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Solar Light Photocatalytic Degradation of Methylene Blue and Methyl Orange Dyes by Ag-ZnO Nanocomposite

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Abstract

A highly efficient silver-assisted ZnO nanocomposite was synthesized using the co-precipitation method, a technique that ensures a controlled and homogeneous formation of the composite material. The high purity of the synthesized nanocomposite was confirmed through detailed FTIR spectra analysis, which showed clear and distinct peaks corresponding to the functional groups present, indicating the absence of significant impurities. To evaluate the photocatalytic capabilities of the nanocomposite, a series of tests were conducted under natural sunlight conditions. These tests employed methylene blue and methyl orange dyes as model organic pollutants, both maintained at a concentration of 10 ppm to simulate common environmental contamination scenarios. Different loadings of the catalyst were tested to determine the optimal amount required for effective dye degradation. The experimental results revealed that a catalyst loading of 0.1 g was the most effective for achieving significant degradation of both dyes within the given parameters. Interestingly, the nanocomposite demonstrated a notably higher photocatalytic degradation efficiency for methylene blue compared to methyl orange, suggesting a preferential interaction or degradation pathway for the former. These findings suggest that the prepared silver-assisted ZnO nanocomposite holds substantial potential for application in industrial wastewater treatment processes. The enhanced degradation of methylene blue indicates that the nanocomposite could be particularly useful in environments where this dye or similar organic pollutants are prevalent. This study offers a promising new pathway for the efficient and cost-effective degradation of organic pollutants in wastewater, highlighting the potential for scalable implementation in industrial settings to address environmental pollution challenges. Further research could focus on optimizing the synthesis process, exploring the degradation mechanisms in greater detail, and testing the nanocomposite against a broader range of pollutants to fully realize its application potential.

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INTRODUCTION

Water pollution, predominantly caused by industrial effluents, poses a significant threat to environmental sustainability and human health. Among the various pollutants, synthetic dyes such as Methylene Blue (MB) and Methyl Orange (MO) are particularly problematic due to their widespread use in textile, paper, and other manufacturing industries, as well as their persistence and toxicity in aquatic environments. Traditional methods of dye removal, including coagulation, adsorption, and biological treatments, often fall short in terms of efficiency and cost-effectiveness. Consequently, there is a growing interest in advanced oxidation processes (AOPs) for the degradation of these pollutants.

Photocatalysis, a promising AOP, leverages the catalytic properties of semiconductors to generate reactive oxygen species (ROS) under light irradiation, facilitating the breakdown of complex organic molecules. Among various photocatalysts, zinc oxide (ZnO) has garnered attention due to its high photosensitivity, stability, and non-toxic nature. However, the wide bandgap of ZnO limits its photocatalytic activity under visible light, necessitating modifications to enhance its efficiency.

The integration of silver nanoparticles (Ag NPs) with ZnO to form Ag-ZnO nanocomposites has emerged as an effective strategy to overcome this limitation. Ag NPs not only act as electron sinks to reduce the recombination of electron-hole pairs but also extend the photoresponse of ZnO into the visible region through surface plasmon resonance (SPR). This synergistic effect significantly enhances the photocatalytic performance of ZnO under solar light irradiation.

This study investigates the solar light photocatalytic degradation of Methylene Blue and Methyl Orange dyes using Ag-ZnO nanocomposites. The synthesis of Ag-ZnO nanocomposites, their structural and optical properties, and their efficiency in degrading MB and MO under solar light are explored. The findings of this research could contribute to the development of efficient and sustainable photocatalytic systems for wastewater treatment.

Dyes are coloured compound which impart colour in visible region and it form a bond with a substrate [1]. The Production of synthetic dyes is on the increase because of their high demand [2]. The industries like textile, leather, paper, printing, cosmetic, petroleum, plastic, food, paints, rubber, and pharmaceutical uses the dyes on major scale [3]. And because of this largest consumer of colourants, the effluents from this industries contain vast quantity of dyes (which are carcinogenic mutagenic and toxic to human) Using during process [4]. The impact of these dyes on the environment due to the potentially carcinogenic property of chemicals [5]

One of the highest consuming materials in dye industry is methylene blue used for colouring silk, wool, cotton, and paper. It is an aromatic heterocyclic basic dye which has molecular weight 319.95 g/mol. It is a cationic dye which molecular formula is C16H18N3ClS and the λmax value is 663nm. The IUPAC Name is [7-(dimethylamino) phenothiazin-3-ylidene]-dimethylazanium;chloride [6]. It is a water soluble dye. It is toxic, carcinogenic, and non-biodegradable and can cause serious threat to human health [7]. Methylene blue is an organic chloride salt with a formula $C_{16}H_{18}ClN_3S$ as presented in Figure 1. It is also called Methylthioninium chloride or Swiss Blue. It is a thiazine dye with antioxidant, cardioprotective properties, antimalarial, and an antidepressant.

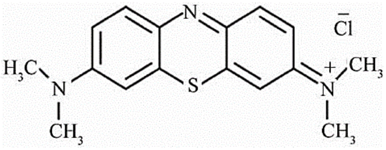


Figure 1. Structure of Methylene Blue [8].

Methyl orange is also one of the most common dyes in the textile industries. Its molecular weight is 327.34 g/mol and Molecular formula is $C_{14}H_{14}N_3NaO_3S$ presented in Figure 2 and the λmax value i463 nm [10].

