Enhancing textile water Decolorization efficiency: Insights from response surface quadratic modelling

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Abstract

Nowadays, textile industries provide larger employers with few required special skills, which shows that it is one of the important industries with major economic role in many countries, which utilizes large amount of water and various chemicals. Like a coin with two sides, the waste water produced from those industries produce large amount of pollutants, which harmful for human and environment. By Photocatalytic method, organic and inorganic pollutants oxidised rapidly, show attractive field of technic for waste water treatment and water purification. An experimental setup consist of a closed box contains UV lamp surrounding aluminium foil is made. Under UV lamp, the synthetic sample is made and treated for four hours in the experimental setup containing TiO_2 and TiO_2-Cu doped catalyst. The background on these technologies as well as the theoryfor enhanced oxidation technology by photocatalysis. This paper specifically give attention on Photocatalytic semiconductor $TiO_2$and the recentlymodified TiO_2photocatalysts and its modification, including the addition of TiO_2 withmetal cupper metal powder, for variety of morphologies of TiO_2 physical modification, which enhance Photocatalytic activity for oxidation process in advance.

Keywords: Optimal parameters, Cu-TiO_2 photocatalysis, Textile wastewater treatment, Response Surface Methodology, ANOVA results, Dosage effects, Irradiation time optimization, Concentration influence, Decolorization efficiency

1. Introduction

Titanium dioxide (TiO_2), most commonly used as conservation and energy storage, pollution control in environmental, semiconductor, sensors, Li batteries and

photovoltaic, because of its unique properties like photo electric property, due to its low cost, high chemical stability which is safety towards humans and environment.Optimization of titanium dioxide as a photocatalyst, which is a semiconductor, commonly used in technical heterogeneous photocatalysis. Through photochemical process like catalytic degradation by inducing visible light,toxic dye degradation of evironmental process can step up (Sanakousar et al, 2021). There have been experiments, in UV or visible area, for the improvement of activities of photocatalysis(Abhishek Sraw et al, 2022). However, for practical use, the titanium dioxidenarrow light response range of photocatalytic system with separation probability in low range of photo induced electron-hole pairs remains unresolved. From the results collected from textile effluent, the reactive dye solution shows no colour removal and in various time period, 50% colour removed. Transition metal with Doped TiO_2, studied extensively for photocatalytic activity and also Response to area in visible light(Park, 2022). However, metal selective modification is one of the frequently used methods to increase the catalyst's photocatalytic effectiveness (ZhengisbekKuspanov et al 2023). Titanium dioxide nanoparticles' efficacy and flaws are assessed using a variety of characterization techniques (Ivana Grcic et al 2023). The choice of characterization techniques is crucial to ensure there is enough data (Dongjie Chen et al, 2020). Characterizations used with great proficiency in TiO_2 assessment(Ivana Grcic, 2023). Using UV reactor of thin gap annular, Photocatalytic oxidation with TiO_2 was used, which breakdown the colour of synthetic effluent in dye in range upto 400 ppm.

2. Materials and methods

2.1. Chemicals

Titanium tetra iso propoxide as well as ethanol of 99.9% purity were purchased from Sigma-Aldrich. Using sol-gel process, Samples of copper-doped TiO_2 were created. In this procedure, particles of solid suspended in liquid are converted into gels (networks particulate of sols) gels. Before creating crystalline TiO_2 nanoparticles by calcination, here two primary reactions involved, they were, hydrolysis and condensation. TTIP is a frequently utilised precursor for the manufacture of TiO_2 nanoparticles. The creation of a three-dimensional network resulted from the hydrolysis of these precursors by adding water (condensation). The resultant mixture was agitated for 24 hours to create a homogenous gel. The produced gel was dried at 80° C in a hot air oven (Eichhorn et al, 2022). Moreover, the gel was powdered and then heated in a furnace for three hours up to 450° C to produce nanopowder of Cu-doped TiO_2. Under UV- irradiation, when TiO_2Doped withmetal or non-metals or co- doping with TiO_2 has been investigated, which shows interesting path towards band gap energy to increase the active surface area.

2.2. Phase and structural characterization

2.2.1Electron microscope for field emission scanning

In FESEM imaging, the secondary electron (SE) mode is preferred over the backscattered electron (BSE) mode. The SE mode allows for better accurate surface pictures of nanoparticles of titanium dioxide, compared to BSE (Ziental et al, 2020). This is important because TiO_2 nanoparticles frequently form agglomerations, which makes it easier to read micrographs. Magnification up to 30,000 times is frequently necessary to observe the morphology of TiO_2 nanoparticles. To characterize, the morphological surface of nanoparticles of TiO_2, up to 200000 times higher magnification has to be reported. They primarily depend on how TiO2 onanoparticles were in before being characterized. Moreover, calcined dry TiO_2 nanoparticles enable for higher magnification observation than uncalcined nanoparticles.

