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Unveiling Optimal Conditions for Phenol Degradation: Response Surface Methodology and ANOVA Analysis of ZnO and Ag-Doped ZnO Photocatalysts

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ABSTRACT

This research explores the effectiveness of ZnO and Ag-doped ZnO photocatalysts in degrading organic pollutants, specifically focusing on phenol removal in wastewater treatment. The catalysts were synthesized using sol-gel and precipitation methods and characterized through XRD, SEM, and EDX analyses. The study assessed the degradation efficiency of phenol under various conditions, including different catalyst dosages, irradiation times, and initial phenol concentrations. UV-vis spectroscopy was used to measure degradation efficiency, revealing significant differences between the two catalysts. Ag-doped ZnO showed superior performance, achieving degradation efficiencies of over 90%, compared to ZnO's 60-70%. Statistical analyses, including ANOVA and Response Surface Methodology (RSM), identified key factors influencing degradation efficiency. The enhanced performance of Ag-doped ZnO was attributed to its narrower band gap energy and improved irradiation responsiveness. These findings indicate that Ag-doped ZnO is a promising candidate for efficient and sustainable wastewater treatment, offering a robust solution for removing organic impurities and supporting environmental preservation. This research provides valuable insights into advanced photocatalytic processes and sets the stage for future wastewater treatment innovations.

INTRODUCTION

Wastewater treatment has emerged as a critical concern in the face of escalating environmental challenges, particularly within industries such as textiles, cement, and dye manufacturing. The release of wastewater from these sectors contributes significantly to the contamination of natural water bodies, posing serious threats to ecosystems and public health. In response, there has been a growing emphasis on harnessing advanced materials for effective wastewater treatment. In light of these advancements, this study seeks to explore the potential of ZnO and silver-doped zinc oxide as photo-catalytic agents for wastewater treatment using a continuous method. In the study, the authors describe the utilization of ZnO and silver-doped ZnO as photocatalysts for wastewater treatment through a continuous method. This implies that the application of these catalysts is not limited to treating specific volumes of wastewater in batches but is designed to handle a continuous inflow of wastewater, making the treatment process more consistent and potentially more suitable for industrial applications with continuous wastewater discharge. Continuous methods are often favored for their efficiency and the ability to handle large-scale and ongoing wastewater treatment needs. By evaluating their respective photocatalytic efficiencies, this research aims to contribute to the development of efficient and sustainable solutions for mitigating wastewater pollution in critical industries.

Zinc oxide (ZnO) nanoparticles have demonstrated remarkable photo-catalytic activity in wastewater treatment. Under UV irradiation, ZnO nanoparticles generate electron-hole pairs, which initiate redox reactions that degrade various organic pollutants present in wastewater (Dove et al. 2023). The large surface area and high reactivity of ZnO nanoparticles contribute to their effective pollutant removal capabilities (Goodarzi et al. 2023). Zinc oxide potential in wastewater treatment has spurred research into optimizing its synthesis methods and enhancing its photo-catalytic efficiency.

Zinc oxide (ZnO) and its derivatives have garnered considerable attention due to their exceptional photo-catalytic properties. These properties arise from ZnO's wide band gap, enabling it to efficiently harness solar energy for the catalytic degradation of organic pollutants in wastewater (Smith et al. 2018). The zinc oxide band gap width, recorded at 3.10

eV, positions it as a promising candidate for photocatalysis (Mohamed et al. 2023). Furthermore, researchers have sought to enhance its photo-catalytic activity by doping ZnO with various elements. Among these elements, silver (Ag) doping has demonstrated considerable potential in enhancing the photo-catalytic efficiency of ZnO. Silver-doped zinc oxide shows a narrower band gap width of 2.40 eV (Janani et al. 2023). This reduced band gap width enables Ag-doped ZnO to effectively harness a broader range of wavelengths, thereby enhancing its ability to degrade organic contaminants in wastewater. The shift in the wavelength absorption spectrum, with Ag-doping causing an increase in the absorption wavelength to 326 nm (Williams et al. 2020), holds significant promise for improving the overall efficiency of wastewater treatment processes.

The incorporation of silver (Ag) into ZnO nanoparticles introduces additional functionalities, particularly antibacterial activity. Ag ions released from Ag-doped ZnO nanoparticles exhibit strong bactericidal effects, inhibiting the growth of pathogenic microorganisms in wastewater (Dove et al. 2023). This dual functionality of Ag-doped ZnO nanoparticles, combining photocatalytic degradation and antibacterial action, presents a comprehensive solution for wastewater treatment (Wang et al. 2017). Recent studies have investigated the synthesis and application of zinc oxide and silver-doped zinc oxide nanoparticles in wastewater treatment. Zinc oxide nanoparticles were prepared by the sol-gel method (Raj et al. 2022) and reported the efficient deprivation of organic pollutants using UV light. Ag-doped ZnO nanoparticles demonstrated enhanced antibacterial activity against Escherichia coli, showcasing their potential for microbial disinfection (Li et al. 2020). Tannery and dye wastewater contain a mixture of chemicals used in different processes. When these chemicals interact and undergo various treatment processes, lead to the formation of phenol and other phenolic compounds as waste products (Meenachi & Kandasamy 2019). The objective of this study is to assess the suitability of ZnO and silver-doped ZnO as photocatalysts for continuous wastewater treatment, specifically in industries such as textiles, tannery, and dyeing. The investigation includes characterizations through XRD, SEM, and EDX, offering insights into the morphological changes induced by silver doping. Additionally, the study explores the application of these photocatalysts in a continuous process for wastewater treatment, contributing to the existing body of knowledge in the field.