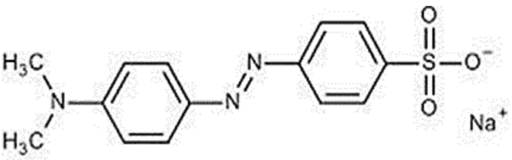


Figure 2. Structure of Methyl Orange

The IUPAC Name of Methyl Orange is sodium4-{[4-(dimethylamino) phenyl]diazenyl}benzene-1-sulfonate[9]. It is populaty used as in PH indicator in titration and found in major industries influent which harmful to environment and human health [4]

One of the great method to remove such harmful dyes from the industrial effluent is photocatalytic degradation [4], based on photocatalyst which is branch of Chemistry that deals with chemical reactions taking place in the presence of light and a photocatalyst [11]. Name itself indicates that is combination of two words: Photo related to photon and Catalyst, which altering the rate of reaction. Many of new class materials with enhanced photocatalytic activity have been designed [12]. Sunlight is one of the best resource among other renewable source now a days photocatalytic degradation process is used for removing such hazardous dyes from water so to prepare visible light photocatalyst is combining the semiconductor and metal material is a very recent trends in the field of the waste water treatments. There are many different processes for to make a photocatalyst such as Oxidation, Sol-gel, Co-precipitation, Hydrothermal [13], etc. But the co-precipitation method is one of the easy and economical one [14]

In Co-precipitation method the soluble salt of the desired metal ion is taken with the alkali medium to formation of the precipitation of metal oxide. The simple Co-precipitation method between the zinc acetate dehydrate and sodium hydroxide is given,

Reaction

$$\mathrm{Zn\ (CH_3COO)_2 + NaOH \longrightarrow Zn\ (CH_3COO)(OH) + NaCH_3COO}$$

$$\mathrm{Zn\ (CH_3COO)\ (OH) + NaOH \longrightarrow ZnO + NaCH_3COO + H_2O}$$

The residual sodium salt $NaCH_3COO$ is removed by ethanol and distilled water washing [15]. In this way the photocatalyst is prepared and used for dye degradation in the effluent. This photocatalytic method proved to be promising method for the treatment of waste water contaminated with organic pollutants [16]. To make the water clear because quality of water is an important aspect which determines it usage for the industrial and domestic purposes [3].

MATERIAL AND METHOD

Material

All the chemicals which required for the synthesis Nano composite and its application as shown in Figure 3 were obtained from the store of school of chemical science KBC North Maharashtra University Jalgaon . All this chemical used without any further purification.

Zinc acetate (company name and purity), Silver nitrate, Sodium hydroxide, Methyl Orange, Methylene Blue, Ethanol and double distilled water.

Figure 3. Chemicals Obtained for Synthesis.

Synthesis of Catalyst

The Ag-ZnO nanocomposite was prepared using a straightforward co-precipitation method. Initially, a zinc acetate solution was made by dissolving 22 grams of zinc acetate in 100 milliliters of distilled water. Concurrently, a silver nitrate solution was prepared by dissolving 0.22 grams of silver nitrate in 100 milliliters of double-distilled water. Additionally, a 2M sodium hydroxide solution was created by dissolving 8 grams of sodium hydroxide in distilled water. An ethanol-water mixture, in a ratio of 9:1, was prepared by mixing 9 milliliters of ethanol with 1 milliliter of water. For the dye solutions, a 10 ppm Methylene Blue solution was prepared by dissolving 10 milligrams of the dye in 1000 milliliters of distilled water, and similarly, a 10 ppm Methyl Orange solution was prepared by dissolving 10 milligrams of the dye in 1000 milliliters of distilled water.

Synthesis Process

In the synthesis process as shown in Figure 4, 100 ml of the zinc acetate solution was mixed with 100 ml of the silver nitrate solution and poured into a 500 ml beaker. To this mixture, 2M NaOH was added dropwise under constant stirring at 1100-1200 RPM. Stirring continued for 60 minutes after the complete addition of NaOH, from 12:00 to 13:00 on 23/03/2023. Following the reaction, the mixture was allowed to stand undisturbed for 22 hours, from 13:00 on 23/03/2023 to 11:00 on 24/03/2023.

The resulting solution was then filtered using Whatman filter paper no. 41 and washed with a 9:1 ethanol-water mixture. The washed product was dried at 100°C for 12 hours, followed by calcination at 600°C for 2 hours. The prepared catalyst was then ready for use.

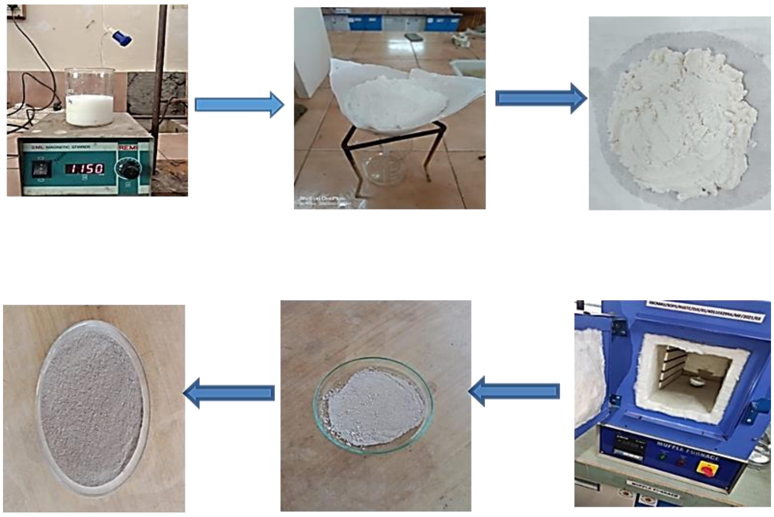


Figure 4. Synthesis Process.