TiO_2 nanoparticles were frequently more heavily charged during image capture, resulting in a white disturbance that may be mistaken for genuine TiO_2 nanoparticles. The centrifuge and storage TiO_2 nanoparticles' forms and sizes could be distinguished from the micrographs with magnifications of up to 30,000 times. By high calcination temperature of 450-700 °C is the capacity to reach such high magnification levels as possible.The ability to use high magnification not only makes TiO_2 nanoparticle observation and interpretation easier, but it also enables precise particles size estimation. The morphological behaviour of the images, obtained with magnifications up to 200,000 times, could be seen. Also, during SEM imaging, the majority of quite almost above 400 ° C, high heat-treating operations, permittedthe sol-gel synthesised of nanoparticles of TiO_2a clear observation (Nasrabadi et al, 2021).

2.2.2 Elemental analysis

When coupled with the apparatus, simultaneously the electron dispersive X-ray (EDX) canperform the analysis of elements based on characteristic X-ray emitted. Due to the use of a single phase, area scans EDX is frequently used to provide an overall elemental analysis of TiO_2nanoparticles. Usually, the elemental analysis comes after the FESEM. In contrast to molecular data, only atomic behaviour of elemental data was analysed by EDX. Using data from area beneath EDX spectrum, sensitivity factor and the accelerating voltage, The atomic per cent (at. %) and weight per cent (wt.%) data were computationally translated. In general, the EDX spectrum's presence of a certain TiO and Cu element strongly supports other characterization like structural and phase analysis(Annin K. Shimi, 2022).

This analysis is also helpful for describing how different conditions affect the related elements, including heat treatment (Athanasekou, 5 June 2017). For instance, the differences in elemental composition shown by the EDX spectra obtained in this work showed how calcination temperatures affected the resulting Cu- TiO_2 nanoparticles.

Higher calcination temperatures were seen to reduce the concentration of oxygen in the EDX spectra. The EDX serves as a crucial instrument for validation of the presence and absence of any other ingredients in additionalform the complexity because current TiO_2 nanoparticle manufacturing via the sol-gel requires numerous variations in chemical parameters (M. Aravind, 2022).

2.3Characterization images

The undoped TiO_2 and doped TiO_2 along with Cu ions, those morphologies were shown in figure (1 & 2) and figure (3 & 4), respectively. It is evident from the surface morphology image of TiO_2 powder that it contains nanoscale spherical particles with a comparatively homogenous size distribution and a propensity to aggregate (Surya Pratap Goutam, 2018). However, the morphology of TiO_2 after Cu doping shows that Cu was loaded onto TiO_2 in the form of rather large agglomerates of tiny particles.