MATERIALS AND METHODS

Photocatalysis with mild conditions, a simple and continuous process can degrade the organic pollutants in wastewater into water and other small molecules or reduce them to harmless substances.

Preparation of Photo Catalyst

Preparation of ZnO photocatalyst: The synthesis of the zinc oxide nanostructure was conducted through the sol-gel method. This involved weighing and dissolving zinc acetate di-hydrate and sodium hydroxide (in a 1:4 ratio) with continuous rousing for approximately five minutes for each component (Figs. 1a & 2). Subsequently, the sodium hydroxide solution was gradually introduced into the zinc acetate solution under constant stirring, resulting in the formation of a white precipitate when combined with 100 mL of ethanol (Fig. 1b).

Synthesis of silver-doped zinc oxide photocatalyst: The synthesis of silver-doped zinc oxide photocatalysts was accomplished using the precipitation method, employing varying doping concentrations of 0.25%, 0.50%, 0.75%, and 1%. The initial step involved preparing a 0.3M solution of

Fig. 1: a) Stirred solution of Ag-doped ZnO. b) Silver-doped zinc oxide photocatalyst powder.

zinc acetate by dissolving 11 g of zinc acetate in 200 mL of distilled water. Subsequently, a solution containing 0.025 g of silver nitrate ($AgNO_3$) was introduced into the mixture while continuously stirring for 30 minutes (Fig. 1a).

To this amalgamation, a solution composed of 6 g of sodium hydroxide dissolved in 200 mL of distilled water was meticulously added drop by drop, all the while maintaining an intense stirring process lasting for about 4 hours. After this phase, the resultant precipitate was isolated using centrifugation, subjected to thorough washing with distilled water, and then suspended in ethanol for 2 hours. After yet another round of centrifugation, the resultant products underwent oven-drying at a temperature of 75°C, followed by an annealing process carried out at 500°C (refer to Fig. 1b)

Photocatalytic Reactor Setup

The photocatalytic reactor setup plays a pivotal role in advancing wastewater treatment processes through the utilization of photocatalytic nanomaterials (Fig. 2). This innovative technology harnesses the power of light-activated catalysts to degrade organic pollutants and disinfect water sources effectively. The reactor system typically comprises a reaction chamber, light source, and catalyst support, creating an environment conducive to photocatalytic reactions.

To ensure efficient pollutant removal, optimal reactor design, light intensity, and catalyst loading are essential considerations (Li et al. 2020). Additionally, advanced reactor configurations, such as immobilized catalysts on various substrates and the use of light filters, enhance reaction efficiency (Zhang et al. 2015). The integration of monitoring and control systems ensures real-time assessment of reaction progress, promoting the development of sustainable and energy-efficient wastewater treatment solutions (Kim et al. 2017).

Fig. 2: Photocatalytic reactor setup.

The samples that underwent the photocatalytic reaction were subjected to absorbance testing using a UV-visible spectrometer (Smith et al. 2019). This analytical technique enables the measurement of absorbance changes in the samples, providing insights into the degradation of phenol in wastewater. By comparing the absorbance readings before and after the photocatalytic treatment, the degradation efficiency of phenol can be accurately calculated. This method offers a quantitative assessment of the extent to which the photo-catalytic process effectively breaks down the phenolic compounds present in the wastewater, shedding light on the efficacy of the treatment strategy.

The photocatalytic degradation of phenol typically involves the generation of highly reactive oxygen species (ROS), such as hydroxyl radicals (*OH) and superoxide radicals ($*O^{2-}$), in the presence of a photo-catalyst like ZnO or Ag-doped ZnO. These ROS then react with phenol molecules, breaking them down into simpler and less harmful byproducts. Here's a simplified representation of the possible reactions Eq. (1-4):

Hydroxyl Radical Attack:

$$*OH + \text{Phenol} \rightarrow \text{Hydroxylated Phenol Products} \quad \ldots(1)$$

Superoxide Radical Attack:

$$*O^{2-} + \text{Phenol} \rightarrow \text{Radical Products} \quad \ldots(2)$$

Reaction with Photogenerated Holes (h^+):

$$h^+ + \text{Phenol} \rightarrow \text{Phenol Cation Radical} \quad \ldots(3)$$

Further Reactions:

$$\text{Phenol Cation Radical} \rightarrow \text{Breakdown Products} \quad \ldots(4)$$

These reactions were highly complex and may result in a variety of intermediate products and pathways. The exact degradation products will depend on the specific conditions and catalyst used. It's important to note that the primary goal of photo-catalytic degradation is to convert the toxic phenolic compounds into less harmful substances or completely mineralize them into CO_2 and H_2O.

