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An Analysis of the Photocatalytic Activities of ZnO Nanoparticles: Factors Influencing Dye Degradation

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Abstract: *Nanometal oxides exhibit size-dependent properties that set them apart from their larger counterparts. Nanometal oxides can manipulate matter at the nanoscale and generate materials with distinct properties and functions due to their unique properties. Nanomaterials have a considerable advantage due to their small size and high ratio of surface area to volume, which makes them suitable for photocatalysis and permits the breakdown of a variety of dyes. As a result of their photocatalytic activity, the use of zinc oxide nanoparticles (NPs) in environmental applications is gaining importance. The photocatalytic efficiency of ZnO NPs was evaluated by determining the progress of dye degradation, such as Methylene Blue (MB), Methyl Orange (MO), and Rhodamine B (RB). Multiple research studies have presented findings that support this specific area of inquiry. Various characteristics of ZnO NPs, such as their crystalline phase, particle size, and surface area, have a significant effect on their photocatalytic properties. Our study will demonstrate the effect of the NP sizes and others factors on dye degradation. In this case, we gathered data from various research projects for data analysis. Our analysis includes descriptive analysis, chi-square test, correlation, and one-way ANOVA Analysis of Variance (ANOVA) using those data. This study concludes the effect of different factors on dye degradation efficiency.*

Keywords: NPs; ZnO NPs, Photocatalytic properties; Dye degradation.

1. INTRODUCTION

Metal oxide nano sized materials are recently shown efficient in different purposes [1]. Metal oxide NPs (MONs) are being explored now in photocatalytic applications [2]. Among various MONs, ZnO NPs are the most studied topic in the field of nanoscience. Because of the high photocatalytic activity of ZnO NPs toward a number of different azo dyes, it is feasible that these particles could find use in waste water treatment [3]. ZnO nanostructures have been shown to be attractive photocatalyst candidates for use in photodegradation because they are non-toxic, affordable, and much more effective at absorbing light from a broad range of the solar spectrum [4]. The bandgap energy of ZnO nps plays an essential role in defining the photocatalytic activity of substances [5]. When subjected to blacklight, ZnO NPs accelerated the degradation of reactive orange and MB, RB, reactive blue, MO, and methyl red. During the dye degradation of MB, modified ZnO NPs showed off their excellent photocatalytic characteristics [6]. MB was effectively broken down by Mg-doped ZnO NPs when these were exposed to both visible light and ultraviolet light. When exposed to UV and visible light, respectively, Ce-doped ZnO NPs were able to photo catalyze the breakdown of several dyes in an effective manner [7]. Research has been conducted on the photocatalytic degradation of MB by a ZnO-based metal organic framework (MOF). The fact that more than 90 percent of the dyes were degraded is an encouraging outcome. In a system that uses photocatalysis, the transformation or reaction takes place on the surface of the catalyst. When photons activate a photocatalyst with energies that are equivalent to or greater than