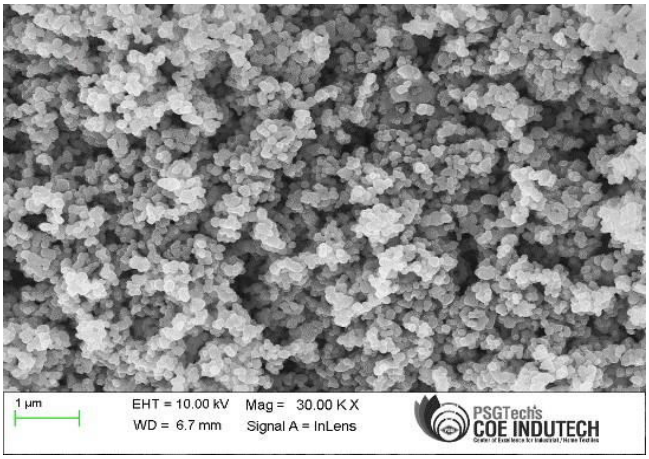


Figure 1 :SEM analysis for TiO_2 at Mag of 30.00 K X

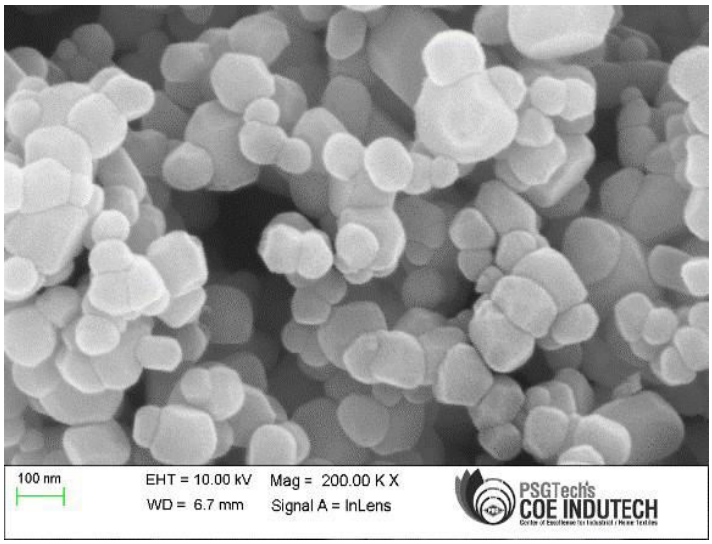


Figure 2 :SEM analysis of TiO_2 at Mag of 200.00 K X

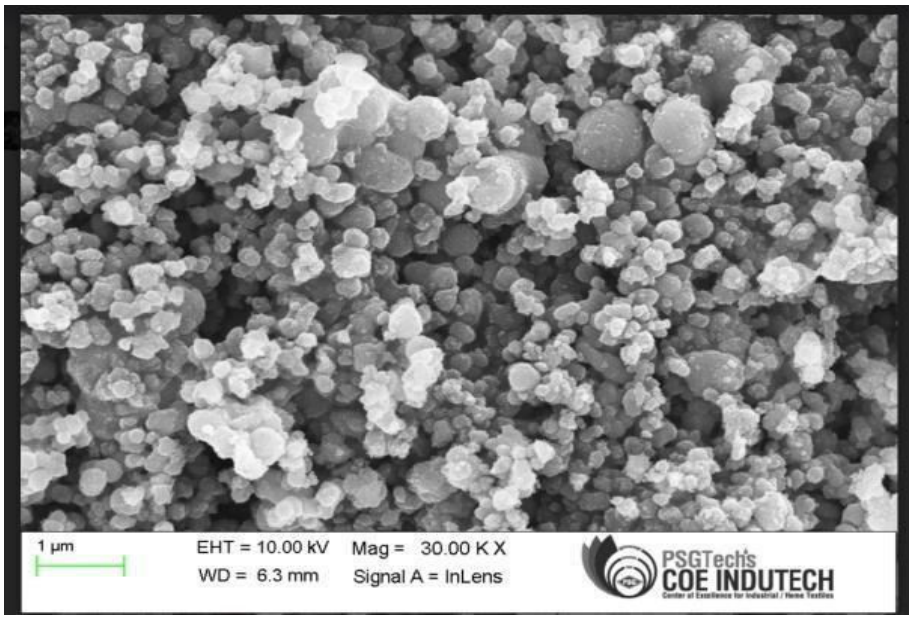


Figure 3: SEM analysis of Cu- TiO_2 at Mag of 30.00 K X

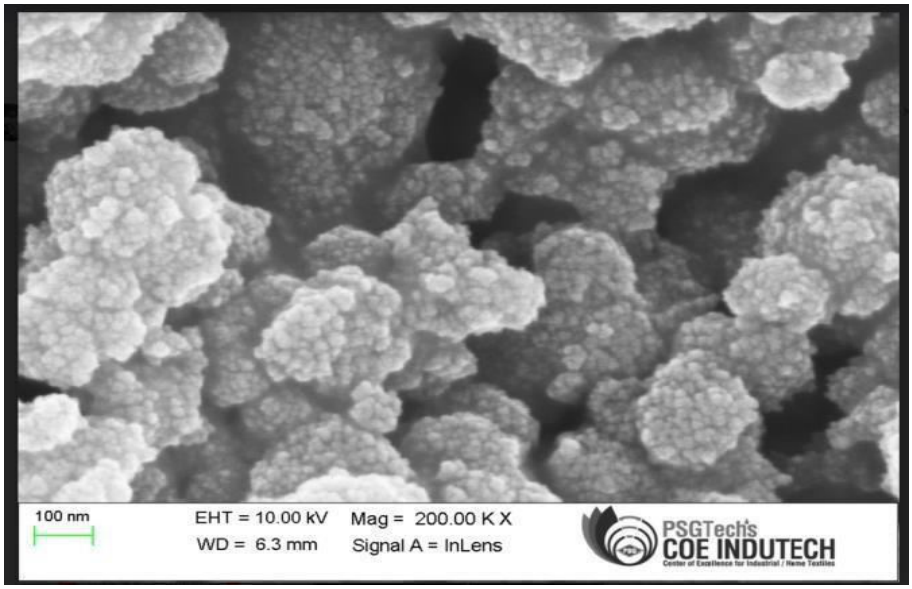


Figure 4: SEM analysis for doped $TiO_2$with Cu at Mag of 200.00 K X

The images above demonstrate the results of a TiO_2, SEM study in which a particle is examined at magnifications of around 30.00 K X and 200.00 K X, allowing us to verify that the obtained particle is in the nano-size range.