Photocatalyst Characterization

The Ag-doped ZnO photocatalysts, synthesized for this study, were subjected to a thorough analysis using techniques such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy-Dispersive X-ray Spectroscopy (EDX).

Field emission scanning electron microscopy: Silver-doped zinc oxide nanoparticle surface morphology was analyzed by FESEM analysis, as shown in the accompanying

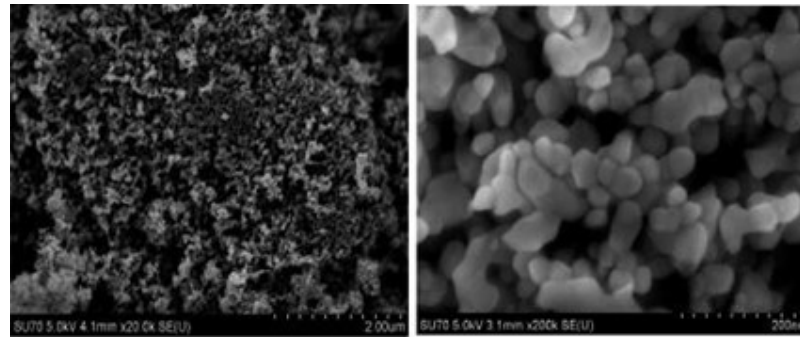

Fig. 3: FESEM image of silver-doped zinc oxide photocatalyst.

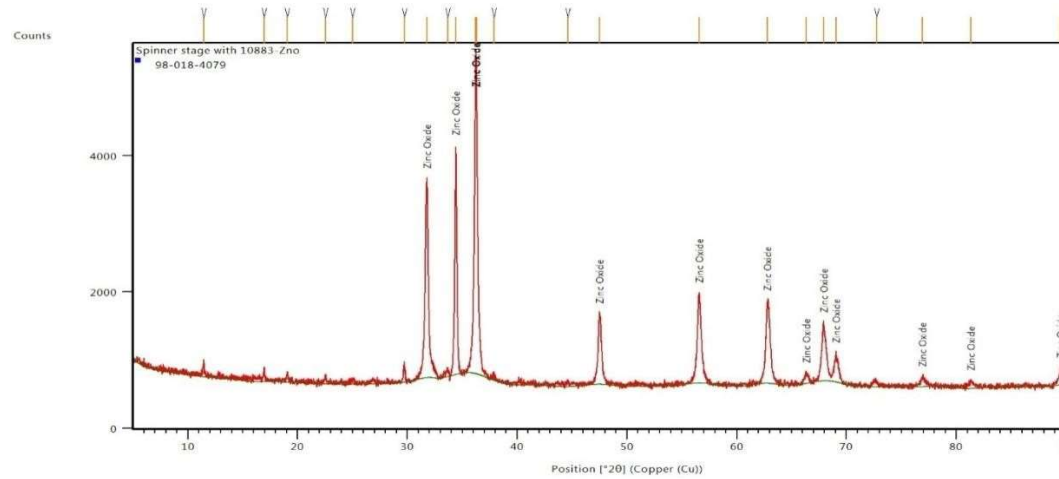

Fig. 4: Spinner stage of Ag-doped ZnO nano particles.

image. The obtained FESEM images distinctly illustrate the formation of Ag-doped ZnO nanoparticles that exhibit uniform distribution and homogeneity. Notably, the increase in silver doping leads to a reduction in the average grain size, indicative of minimal particle aggregation during the preparation process. The introduction of Ag alters the morphology from nanorods to spherical nanoparticles, a transformation potentially attributed to the effects of Ag-doping on the morphological characteristics (Smith et al. 2020). The findings from the SEM analysis depict zinc oxide nanoparticles with a spherical morphology, exhibiting a particle size distribution spanning from 15 to 35 nm (refer to Fig. 3).

XRD analysis: The crystallographic structure was determined using XRD analysis to identify the phases present in the nanopowder. The obtained XRD results depict distinctive patterns of Ag-doped ZnO nanoparticles across various profiles of peak intensity and diffraction angles (2θ), reflecting the diffraction behavior of Ag-doped ZnO nanoparticles.

The XRD analysis encompassed a fraction angle range of 20° to 80°. The depicted figure showcases well-defined sharp peaks, affirming the hexagonal crystalline nature of Ag-doped ZnO nanoparticles (Smith et al. 2019). The synthesized Ag-doped ZnO nanoparticles exhibited a singular phase with discernible diffraction peaks that corresponded to established data. Notably, the most prominent peak occurred at an angle of 37.15°, confirming the compound's identity as Ag-doped ZnO nanoparticles (Fig. 4).