Photocatalytic Degradation of Methylene Blue and Methyl Orange

In this study, sunlight served as the visible light source for the photocatalytic degradation experiments as shown in Figure 5. Various loadings of the Ag-ZnO catalyst (0.2 g, 0.1 g, 0.05 g, and 0.025 g) were used with 100 ml solutions of 10 ppm Methylene Blue and 10 ppm Methyl Orange. Prior to sunlight irradiation, each catalyst loading was separately added to the dye solutions and stirred in the dark for 30 minutes to reach adsorption-desorption equilibrium. Photocatalytic activity was then tested from 11:00 am to 3:00 pm with constant stirring at 500 RPM. During the degradation process, 3 ml samples were withdrawn at 30-minute intervals for Methyl Orange and at 10-minute intervals for Methylene Blue. The absorbance of these samples was measured using a spectrophotometer. The percentage of dye removal was subsequently calculated based on the absorbance data.

Formula

$$\%\ \text{Dye Removal} = \frac{Concentration-Absorbance}{Concentration}\times 100$$

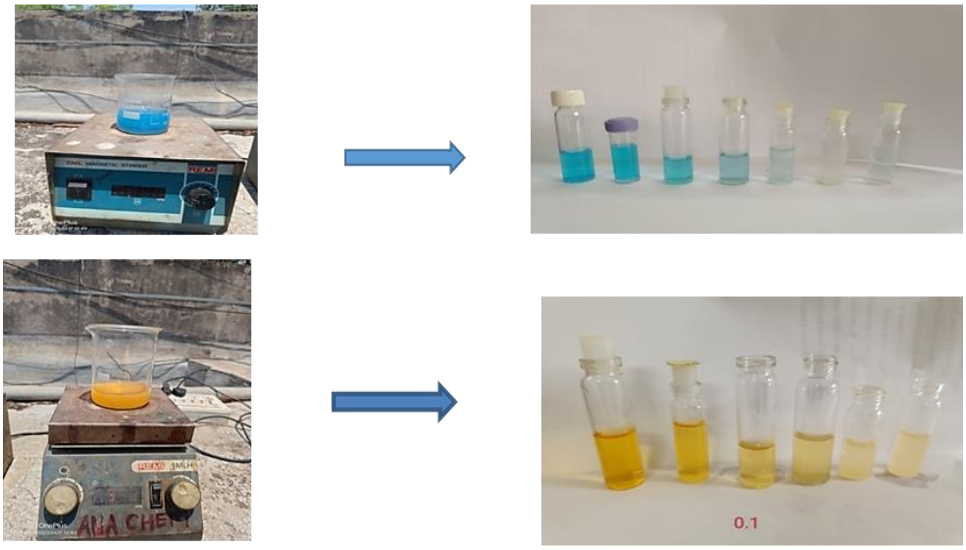


Figure 5. Photocatalytic degradation experiments.

RESULT AND DISCUSSION

Characterization

UV - Visible Spectra

The UV-Visible spectra were obtained to determine the λmax values of the prepared Methylene Blue and Methyl Orange dye solutions. Figure 6 displays these spectra, showing a λmax value of 663 nm for Methylene Blue, represented by the blue line, and a λmax value of 463 nm for Methyl Orange, represented by the orange line. The absorbance of the samples withdrawn during the photocatalytic degradation experiments (as described in section 3.3) was measured at these λmax values.

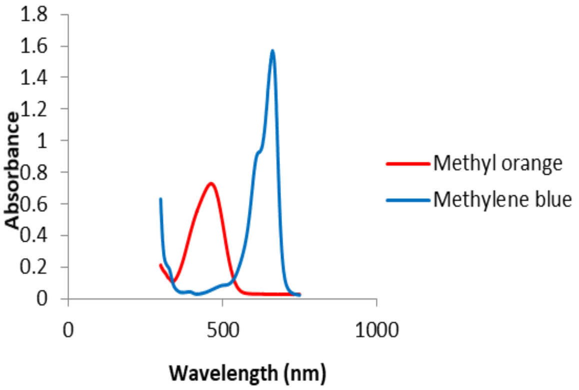
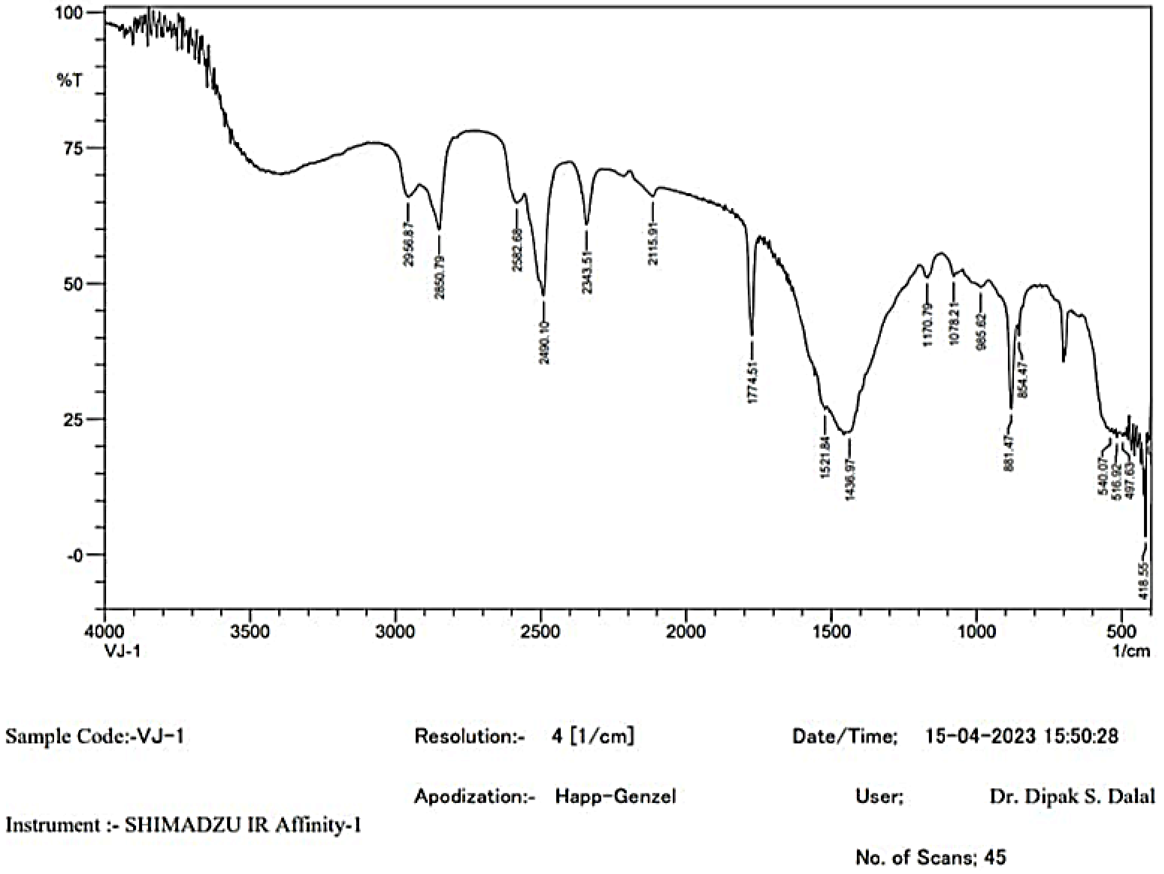