2.3. EDX analysis for TiO_2 and Cu-TiO_2

The provided data is from an Energy-Dispersive X-ray Spectroscopy (EDX) report, which is used to determine the elemental composition of a sample. In this case, the analysis is

for TiO_2 nanoparticles (figure 5 & 6). Atomic Percentage (at%) represents the proportion of each element in the sample at the atomic level. In this case, oxygen makes up approximately 31.05% of the atoms, while titanium makes up around 68.95% of the atoms in the TiO_2 nanoparticles. Sigma Weight Percentage (wt %) value provides information about the weight percentage of each element within the sample. Weight percentage takes into account the atomic weights of the elements. In this case, oxygen constitutes about 3.28% of the weight of the sample, and titanium constitutes about 12.22% of the weight of the sample. The atomic percentage reflects the stoichiometry of TiO_2, where the ratio of titanium to oxygen atoms is approximately 1:2. The weight percentage reflects the mass contribution of each element, taking into account their atomic weights, and it shows that titanium, being a heavier element, has a greater weight percentage in the sample.

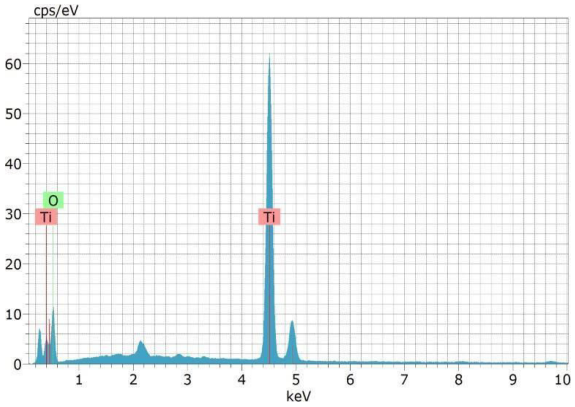


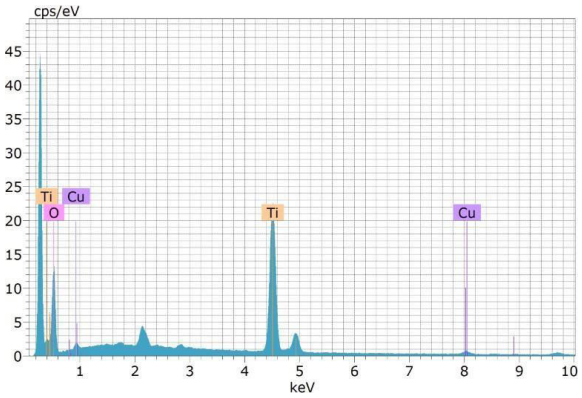
Figure 5: EDX analysis for TiO_2

Spectrum: TiO2

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Titanium	K-series	38.40	57.41	31.05	3.28
Oxygen	K-series	28.50	42.59	68.95	12.22
	Total:	66.90	100.00	100.00	

Figure 6: Elemental analysis for TiO_2

The provided EDX (Energy-Dispersive X-ray Spectroscopy) report contains information about the elemental composition of Cu-TiO_2 nanoparticles, specifically the atomic percentage (at%) and sigma weight percentage (wt%) of oxygen, titanium, and copper in the sample (figure 7 & 8). EDX is a technique used to determine the elemental composition of a material by analysing the X-rays emitted when a sample is bombarded with high-energy electrons.This data indicates that oxygen is the most abundant element in the Cu-TiO_2 nanoparticles, with an atomic percentage of 82.20% and a sigma weight percentage of 10.28%. This suggests that the nanoparticles are predominantly composed of oxygen.Titanium and copperhave an atomic percentage of 16.83% & 0.97% and a sigma weight percentage of 1.39%& 0.22%. This indicates the presence of titanium in the nanoparticles, but it is significantly lower in concentration compared to oxygen.