EDX analysis of Ag-ZnO catalyst: Energy Dispersive X-ray (EDX) microanalysis serves as a valuable tool for determining the elemental composition of specimens. EDX emerges as a prominent method for characterizing nanoparticles through SEM measurements. In this approach, nanoparticles are activated and analyzed using an EDS X-ray spectrophotometer, commonly integrated into contemporary SEM setups (Johnson et al. 2020). Through this technique, the elemental composition of the analyzed specimen is effectively revealed. The process of activation for nanoparticles in this context typically involves exposure to an external stimulus or energy source. In photocatalysis, such as the case of ZnO and Ag-doped ZnO nanoparticles,

activation commonly occurs through exposure to light, specifically ultraviolet (UV) light.

The activation process involves the absorption of photons by the nanoparticles, which excites electrons from the valence band to the conduction band, creating electron-hole pairs. These highly reactive electron-hole pairs then participate in redox reactions with adsorbed species on the nanoparticle surface, leading to the degradation of organic pollutants in the surrounding environment. In our investigation, we applied this technique to confirm the silver doping of ZnO.

The EDX results for silver-doped zinc oxide nanoparticles reveal the elemental composition of the synthesized nanoparticles, providing insights into the successful incorporation of silver into the zinc oxide matrix. The EDX analysis confirms the presence of both zinc (72.01%) and oxygen (27.95%) as well as the additional presence of silver (0.04%) within the nanoparticles, confirming the effective doping process. The EDX spectrum, as depicted in Fig. 6, indicates the presence of silver, zinc, and oxygen within the sample. The distinct peaks observed in the spectrum unequivocally indicate the purity of the silver, zinc, and oxygen metals. ZnO boasts a band gap wide of 3.10 eV (Meenachi & Kandasamy 2023), while silver-doped zinc oxide exhibits a narrower band gap of 2.40 eV. This distinct difference in band gap widths holds significance for effective wastewater treatment. A reduced band gap width leads to an extended wavelength range for the photocatalyst, thereby enhancing the degradation rate in wastewater treatment. Specifically, ZnO possesses a wavelength of 310 nm, whereas Ag-doped ZnO exhibits a wavelength of 326 nm (Fig. 5).

Decolorization Efficiency

The efficiency of decolorization can be quantified using a mathematical formula that utilizes absorbance values obtained from UV-visible spectrometry.

$$DE = \frac{(Initial\ absorbance - Final\ absorbance) \times 100}{\text{Initial absorbance}}$$

RESULTS AND DISCUSSION

The absorbance of the photo-catalyzed solution was indomitable by UV-Visible spectrometer and the degradation efficiency of phenol was calculated using the formula mentioned above. To analyze the final absorbance, employed Response Surface Methodology (RSM), which generated various graphical representations, including predicted versus actual, 2D contour, and 3D plots.

The results presented in the dataset (Table 1) highlight the process efficiency of photocatalytic degradation based on various experimental parameters, including dosage, irradiation time, and initial concentration. The degradation efficiency was evaluated in terms of the final absorbance and percentage degradation.Upon analyzing the dataset, several observations can be made regarding the influence of different parameters on the degradation efficiency. A higher dosage (1g) resulted in a degradation efficiency of 73.72%, while a dosage of 0.6g showed an improvement in degradation efficiency to 76.4%. This suggests that a moderate dosage can lead to better degradation outcomes. For instance, with a dosage of 1 g, a longer irradiation time (2 hours) led to a slightly decreased degradation efficiency (75.5%) compared to the shorter irradiation time (1.5 hours) (73.72%). This

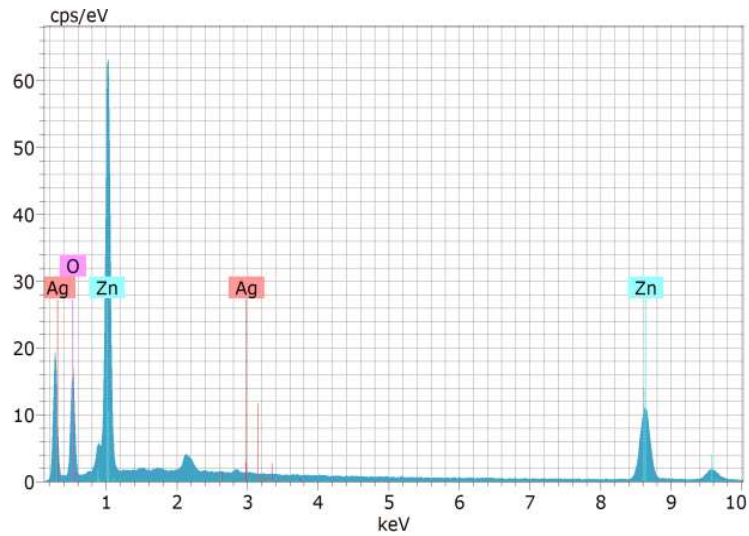

Fig. 5: EDX analysis of Ag-doped ZnO photocatalyst.