the bandgap energy of the photocatalyst, the energy of the photon is absorbed by the electrons in the photocatalyst. When the energy level exceeds the bandgap energy, electrons can be excited from the valence band to the conduction band, resulting in the creation of a vacancy known as a "hole" in the valence band. It is noteworthy that the energy level of the bandgap cannot produce the hole. The bandgap symbolizes the energy difference among the valence and conduction bands. Moreover, semiconductor holes do not immediately release hydroxide radicals. Photocatalysis is a process in which a semiconductor material produces hydroxide radicals through the interaction of photoexcited electrons and holes with water molecules or other reactants. The energy level of the bandgap can not exhibit a direct proportionality to the emission of hydroxide radicals [8] [9]. ZnO NPs are only industrially employed in sunscreens that require UV protection because of the photocatalytic properties of the material [10]. When ZnO is subjected to ultraviolet radiation, the result is the production of reactive free radicals [11]. When a material is subjected to UV radiation, the electrons in ZnO are the ones that are ultimately accountable for the production of electron-hole pairs. The particle size, shape, and manufacturing method all had an impact on the photocatalytic properties of ZnO in the UV-induced degradation of dyes like MO [12]. It is possible to improve the overall efficiency of the photocatalytic process by making adjustments to the particle size and shape of ZnO photocatalysts, as well as the production conditions and manufacturing procedures. Our industries produce a huge amount of waste water [13]. Among these dye-contaminated waters, some are more harmful. So, before disposing of it, it must be treated. By using the photocatalytic property of ZnO NPs, dye degradation can take place as a treating agent. Various ZnO NPs such as Graphene/ZnO, GO/ZnO, α-Fe2O3/ZnO, ZnO/-Mn2O3, ZnO/WO3, Eu/ZnO, etc. are proven as efficient photocatalysts in water treatment by doing dye degradation. But which parameters are directly related to the degradation efficiency variation is still a topic of observation. We investigated data to find the factors affecting dye degradation efficiency through our analysis of the data. For that we had to conduct descriptive analysis, chi-square test, correlation and one way ANOVA test. A sort of data analysis called descriptive analysis helps in precisely defining, showing, or summarizing data points so that patterns can emerge that fulfill all of the needs of the data. This type of analysis can also be used to summarize the data [14]. The chi-square test is a statistical procedure that compares observed and expected results [15]. The objective of this test is to determine whether a discrepancy between observed and expected data is due to coincidence or a relationship between the variables being examined. The correlation coefficient measures the intensity of the assumed linear association between the variables under consideration [16]. One-way ANOVA is typically employed when there is a single independent variable or factor, and the objective is to determine whether variations or various levels of that factor have a measurable impact on a dependent variable [17]. The study aims to find the factors are significantly associated with the dye degradation efficiency of ZnO NPs.