Spectrum: TiO2-CU

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Oxygen	K-series	25.40	60.26	82.20	10.28
Titanium	K-series	15.56	36.92	16.83	1.39
Copper	K-series	1.19	2.82	0.97	0.22
	Total:	42.15	100.00	100.00	

Figure 7: EDX analysis for Cu-TiO_2 Figure 6: Elemental analysis for Cu-TiO_2

2.4. Decolourization efficiency

Decolourization efficiency can be calculated with a mathematical equation with absorbance calculated from a UV-vis spectrometer.

DE = ((Absorbance Initially – Absorbance Finally) *100)/ Absorbance Initially

3. Result and discussion

3.1 Photodegradation efficiency of Cu-TiO_2

The provided data and ANOVA results pertain to a Response Surface Linear Model used in a study on the decolorization (color removal) of textile water through photo-degradation using copper titanium oxide. This model aims to understand the relationship between the factors (Dosage, Irradiation time, Concentration) and their impact on the percentage of decolorization. From the data (Table 1) contains information about the factors (Dosage, Irradiation time, Concentration) and the corresponding percentage of decolorization in textile wastewater for different runs (figure 8). Each run represents a specific combination of factor levels

Table:1 RSM Results for decolourisation using Cu-TiO_2

Run	Factor 1 Dosage(g)	Factor 2 irradiation time (min)	Factor 3 concentration (ppm)	Decolourisation (%)
1	2.5	150	30	71.16
2	1	60	30	73.22
3	1.75	90	30	75.65
4	1.5	120	30	73.66

5	1.25	60	30	71.96
6	1.75	60	10	88.754
7	1.5	90	10	83
8	1	60	10	85.48
9	1.25	60	20	81.84
10	1	120	20	78.6
11	1.5	90	20	80.282
12	1.25	60	40	69.44
13	1	90	40	68.34
14	1.5	120	40	67.58
15	1	90	50	62.48
16	1.5	120	50	62.74
17	2	150	50	64.64

The model's sum of squares (SS) indicates the total variability explained by the factors. In this case, the model explains a significant amount of variability with an F-value of 92 and a very low p-value (< 0.0001), indicating that the model is significant. The factor "Dosage" has a sum of squares that indicates the variability explained by this factor alone. However, the F-value (1.133) and the associated p-value (0.3064) suggest that the Dosage factor is not significant in explaining the variability in decolorization. The factor "Irradiation time" has a sum of squares and its F-value (2.647) and the p-value (0.1277) suggest that Irradiation time is not statistically significant in explaining the variability in decolorization. The factor "Concentration" has a substantial sum of squares, and its F-value (227.23) has a very low p-value (< 0.0001), indicating that Concentration is highly significant in explaining the variability in decolorization.

This means that changes in the concentration of copper titanium oxide have a significant impact on the decolorization process. The residual sum of squares represents the unexplained variability in the model. It's relatively small compared to the total variability, suggesting that most of the variation in decolorization is

accounted for by the factors included in the model.The total sum of squares represents the overall variability in the data. Based on the ANOVA results (Table 2), the model is significant, indicating that the factors collectively have a significant impact on decolorization. Dosage and Irradiation time are not statistically significant factors in this study. Concentration is highly significant, suggesting that changes in copper titanium oxide concentration significantly affect the decolorization process.

Table 2: ANNOVA results for decolourisation using Cu-TiO2

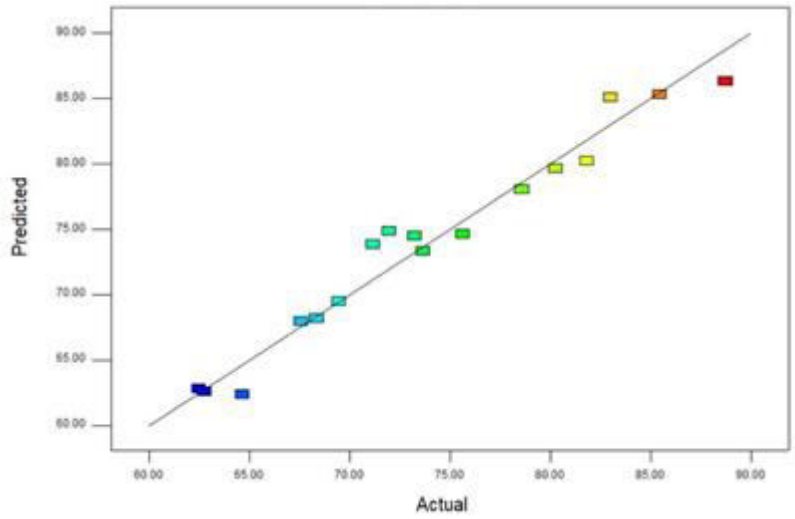


Figure 8: Graphical representation of decolourization efficiency of actual and predicted with response surface methodology.