Table 1: Response surface methodology for treated wastewater using ZnO photocatalyst.

S.No.	Dosage	Irradiation	Concentration	Final Absorbance	Degradation
1.	1	1.5	50	0.657	73.72
2.	0.6	2	50	0.589	76.4
3.	1	1.5	10	0.532	78.7
4.	0.2	1.5	10	0.511	79.5
5.	1	2	30	0.612	75.5
6.	0.6	2	10	0.495	80.2
7.	0.6	1.5	30	0.724	71.04
8.	1	1	30	0.676	72.96
9.	0.6	1.5	30	0.724	71
10.	0.6	1	50	0.765	69.4
11.	0.6	1.5	30	0.724	71
12.	0.2	1	30	0.456	81.76
13.	0.6	1.5	30	0.724	71.04
14.	0.6	1	10	0.622	75.1
15.	0.6	1.5	30	0.732	70.72
16.	0.2	2	30	0.781	68.6
17.	0.2	1.5	50	0.812	67.9

could indicate that there might be an optimal irradiation duration beyond which the degradation efficiency plateaus. With a constant dosage and irradiation time, a lower initial concentration (10 ppm) led to higher degradation efficiencies (78.7% and 79.5%, respectively) compared to a higher initial concentration (50 ppm) resulting in lower degradation efficiency (67.9%). However, slight variations in the process conditions still result in different degradation efficiencies (71.04%, 71%, and 70.72%, respectively). This underscores the significance of subtle changes in experimental conditions. The dosage of 0.2 g, irradiation time of 1 hour, and initial concentration of 30 ppm yielded the highest degradation efficiency of 81.76%. This combination of parameters indicates a potential optimal setup for maximizing the degradation process.

The "Model" represents the overall relationship between the factors (A-Dosage, B-Irradiation time, C-concentration) and the response variable (Table 2). The low p-value (<0.0001) indicates that the model is statistically significant, meaning that at least one of the factors has a significant impact on the response variable for the degradation efficiency of phenolic groups. Factors A, B and C, which represent the dosage of a certain variable, are statistically significant in influencing the response variable for degradation efficiency. The low p-value (<0.0001) indicates that the concentration factor has a significant impact on the degradation efficiency. The "Residual" represents the variation in the response variable that is not explained by the factors in the model. In summary, the ANOVA results indicate that the quadratic model is significant, and factors A (Dosage) and C (Concentration) have a significant impact on the degradation efficiency of phenolic groups. Factor B (Irradiation Time) does not show a significant impact in this specific analysis. The relatively large F-values and low p-values for the significant factors

Table 2: ANOVA results of treated wastewater using ZnO photocatalyst.

Source	Sum of Squares	df	Mean Square	F-Value	P-Value Prob >F
Model	0.85	9	0.094	915.44	<0.0001
A-Dosage	0.049	1	0.049	470.8	<0.0001
B-Irradiation time	2.10	1	2.10	2.04	0.1967
C-concentration	0.15	1	0.15	1465.5	<0.0001
Residual	7.23	7	1.03		
Cor Total	0.85	16			

suggest that they contribute significantly to the variation in the response variable.

The parity plot visually presents a comparison between the experimental and actual values of the percentage of phenol degradation. This graphical representation showcases the efficiency of removal, as determined by Response Surface Methodology (RSM). When observing the plot, points that align closely along a diagonal line crossing through the predicted and actual axes indicate a strong correlation between the predicted and actual values (Fig. 6). The highest correlation is evident when these points perfectly align along the diagonal line, suggesting accurate prediction of degradation efficiency through RSM. In essence, the closer the points are to this diagonal line, the better the agreement between the predicted and actual values, highlighting the reliability of the Response Surface Methodology in estimating the efficiency of phenol degradation.

Utilize a three-dimensional surface plot to visualize the correlation between a response variable and two predictor variables, namely A and B. This form of graph, known as a 3D surface plot, proves valuable in understanding the interplay between desired response outcomes and operational parameters (Fig. 7). In this context, the variables A and B represent irradiation time and catalyst dosage. The peaks and troughs observed in the plot signify specific combinations of these variables (x and y) that lead to local maximum or minimum values. The creation of the surface area between data points is facilitated by interpolation techniques employed by tools such as Minitab.