Figure 6. UV-Visible spectra (λmax).

Catalyst Characterisation

The FTIR spectrum of the prepared ZnO nanocomposite is shown in Figure 7. From these FTIR results, the functional groups present in the nanocomposite can be identified. The band at 496.63 cm−1−1 is attributed to ZnO stretching vibrations. The band at 540 cm−1−1 corresponds to Zn-O stretching vibrations, and the band at 881.47 cm−1−1 is related to the tetragonal Zn-O bonding in the nanocomposite. The band at 1521 cm−1−1 indicates the presence of O-H stretching vibrations, while the band at 2956.87 cm−1−1 is associated with the CO_{22} in the sample. These results confirm the successful synthesis and purity of the Ag-ZnO nanocomposite.



Sample Code:-VJ-1
Resolution:- 4 [1/cm]
Date/Time; 15-04-2023 15:50:28
Apodization:- Happ-Genzel
User; Dr. Dipak S. Dalal
Instrument :- SHIMADZU IR Affinity-1
No. of Scans; 45

Figure 7. FTIR Spectra.

Photocatalytic Activity for Methylene Blue

A photocatalytic study was conducted to evaluate the efficiency of the prepared Ag-ZnO photocatalyst with varying catalyst loads ranging from 0.025 g to 0.2 g per 100 ml solution of Methylene Blue. Absorbance measurements were taken at 663 nm, and the data are presented in Tables 1-4. The experimental results are illustrated in Figures 8-11, corresponding to the different catalyst loadings.

The results indicate that 99% of the Methylene Blue dye was degraded within 50 minutes. The figures show an increasing trend in the percent dye removal, highlighting the photocatalytic efficiency. Notably, a catalyst loading of 0.2 g per 100 ml was the most effective in degrading the dye compared to the other loadings, demonstrating superior photocatalytic performance.

Table 1. Dye Removal of Methyl Orange dye with Catalyst loading 0.2 g/100 mL

Table 1		**Catalyst= 0.2 gm**		
S.N	***Time(min)***	***Absorbance***	***Concentration***	***%Dye Removal***
1	10ppm	1.481	11.92431562	87.58
2	Dark	1.146	9.22705314	90.38938555
3	30	0.136	1.095008052	98.85947333
4	60	0.108	0.869565217	99.09428764
5	90	0.055	0.442834138	99.5387576
6	120	0.03	0.241545894	99.74841323
7	150	0.019	0.152979066	99.84066172

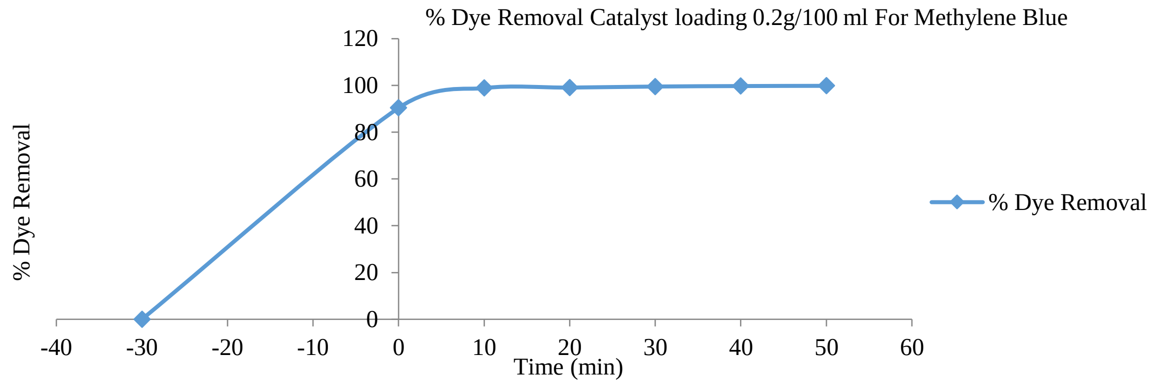


Figure 8. % Dye Removal of Methyl Orange dye with Catalyst loading 0.2g/100 mL.

Table 2. Dye Removal of Methyl Orange dye with Catalyst loading 0.1 g/100 ml.