Sources	Sum of squares	df	Mean square	Values of F	Values of P: (F<Prob)
Model	972.15	3	324.05	113.27	< 0.0001
A-Dosage	3.24	1	3.24	1.13	0.3064
B-Irradiation time	7.57	1	7.57	2.64	0.1277
C-concentration	650.06	1	650.06	227.23	< 0.0001
Residual	37.19	13	2.86		
Cor Total	1009.34	16			

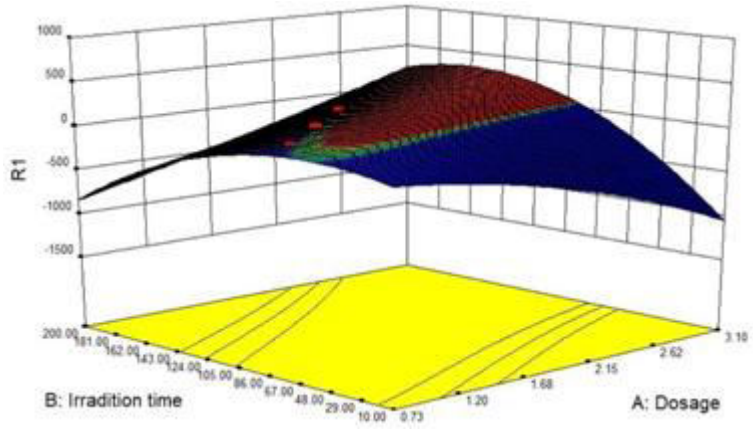


Figure 9a: 3D plot for irradiation time and dosage with a dye concentration of 50ppm

Dosage refers to the amount of copper titanium oxide used in the process. The data shows that (from figure 9a, 9b & 9c) decolorization varies with dosage, e.g., higher dosages (2.5 g) are associated with a decolorization percentage of 71.16%, while lower dosages (1 g) yield higher decolorization percentages 73.22% to 85.48%). The relationship may not be linear, and an optimal dosage for maximum decolorization needs to be identified. Irradiation time is the duration of exposure to light during the photo-degradation process. The data indicates that longer irradiation times (e.g., 150 min) correspond to higher decolorization percentages (64.64% to 71.16%). Shorter irradiation times (e.g., 60 min) show a wider range of decolorization percentages. Concentration represents the amount of copper titanium oxide in parts per million. Higher concentrations (30 ppm) show a range of decolorization percentages (71.16% to 75.65%), while lower concentrations (10 ppm) result in higher decolorization percentages (83% to 88.754%).

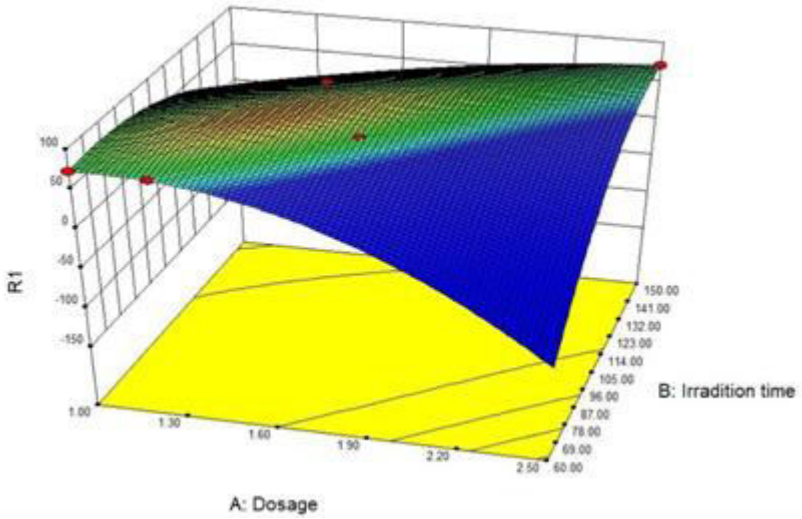


Figure 9b: 3D plot for Irradiation time and dosage with a dye concentration of 30ppm