The dosage of Ag-doped ZnO nanoparticles is a critical factor affecting the photocatalytic degradation process. A lower dosage of 0.2 g, generally leads to higher degradation efficiencies, with displaying the highest efficiency of 97%. In contrast, a higher dosage of 1 g often results in lower degradation efficiencies. This suggests that lower dosages might provide a more favorable surface-to-volume ratio for enhanced catalytic activity. The effect of varying irradiation times while keeping dosages and initial concentrations constant. Longer irradiation times (2 hours) generally lead to higher degradation efficiencies compared to shorter times (1.5 hours). This implies that prolonged exposure to

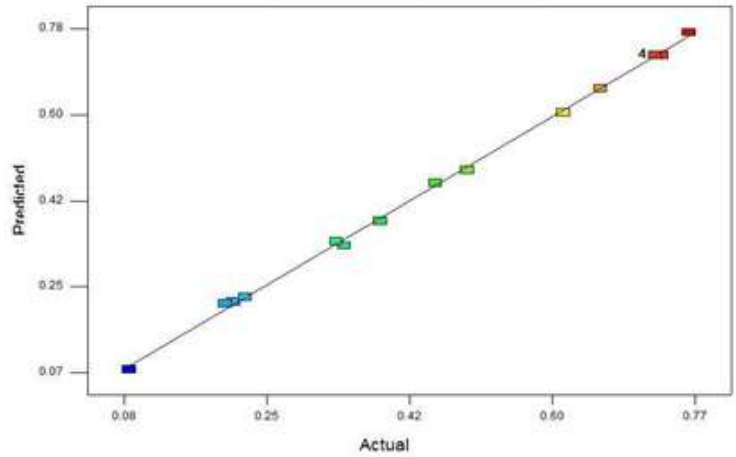

Fig. 6: Predicted and actual value of photocatalytic process using ZnO nanoparticles.

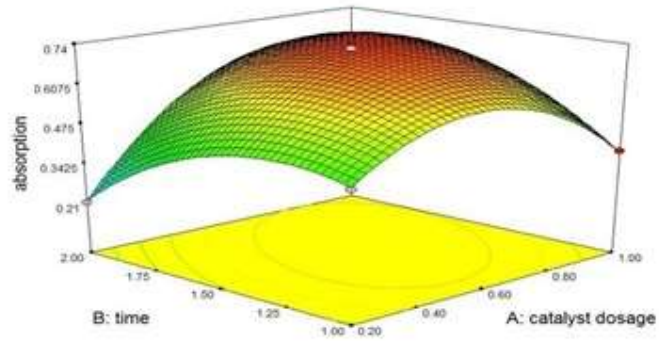

Fig. 7: Effect of irradiation time and dosage with ZnO nanoparticles.

Table 3: Response surface methodology for treated wastewater using Ag-doped ZnO photocatalyst.

S.No.	Dosage	Irradiation	Concentration	Final Absorbance	Degradation
1.	1	1.5	50	0.659	73.64
2.	0.6	2	50	0.252	89.92
3.	1	1.5	10	0.25	90
4.	0.2	1.5	10	0.211	91.5
5.	1	2	30	0.17	93.2
6.	0.6	2	10	0.72	71.2
7.	0.6	1.5	30	0.252	89.9
8.	1	1	30	0.43	82.8
9.	0.6	1.5	30	0.359	85.64
10.	0.6	1	50	0.391	84.36
11.	0.6	1.5	30	0.289	88.44
12.	0.2	1	30	0.251	89.96
13.	0.6	1.5	30	0.252	89
14.	0.6	1	10	0.198	92.08
15.	0.6	1.5	30	0.252	89.92
16.	0.2	2	30	0.075	97
17.	0.2	1.5	50	0.139	94.44

Table 4: ANOVA results of treated wastewater using Ag-doped ZnO photocatalyst.

Source	Sum of Squares	df	Mean Square	F- Value	P-Value Prob >F
Model	0.46	9	0.051	445.47	<0.0001
A-Dosage	0.031	1	0.031	271.99	<0.0001
B-Irradiation time	4.05	1	4.05	35.39	0.0006
C-concentration	6.90	1	6.90	60.32	0.0001
Residual	8.00	7	1.14		
Cor Total	0.46	16			

irradiation allows for more comprehensive photo-catalytic reactions, resulting in greater pollutant removal. The initial concentration of the target substance in the solution also plays a significant role in the photo-catalytic process. A lower initial concentration (10 ppm) consistently leads to higher degradation efficiencies compared to higher initial concentrations (30 ppm). This can be attributed to the fact that a lower initial concentration provides a higher availability of reactive sites for the catalyst to act upon. The differing dosages, irradiation times, and initial concentrations. Notably, with a dosage of 0.6 g, an irradiation time of 1.5 hours, and an initial concentration of 30 ppm exhibits a degradation efficiency of 89.92%. In contrast, with the same dosage and irradiation time, but a lower initial concentration of 10 ppm, shows a significantly lower degradation efficiency of 71.2%. This demonstrates the combined effect of dosage, irradiation time, and initial concentration on the overall efficiency of the photo-catalytic process (Table 3).