Table 2		**Catalyst= 0.1 gm**		
S.N.	***Time(Min)***	***Absorbance***	***Concentration***	***% Dye Removal***
1	10ppm	1.319	10.61996779	87.58
2	Dark	1.317	10.60386473	87.59883244
3	30	0.744	5.990338164	92.99432903
4	60	0.451	3.631239936	95.75328279
5	90	0.207	1.666666667	98.05084155
6	120	0.09	0.724637681	99.1525398
7	150	0.053	0.426731079	99.50094011

Table 3. Dye Removal of Methyl Orange dye with Catalyst loading 0.05 g/100 ml

Table 3		**Catalyst =0.05 gm**		
S.N	***Time(min)***	***Absorbance***	***Concentration***	***% Dye Removal***
1	10ppm	1.319	10.61996779	87.58
2	Dark	1.446	11.64251208	86.38413949
3	30	0.899	7.238325282	91.53481425
4	60	0.463	3.727858293	95.6402881
5	90	0.355	2.858293076	96.65724033
6	120	0.206	1.658615137	98.06025777
7	150	0.099	0.797101449	99.06779378

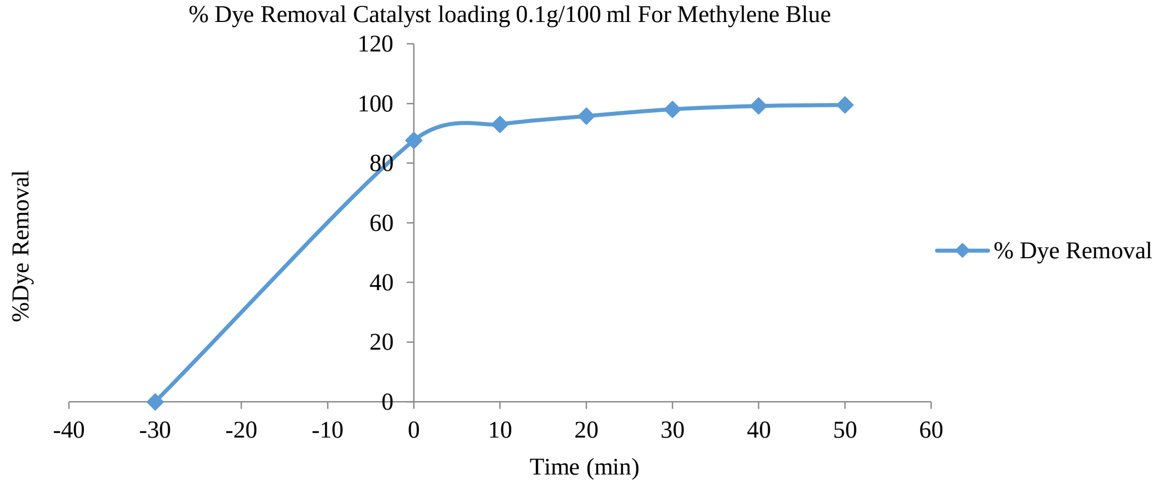


Figure 9. % Dye Removal of Methyl Orange dye with Catalyst loading 0.1 g/100 ml.

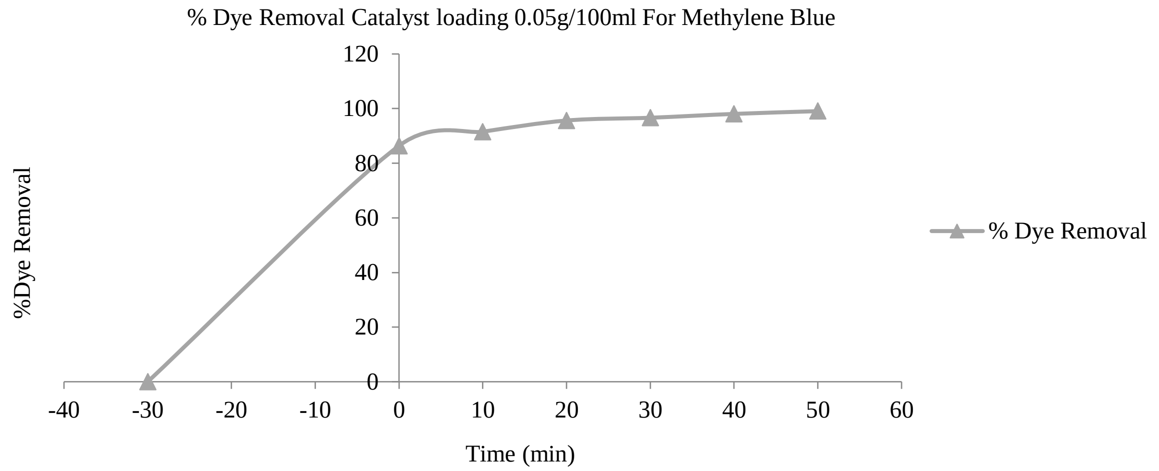


Figure 10. % Dye Removal of Methyl Orange dye with Catalyst loading 0.05 g/100 ml.

Table 4. Dye Removal of Methyl Orange dye with Catalyst loading 0.025 g/100 ml.

Table 4		**Catalyst =0.025**		
S. N.	***Time(min)***	***Absrbance***	***Concentration***	***% Dye Removal***
1	10ppm	1.321	10.63607085	87.58
2	Dark	1.327	10.68438003	87.52358819
3	30	1.222	9.838969404	88.51079485
4	60	0.997	8.027375201	90.6262377
5	90	0.879	7.077294686	91.73566994
6	120	0.788	6.344605475	92.59124905
7	150	0.397	3.196457327	94.59124905