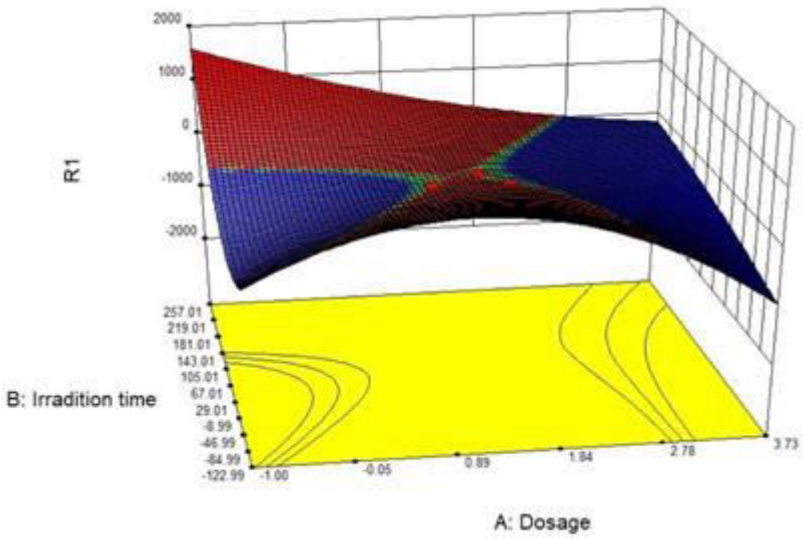


Figure 9c: 3D plot for Irradiation time and dosage with a dye concentration of 10ppm

The efficiency of decolorization is influenced by the interactions between these factors. It seems that there might be optimal conditions where a specific combination of dosage, irradiation time, and concentration results in maximum decolorization. A response surface methodology analysis, considering interactions and quadratic effects, could help identify the optimal conditions for maximum decolorization efficiency. The ANOVA results can provide statistical insights into the significance of each factor and their interactions. A significant p-value for a factor indicates that the factor has a significant impact on decolorization. Consider interactions between factors as they may also contribute significantly to the variability in decolorization.

3.2. **Response surface methodology for titanium dioxide**

To begin, preliminary tests were carried out utilising the single-factor research method to identify the main experimental parameters influencing the photocatalytic Reaction treatment. Catalytic dose, primary dye concentration, and time required for degradation were all factors considered. RSM used three selected experience parameters as independent variables and the percentage of methylene blue degradation as dependent variables to optimise the response. Through 17 sets of experiments, the Box- Behnken test design, which is used for the combined effects investigation of three variables which is independent on response (Table 3). The below analysis table shows the levels and ranges of variables which is independent. The Box-Behnken plan is used because it is highly effective, which was not involved at any point at the peaks in cubic region modelled by theboundary in upper region.

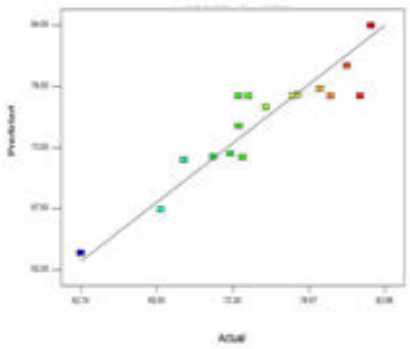


Figure 10: Graphical representation of Actual vs Predicted values

Table 3 :Response surface methodology results for titanium dioxide

Run	Catalyst Dosage (gm)	Time (Min)	Concentration (Mg/L)	Removal (%)
1	1.00	150	30	69.94
2	1.75	150	10	79.44
3	1.00	60	30	77.89
4	1.00	105	50	81.33
5	1.75	105	30	80.2
6	1.75	60	10	75.68
7	2.50	105	10	83.00
8	1.75	60	50	73.78
9	1.75	90	30	77.58
10	2.50	60	30	74.04
11	1.75	105	30	73.76
12	2.50	105	30	71.98
13	1.75	120	30	82.24
14	1.75	105	30	74.45
15	2.50	105	50	62.72
16	1.00	105	10	73.2
17	1.75	105	50	68.34

The independent variables' ideal levels were determined using response surface analysis of the independent and dependent variables. The table and Figure outline the designed experiments as well as the actual and projected response values (figure 10). The decomposition of colour in the dye is represented graphically with the X and Y axes, the effect of variables which was independent of actual, predicted points present in the graph has shown the distribution of catalyst over the dye under the influence of ultraviolet

radiation that is the representation below mentioned in the graph. The point depicted in the graph above is based on the results of the RSM Table 3. After completing 17 runs with the respective decolourization efficiency formula, we can measure the percentage degradation in Table 3 for using a catalyst such as titanium dioxide by plotting the degradation efficiency values against the value predicted by the design expert based on our initial inputs such as concentration, catalyst dosage, and irradiation time. It calculated the degrading efficiency of colour removal in the table using these criteria.

