
39. Aljeboree AM, Radia ND, Jasim LS, Alwarthan AA, Khadhim MM, Washeel Salman A, et al. Synthesis of a new nanocomposite with the core TiO₂/hydrogel: Brilliant green dye adsorption, isotherms, kinetics, and DFT studies. *Journal of Industrial and Engineering Chemistry*. 2022;109:475-485.