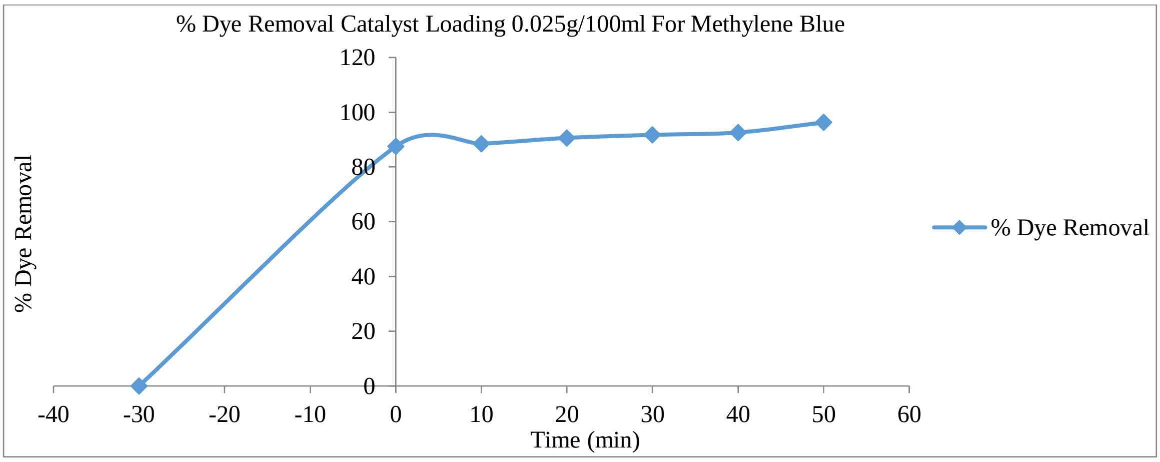


Figure 11. % Dye Removal of Methyl Orange dye with Catalyst loading 0.025 g/100 ml.

Photocatalytic Activity for Methyl Orange

Similarly, the photocatalytic activity for Methyl Orange was evaluated using the same range of catalyst loadings (0.025 g to 0.2 g per 100 ml solution). Absorbance measurements were taken at 463 nm, and the data are presented in Tables 5-8. The experimental results are illustrated in Figures 12-15, corresponding to the different catalyst loadings. The results show that 98% of the Methyl Orange dye was degraded within 150 minutes. The figures display an increasing trend in percent dye removal, indicating the effectiveness of the photocatalytic process. Among the tested loadings, a catalyst loading of 0.1 g per 100 ml was the most efficient, showing the highest rate of dye degradation compared to the other loadings.

Table 5. Dye Removal of Methyl Orange dye with Catalyst loading 0.2 g/100Ml.

Table 5		**Catalyst = 0.2 gm**		
S.N.	***Time (min)***	***Absorbance***	***Concentration***	***% Dye Removal***
1	10ppm	0.99	7.194767442	86.24000024
2	Dark	0.895	6.504360465	87.56040428
3	30	0.756	5.494186047	89.49236389
4	60	0.622	4.520348837	91.35482854
5	90	0.482	3.502906977	93.30068713
6	120	0.294	2.136627907	95.91369724
7	150	0.106	0.770348837	98.52670734

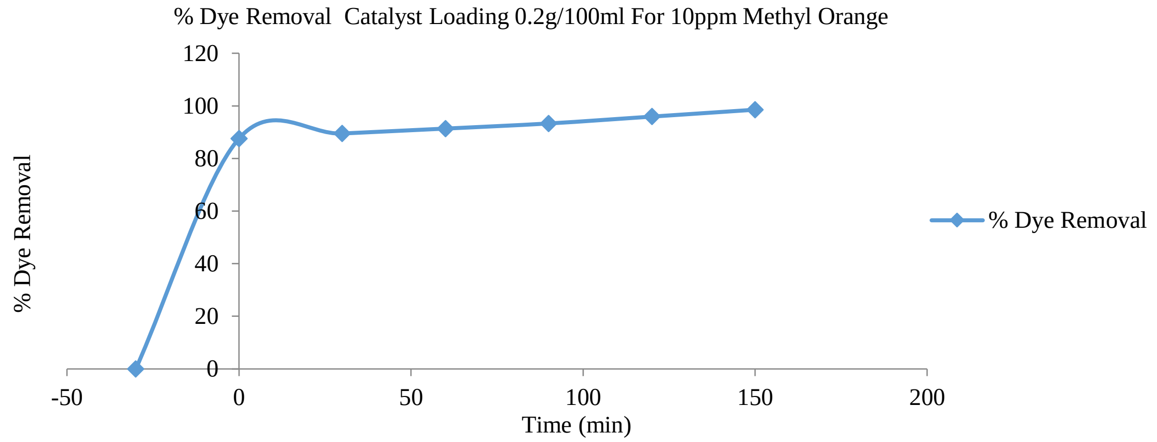


Figure 12. % Dye Removal of Methyl Orange dye with Catalyst loading 0.2 g/100Ml.

Table 6. Dye Removal of Methyl Orange dye with Catalyst loading 0.1 g/100 ml.

Table 6		**Catalyst = 0.1 gm**		
S. N.	***Time (min)***	***Absorbance***	***Concentration***	***% Dye Removal***
1	10ppm	0.841	6.111918605	86.24
2	Dark	0.791	5.748546512	87.05807372
3	30	0.733	5.327034884	88.00703924
4	60	0.222	1.613372093	96.36775268
5	90	0.105	0.763081395	98.28204518
6	120	0.092	0.668604651	98.49474435
7	150	0.069	0.501453488	98.87105826