2. METHODOLOGY

We have 47 data of ZnO NPs for data analysis. There 4 variables of the data such as, Size, Efficiency, Dye name and Duration of work of ZnO NPs. There, we perform descriptive and cross-sectional study analysis to make our result more precise and to find factor affecting the efficiency of NPs. Also, perform correlation to make sure that the result of association. We use SPSS-version 25 for the data analysis. We make the variables categorical for convenience of the data analysis. We make the variables categorical for convenience of the data analysis.

Table 1: Table of categorical variables introduction

Variables Name	Category	Description
Efficiency of NPs	Most Efficient	Which efficiency is 80% or more
	Efficient	Efficiency less than 80%
Size of NPs	1 is (<=30)	Size is 30 nm or less
	2 is (>30)	Size is above 30
Dye Name	1	MO
	2	MB
	3	RB
Duration of dye degradation	Not time consuming	Time less or equal to 3 hr
	Time consuming	Time greater than 3 hr

3. COLLECTED DATA

Table 2: ZnO NPs Table of Different Size and Efficiency.

Nanoparticle	Size (nm)	Dye name	Efficiency (%)	Time (min)	Ref.
Graphene/ZnO	23.6	MO	97.10	360	[18]
GO/ZnO	35	MO	95	120	[19]
α-Fe2O3/ZnO	56.7	MO	100	180	[20]
ZnO/-Mn2O3	50	MO	90	210	[21]
2% ZnO/WO3	19.28	MO	100	180	[22]
1 mol% Eu/ZnO	5.67	MO	95.30	180	[23]
ZnO (0.4g/l)	17.3	MO	95	120	[24]
ZnO nano powder	27	MO	98.10	45	[25]
ZnO powder	50	MO	80	120	[25]
Fe3O4/ZnO core/shell magnetic NPs	25-30	MO	83	360	[26]
Cu/ZnO	28.5	MO	88	240	[27]
ZnO nanorods on indium-tin oxide substrate	80-90	MO	71	150	[28]
ZnO NP	15-25	MO	81	100	[29]
porous graphene/ZnO nanocomposite	32-72	MO	100	150	[30]
ZnO:Eu(1%)-W	16.2	MO	10	150	[31]
ZnO:Eu(10%)-M	5.6	MO	100	60	[31]
ZnO:Eu(3%)-W	16.2	MO	62	150	[31]
ZnFe2O4@ZnO	17	MO	99	240	[32]
Ag-ZnO	64.32	MO	92	30	[33]
Cu-doped ZnO nanorods	9.46	MO	99	120	[34]
ZnO NPs	20–30	MB	81	240	[35]
FSP-derived ZnO NPs	47	MB	70	60	[36]
ZnO NPs (M8-ZnO)	22	MB	90	120	[37]
ZnO NPs synthesized by ppt method	30	MB	81.02	180	[38]
ZnO NPs synthesized by sol-gel method	28	MB	92.48	180	[38]
ZnO–Si	32	MB	90	60	[39]
ZnO@GO	15 ± 5	MB	98.50	15	[40]
Gd doped ZnO	39.63	MB	93	90	[41]
Ni–Th–ZnO	30.58	MB	93	180	[42]
Zn98Ca2O	26.09	MB	89	120	[43]
Mn-ZnO	28.6	MB	88	120	[44]
ZnO NP grown on silica	33.8–89.8	MB	71.70	150	[45]
ZnONp**	98	MB	78	60	[46]
amine modified ZnO NPs	7.51	MB	93.80	25	[47]
polyaniline/ZnO nanocomposite	10-30	MB	94	360	[48]
ZnO NP	28	RB	95	70	[49]
ZnE4T (spherical NPs)	29	RB	84	120	[50]

ZnE5T (nanosheets)	31	RB	78	120	[50]
ZnE6T (hexagonal prismatic NPs)	32	RB	75	120	[50]
ZnO Nps	18.3	RB	74	180	[51]
CR –ZnONPs	13.33	RB	98	200	[52]
ZnO NPs	20.37	RB	46	180	[53]
Ag–ZnO	30	RB	85	300	[54]
5- SeZO	7.91	RB	99.21	150	[55]
CAB-ZnO	21	RB	60	480	[56]
ZnO nanofiber	78	RB	60	120	[57]
ZnO nanoparticle	30	RB	28	120	[57]

4. RESULTS & DISCUSSION

We perform bar plot for those variables in Chi-square test Which shows the result given below,
Figure 1 shows the descriptive analysis of Efficiency wise size of ZnO NPs. Where we see 12.77% most efficient NPs size are less than or equal to 30 and 17.02 percent size are greater than 30. On the other hand, 53.19% efficient ZnO NPs size are <=30 and 17.02% NPs size are above 30.