Table 4 : ANOVA data: For TiO_2response surface quadratic model

Sources	Summation of squares	d f	MeanSquare	Value of F	Value of P F<prob
Model	386.54	9	42.94	4.43	0.0312
A-catalyst dosage	14.04	1	14.04	1.44	0.26
B-time	17.08	1	17.08	1.76	0.22
C-concentration	78.93	1	78.93	8.14	0.02
AB	8.67	1	8.67	0.89	0.37
AC	201.49	1	201.49	20.80	0.002
BC	21.16	1	21.16	2.18	0.18
A*2	12.35	1	12.35	1.27	0.29
B*2	25.69	1	25.69	2.65	0.14
C*2	3.15	1	3.15	0.32	0.58
Residual	67.80	7	9.68		
Standard devi.	3.11		R-Squared	0.8507	
Mean	75.27		Adj R- Squared	0.658	
C.V. %	4.13		Pred R- Squared	0.29	
Press	320.4629		Adeq precision	8.57	

Anova tables show the contribution of a single component to the variation in response (from table 4). The greater the value, the greater the variation. In addition, each factor has a p-value; if it is less than 0.05 (confidence level), the factor effect is considered significant. It also tells you how many degrees of freedom you have when estimating inaccuracy. If there is no degree of freedom for error estimates, the design is saturated, and stepwise regression must be used forward or backwards. The contribution of catalyst dose, irradiation time, and concentration in the aforesaid ANOVA offers us the clearance possibility of a combination of the independent variables in the table, whether obtained is significant or not. The given or taken experimental data are mismatched, when the

value of prob equalise to 0.0999 or greater than that, for the colour removal process. If the value of p is less than 0.099, then the colour removal process is significant when it comes to our experimental data with the combination of irradiation time, catalyst dosage, and concentration.

3.3. **Representation models for the colour removal process using RSM**

For the expected responses (Y1, Y2), RSM was used to generate three-dimensional (3D) and two-dimensional (2D) contour plots. To facilitate visualization and in establishing the type of interactions between the test factors, the response surfaces for colour removal efficiency and deterioration are presented in Figure 11. These plots can also be used to evaluate the effect of the independent variables (time, concentration, and catalyst dosage), as well as their interactions, on the colour removal and degradation of landfill leachate. Because the model has several parts, two response surface diagrams were created for each answer (Y1, Y2), with one factor used consistently in each diagram.

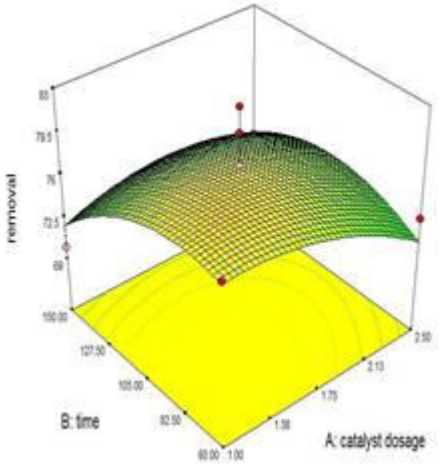


Figure 11: three-dimensionalplot surface for TiO_2

The 3D plot represents the estimated value of the quadratic model for the roughness value of the design machining parameters with catalyst dosage vs irradiation time the distribution of the point from the percentage of not 62% of degradation efficiency due to this range of values showing the dome-shaped plot in 3D for the colour removal for the respective catalyst dosage and irradiation time. The distribution colour removal of dye at different concentrations is around 30ppm in the second 3d plot where the point of A that is catalyst dosage lies between the points (from 59.22 to 2.75) then the length of the other side varies from the difference of (from 69.0 to 59.26).

Conclusion

The work shows the experimental study of the photocatalytic performance of photocatalyst nanoparticle TiO_2 and Cu-doped TiO_2 decolourization efficiency. Here the

more efficiency photocatalyst performed by Cu doped with TiO_2,due to having high band gap that can easily absorbed the dye compound. In summary, the results suggest that the efficiency of decolorization is influenced by dosage, irradiation time, and concentration. The relationship is likely not linear, and there may be optimal conditions for achieving maximum decolorization efficiency. Further statistical analysis, possibly using response surface methodology, would be beneficial to identify the optimal factor levels for achieving the highest decolorization percentage.

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