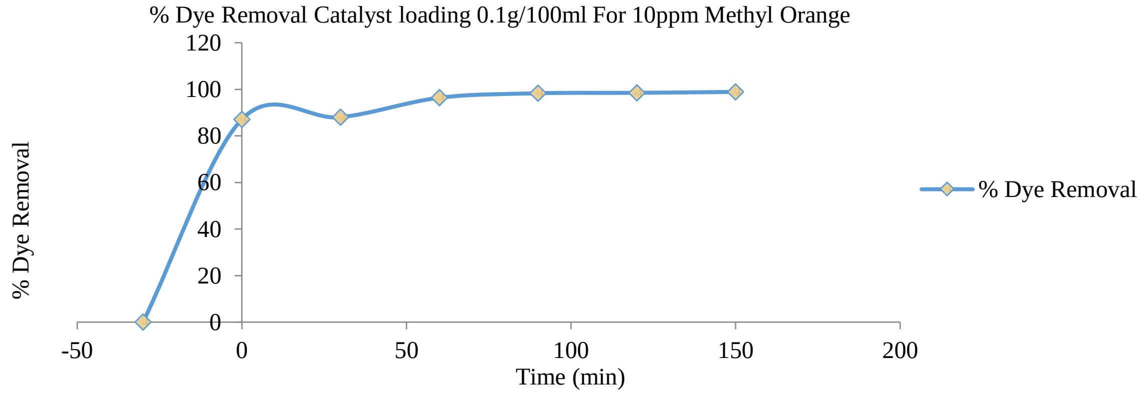


Figure 13. % Dye Removal of Methyl Orange dye with Catalyst loading 0.1 g/100 ml.

Table 7. Dye Removal of Methyl Orange dye with Catalyst loading 0.05 g/100 mL.

Table 7	**Catalyst=0.005**			
S.N.	***Time(min)***	***Absorbance***	***Concentration***	***% Dye Removal***
1	10ppm	0.99	7.194767442	86.24
2	Dark	0.895	6.504360465	87.56040404
3	30	0.866	6.293604651	87.96347475
4	60	0.712	5.174418605	90.10391919
5	90	0.528	3.837209302	92.66133333
6	120	0.486	3.531976744	93.24509091
7	150	0.292	2.122093023	95.94149495

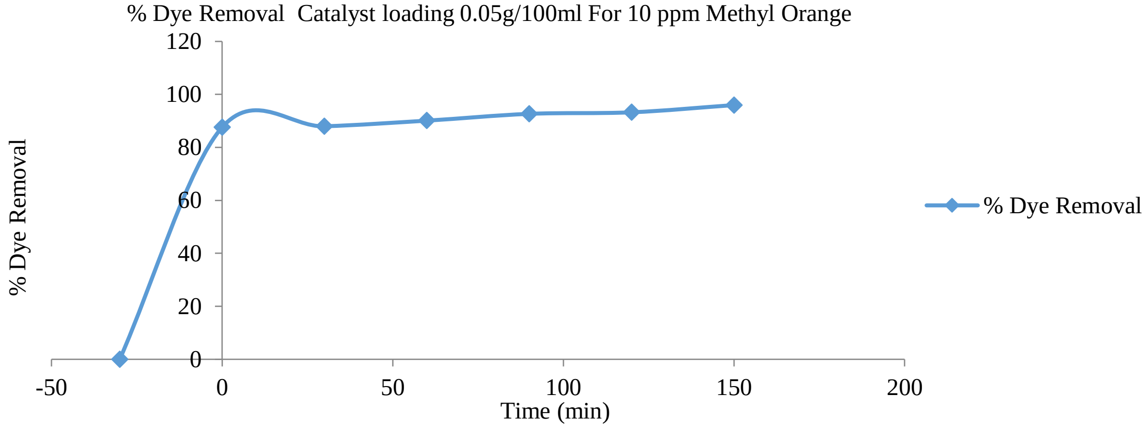


Figure 14. % Dye Removal of Methyl Orange dye with Catalyst loading 0.05 g/100 ml

Table 8. Dye Removal of Methyl Orange dye with Catalyst loading 0.025 g/100 ml.

Table 8	**Catalyst=0.025**			
S.N.	***Time(min)***	***Absorbance***	***Concentration***	***% Dye Removal***
1	10ppm	0.95	6.904069767	86.24
2	Dark	0.921	6.693313953	86.6600421
3	30	0.891	6.475290698	87.09456842
4	60	0.65	4.723837209	90.58526316
5	90	0.523	3.800872093	92.42475789
6	120	0.439		93.64143158
7	150	0.422		93.88766316

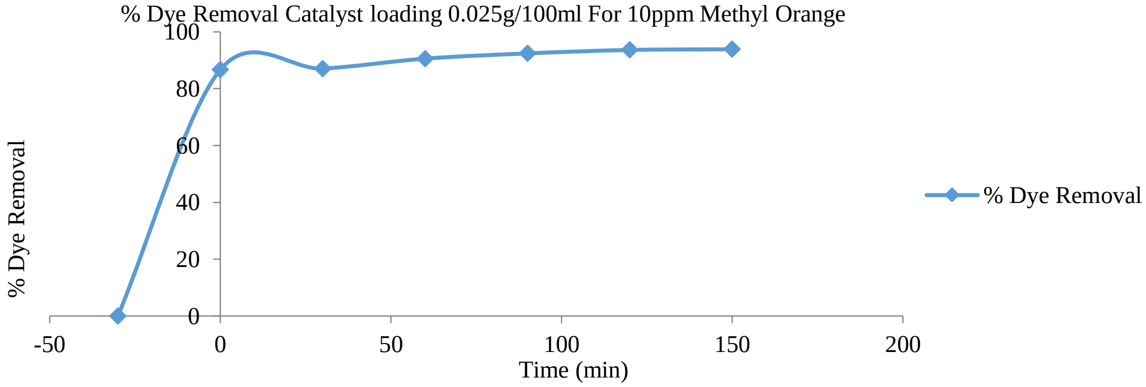


Figure 15. % Dye Removal of Methyl Orange dye with Catalyst loading 0.025 g/100 ml.