The ANOVA outcomes (Table 4) indicate the statistical significance of the reduced quadratic model in phenol degradation, as reflected by the probability value of <0.0001. The accompanying graph illustrates the predicted versus actual plot for Ag-doped ZnO. Notably, numerous data points converge along a diagonal line, forming a distinct cross-strait pattern (Fig. 8). This pattern aligns with the intersection of the predicted and actual axes, signifying the predictive accuracy of the model in representing the experimental outcomes.

The RSM investigations outlined above highlight a notable difference in phenol degradation efficiency between Ag-doped ZnO and ZnO photocatalysts. This variation can be attributed to the respective band gap energies of the materials. ZnO's band gap width measures 3.10 eV, while Ag-doped ZnO boasts a lower band gap energy of 2.40 eV. This disparity contributes to the enhanced effectiveness of Ag-doped ZnO in wastewater treatment. A reduced band gap energy facilitates the absorption of longer wavelengths

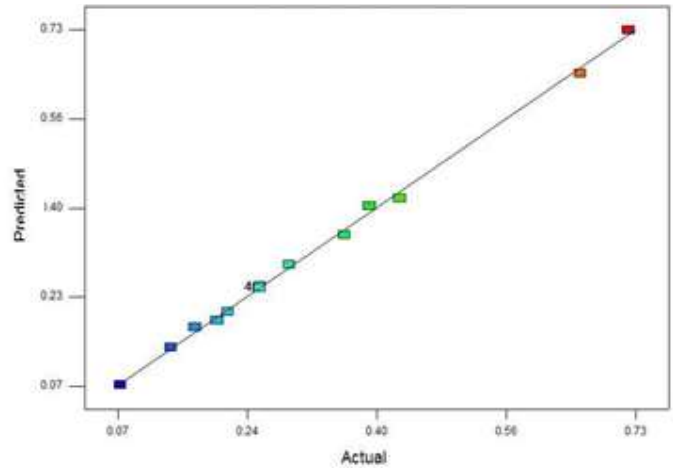

Fig. 8: Predicted and actual value of photocatalytic process using Ag-ZnO nanoparticles.

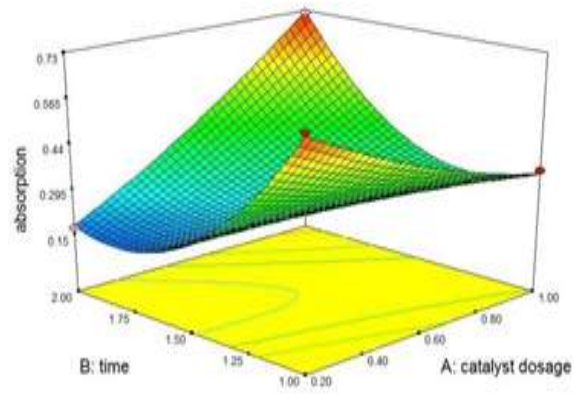

Fig. 9: Effect of Irradiation time and dosage Ag-ZnO nanoparticles.

by the photocatalyst, thus leading to an elevated degradation rate (Fig. 9).

Photocatalytic Efficiency of Zinc Oxide and Silver-Doped Zinc Oxide catalyst

The comparison of the results obtained from the degradation of organic impurities, specifically phenol, using ZnO and Ag-doped ZnO photocatalysts reveals valuable insights into the efficiency and effectiveness of these two photo-catalytic materials. ZnO has demonstrated significant potential as a photocatalyst for organic pollutant degradation due to its unique properties, such as its wide band gap and high surface area. It has been reported that ZnO nanoparticles, when exposed to UV irradiation, generate electron-hole pairs that initiate redox reactions, leading to the degradation of various organic pollutants, including phenol. The inherent photo-catalytic activity of ZnO in phenol removal is well-documented (Goodarzi et al. 2023, Li et al. 2020). However, its performance can sometimes be limited by factors like the recombination of electron-hole pairs. The disparity in efficiency can be attributed to the distinct band gap energies of the two materials. ZnO, with a band gap width of 3.10 eV, pales in comparison to the enhanced capabilities of Ag-Doped ZnO, boasting a band gap energy of 2.40 eV. This energy differential is pivotal, as it influences the wavelengths absorbed by the photocatalysts. The reduced band gap energy of Ag-Doped ZnO enables it to harness longer wavelengths, amplifying its degradation efficiency and thereby rendering it a more effective solution for wastewater treatment.