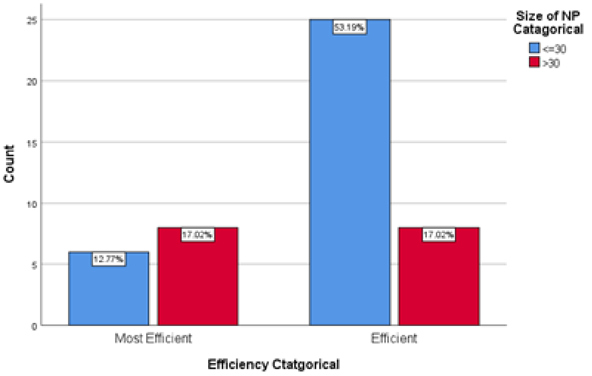

Fig. 1. Size vs Efficiency bar chart

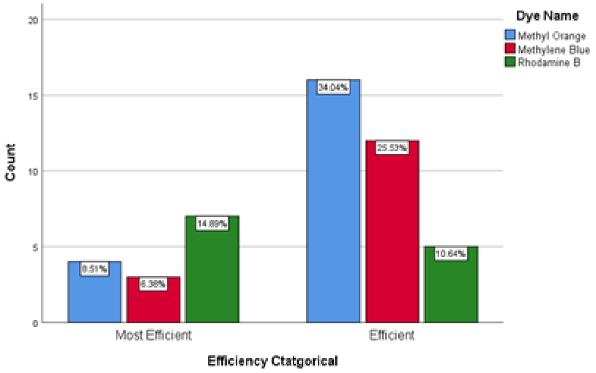

Fig. 2: Dye vs Efficiency bar chart

Figure 2 shows that 8.51% most efficient NPs of our data degrade MO dye and shows their efficiency, where 34.04% NPs shows their best efficiency by degrading MO dye. The percentage of most efficient and percentage of efficient NPs in degradation of MB dye are 6.38% and 25.53% respectively. Also, we see the percentage of most efficient and rate of efficient NPs in RB degradation are 14.89% and 10.64% respectively.

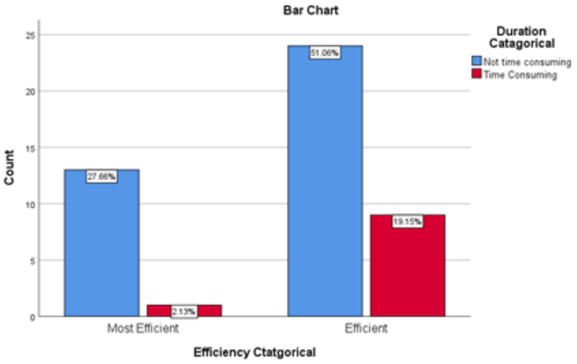

Fig. 3: Duration of dye degradation vs Efficiency bar chart

Figure 3 shows that 27.66% most efficient NPs are not time consuming and 2.13% are time consuming. On the other hand, 51.06% efficient NPs are not time consuming and 19.15% are time consuming.

We perform Chi-square test for finding associated variables with the efficiency of ZnO NPs in SPSS. Where we see the result as,

Table 3: Chi-square test result

Variables	**Chi-square test with Efficiency**	
	Chi-square value	**P-value**
Size of NP	4.739^a	0.029
Dye	6.279^a	0.043
Duration of dye degradation	2.378^a	0.242

Where we see that the P-value of Size of ZnO NPs and P-value of Dye of Chi-square test with efficiency are 0.045 and 0.044 respectively. We interpret that there are significant association of ZnO NPs size and degraded dye with the dye degradation efficiency. That means there are effects of NPSs size and variation of dye on degradation efficiency of ZnO NPSs. We also see that the p value of duration of dye degradation is 0.242, which means there is no effect of duration in efficiency of dye degradation of ZnO NPs.

Now we check the strength of the association. We consider the symmetric measure of chi-square test table for checking the strength. We have two associated variables, which are Size and Dye. The symmetric tables are

Table 4: Table of Symmetric Measures of Size & Efficiency

		Value	**Approximate Significance**
Nominal by Nominal	Phi	-.318	.029
	Cramer's V	.318	.029
N of Valid Cases		47	

The table 4 is 2 by 2 in size because the variables (Size and Efficiency) hold two labels. So, we consider the Phi-coefficient value. We know for the value of Phi-coefficient under 0.2, Between 0.2 and 0.3 and above 0.3 interpret week, moderate and strong association respectively. We see the Phi value for size and efficiency is -0.318. The value 0.318 interpret that there is strong association between Size and Efficiency. The negative sign interpreted opposite relation between those variables. That means if the size increase, the efficiency of photocatalysis will decrease. If the size decrease, the efficiency will increase.

Table 5: Table of Symmetric Measures of Dye & Efficiency

		Value	Approximate Significance
Nominal by Nominal	Phi	.365	.043
	Cramer's V	.365	.043
N of Valid Cases		47	

The tables are two by three in size. Because Dye has three labels. So, we consider the Cramer's V coefficient for interpreting the result. The value of Cramer's V is 0.365, which shows the strong relationship between Dye and Efficiency. Because, we know if the value is above 0.3, it will interpret the strong association.