CONCLUSION

The photocatalytic degradation of Methylene Blue and Methyl Orange dyes was investigated using an Ag-ZnO nanocomposite, successfully prepared via the co-precipitation method. FTIR spectra confirmed the composition and purity of the synthesized nanocomposite. This nanocomposite effectively harnesses natural sunlight for the photocatalytic degradation of both dyes.

Catalyst loadings of 0.1 g and 0.2 g demonstrated high degradation efficiencies, achieving approximately 99% and 98% degradation, respectively. Figures 16 and 17 clearly illustrate the degradation efficiency, showing that Methylene Blue degrades within 50 minutes of natural solar light exposure, whereas Methyl Orange requires 150 minutes for complete degradation under similar conditions. This study highlights the potential of Ag-ZnO nanocomposite as an efficient photocatalyst for the removal of organic dyes from wastewater using solar energy (Tables 9, 10).

Table 9. Dye Removal of Methylene blue dye.

Methylene Blue				
Time (min)	***0.2 gm***	***0.1 gm***	***0.05 gm***	***0.025 gm***
0	90.38939	87.598832	86.384139	87.5235882
10	98.85947	92.994329	91.534814	88.5107949
20	99.09429	95.753283	95.640288	90.6262377
30	99.53876	98.050842	96.65724	91.7356699
40	99.74841	99.15254	98.060258	92.5912491
50	99.84066	99.50094	99.067794	96.2674186

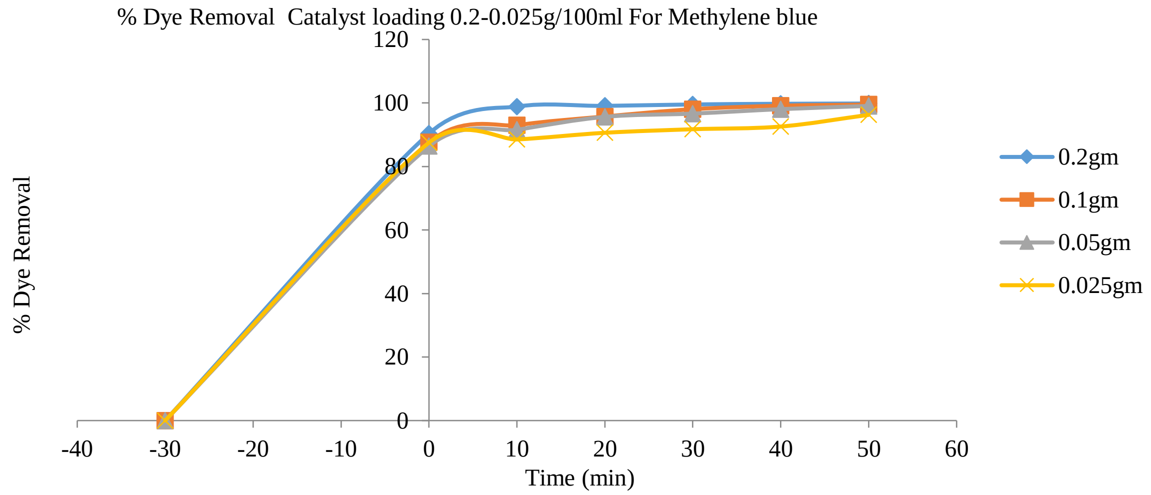


Figure 16. % Dye Removal of Methylene blue dye.

Table 10. Dye Removal of Methyl Orange blue dye.

Methyl Orange				
Time (min)	**0.2 gm**	**0.1 gm**	**0.05 gm**	**0.025 gm**
0	87.560404	87.0581	87.560404	86.6600421
30	89.492364	88.007	87.9634748	87.0945684
60	91.354829	96.3678	90.1039192	90.5852632
90	93.300687	98.282	92.6613333	92.4247579
120	95.913697	98.4947	93.2450909	93.6414316
150	98.526707	98.8711	95.971495	93.8876632

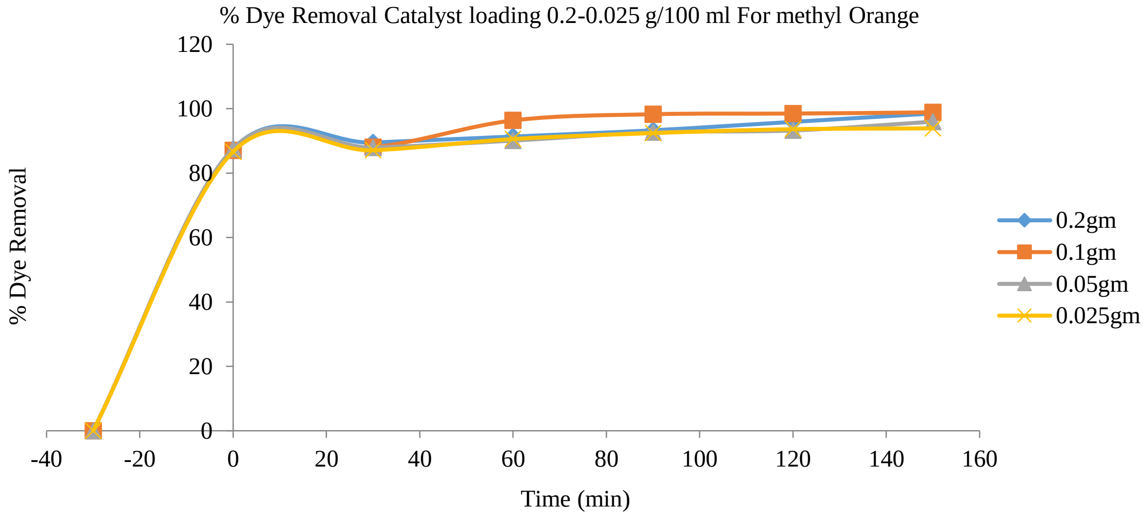


Figure 17. % Dye Removal of Methyl Orange blue dye.

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