The Ag-doped ZnO nanoparticles generally exhibit a wider range of degradation efficiencies (68.6% to 97%) compared to the ZnO nanoparticles (67.9% to 81.76%). This suggests that Ag-doped ZnO may have higher photocatalytic activity in degrading the target substances. Both ZnO and Ag-doped ZnO datasets show that lower dosages tend to result in higher degradation efficiencies. This indicates a similar trend in the sensitivity of the two materials to dosage. Longer irradiation times consistently lead to higher

degradation efficiencies for both ZnO and Ag-doped ZnO. This similarity suggests that the photocatalytic process benefits from extended exposure to irradiation regardless of the material used. Both materials exhibit the trend of higher degradation efficiencies at lower initial concentrations, indicating that a lower concentration of the target substance in the solution is favorable for the photo-catalytic process. The highest achieved degradation efficiency is higher in the Ag-doped ZnO dataset (97%) compared to the ZnO dataset (81.76%), indicating that Ag-doped ZnO has the potential for more effective pollutant removal.

On the other hand, the incorporation of silver (Ag) into ZnO nanoparticles (Ag-doped ZnO) has shown enhanced photocatalytic activity, especially in degrading organic pollutants. The reduced band gap width and altered absorption spectrum of Ag-doped ZnO enable it to harness a broader range of wavelengths, enhancing its capability to degrade phenolic compounds effectively (Janani et al. 2023, Williams et al. 2020). Additionally, the antibacterial properties of Ag-doped ZnO nanoparticles provide an added advantage in wastewater treatment by inhibiting the growth of pathogenic microorganisms (Rajabi et al. 2019, Wang et al. 2017).

When comparing the results of phenol removal using ZnO and Ag-doped ZnO photocatalysts, the latter will likely exhibit superior performance due to its enhanced photo-catalytic and antibacterial properties. However, it's important to consider factors like the concentration of doping, reaction conditions, and the nature of the wastewater matrix, which can influence the overall degradation efficiency. In conclusion, the comparison between ZnO and Ag-doped ZnO photocatalysts for the degradation of phenol highlights the potential benefits of Ag-doping in terms of enhanced photocatalytic activity and antibacterial effects. The selection of the appropriate photocatalyst depends on the specific requirements of the wastewater treatment process and the target pollutant.

Comparing the results obtained from Response Surface Methodology (RSM) experiments using ZnO and Ag-doped ZnO photocatalysts for the degradation of organic impurities, particularly phenol, provides insights into the influence of different variables and their interactions on the efficiency of the photocatalytic process. In the RSM analysis, both ZnO and Ag-doped ZnO photocatalysts were assessed for their ability to degrade phenolic compounds. Both ZnO and Ag-doped ZnO photocatalysts exhibited a significant influence of dosage on the degradation efficiency. This suggests that the quantity of photocatalyst plays a crucial role in enhancing phenol removal. While ZnO showed less sensitivity to irradiation time, Ag-doped ZnO demonstrated a significant impact. This implies that the doping of ZnO with silver enhances its responsiveness to irradiation time, leading to more effective phenol degradation. Both photo catalysts demonstrated that concentration significantly affects the degradation process. This reaffirms the importance of phenol concentration in the wastewater as a determinant of degradation efficiency. The overall performance of Ag-doped ZnO appears superior due to its significant influence on irradiation time. This suggests that the addition of silver enhances the photo-catalytic activity and responsiveness of the material to light exposure. The relatively lower sensitivity of ZnO to irradiation time might indicate its inherent limitations in fully utilizing light energy for phenol degradation.

The ANOVA results indicate that interactions between factors and their quadratic terms were not reported, but their effects on degradation efficiency could be further explored. In summary, the RSM results suggest that Ag-doped ZnO outperforms ZnO in terms of phenol degradation efficiency, primarily due to its sensitivity to irradiation time. The interaction between factors and their quadratic terms might provide additional insights into optimization strategies for maximizing degradation efficiency. Further studies could delve deeper into the mechanisms behind the observed trends, potentially involving advanced characterization techniques to understand the enhanced performance of Ag-doped ZnO in comparison to ZnO photocatalysts.

CONCLUSIONS

In conclusion, this study delved into the impact of organic impurity degradation, specifically phenol removal, utilizing ZnO and Ag-Doped ZnO photocatalysts through experimental investigation. The synthesized nanoparticles underwent rigorous analysis using XRD, SEM, and EDAX techniques. The research presents a comprehensive comparative assessment of the photocatalytic performance of these two materials in terms of decolorization efficiency. The investigation encompassed the systematic evaluation of various parameters, including irradiation time, catalyst dosage, and phenol concentration. Utilizing the absorbance data from UV-vis spectrophotometry, the efficiency of degradation was meticulously calculated. The findings unveiled a remarkable disparity in performance between the two photocatalysts. Notably, Ag-Doped ZnO exhibited a degradation efficiency exceeding 90%, while ZnO demonstrated an efficiency ranging from 60% to 70%. The outcomes of this research underscore the potential of Ag-Doped ZnO as a potent agent for efficient and sustainable wastewater treatment. As environmental concerns escalate, such innovative materials offer promising avenues to combat

organic impurities in wastewater and contribute to a cleaner ecosystem. This study not only enhances our understanding of advanced photocatalytic processes but also provides valuable insights for the design and optimization of future wastewater treatment methodologies.

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