To be sure about the Size vs Efficiency negative association, we perform the Bivariate correlation between size and efficiency of ZnO NPs. Where we see,

Table 6: Table of Correlation

Correlations

		Efficiency Categorical	Size of NPS Categorical
Efficiency Categorical	**Pearson Correlation**	1	-.318
	Sig. (2-tailed)		.030
	Sum of Squares and Cross-products	9.830	-3.234
	Covariance	.214	-.070
	N	47	47
Size of NP Categorical	**Pearson Correlation**	-.318	1
	Sig. (2-tailed)	.030	
	Sum of Squares and Cross-products	-3.234	10.553
	Covariance	-.070	.229
	N	47	47

The table 6 shows the correlation between Efficiency and Size of ZnO NPs is -0.318. So, we found the negative correlation between size and efficiency. Thus, there is a negative relation among these variants.
If the size increases, the efficiency of Zno will decrease. If the size decreases, the efficiency will increase.

To find the best degraded dye by photocatalysis with ZnO NPs, we perform One Way ANOVA between Dye and Efficiency. Findings given below,

Table 7: Descriptive Analysis Table of One-way ANOVA Test

	N	Mean	Std. Deviation	Std. Error
MO	20	1.8000	.41039	.09177
MB	15	1.8000	.41404	.10690
RB	12	1.4167	.51493	.14865
Total	47	1.7021	.46227	.06743

From One way ANOVA we see the P-value is 0.43, which also shows the variables are significant. Then we see in the table 7 RB dye have minimum mean. Thus, the RB is most feasible dye for the dye degradation among our studied dyes. The mean values of another two dyes are approximately similar. Now we find the feasible degraded dye between MO and MB.

To obtain the significant mean difference between different dye we see the table of Post Hoc Test from One Way ANOVA, which revealed the mostly degraded dye in dye degradation which is catalyzed by ZnO NPs. The table is given below,

Table 8: Table of Post Hoc Test

(I) Dye Name	(J) Dye Name	Mean Difference (I-J)	Std. Error	Sig.
MO	MB	.00000	.15027	1.000
	RB	.38333*	.16065	.021
MB	MO	.00000	.15027	1.000
	RB	.38333*	.17039	.030
RB	MO	-.38333*	.16065	.021
	MB	-.38333*	.17039	.030

The table 8 shows that there was no significant mean difference between MO and MB. Because the mean difference is near to 0. Two dyes are equivalently degraded in degradation. So, the other parameters such as cost and availability of dye will determine their feasibility.

We found that there was a relationship between the amount of time the experiment was carried out for, the type of dye that was used, and the size of the ZnO NPs that were used. The Chi-square test demonstrated the existence of an association that is statistically significant between size and effectiveness. A substantial association was found between dye and efficiency, according to the findings of the Chi-square test, which was also conducted. However, there was not a significant association between the

amounts of time it took for the dye degradation. Using the Chi-square test and the correlation, we were able to determine that there is a significant and negative link between size and efficiency. In addition to this, we discovered that there is a meaningful connection between the Dye and the photocatalytic efficiency of ZnO NPs. When it came to the degradation of dye catalyzed by ZnO NPs, we found that RB was the most feasible and effective in dye degradation. When it came to the degradation of the dye, MO and MB were equivalently identical to one another. As the correlation between size and efficiency was negative, we reached at the finishing that the size of ZnO NPs is strongly associated with an inversely related and significant connection.

5. CONCLUSION

In the conclusion we have descriptive analysis of ZnO NPs. We observed the dye-degradation by ZnO NPs with Size, Dye and Duration of work. There was significant relation between size & efficiency from Chi-square test. The relation between dye & efficiency from Chi-square test was also significant. But there was no significant between Duration of dye degradation and Efficiency. From Chi-square test and Correlation, we found strong and inverse relationship of size with efficiency. Also, we had strong relation between Dye & Efficiency of ZnO NPs. We found that RB was most feasible for dye degradation of ZnO NPs. MO and MB were equivalent in dye degradation. So, we conclude that the size of ZnO NPs have strong and opposite relation. The Dye has strong relation with the efficiency. RB is most efficient degraded dye.

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