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OPTIMIZATION OF PHOTOCATALYTIC DEGRADATION OF PARA-NITROPHENOL IN VISIBLE LIGHT BY NITROGEN AND PHOSPHORUS CO-DOPED ZINC OXIDE USING FACTORIAL DESIGN OF EXPERIMENT

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Abstract

In this study, Nitrogen and Phosphorous co-doped Zinc Oxide (NPZ) was prepared through a solvent free reaction. The NPZ was characterized by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy. The photocatalytic activity of the catalyst was investigated by monitoring the degradation of para-nitrophenol (PNP) under visible light irradiation and the process was optimized using factorial design of experiment. The factors investigated were initial concentration of para-nitrophenol, catalyst loading, pH and irradiation time. The characterization results revealed a successful doping of ZnO by nitrogen and phosphorus and an improvement in the surface morphology of the catalyst. The photocatalyst exhibited improved photocatalytic activity under visible light by 73.8%. The statistical analysis of the optimization result showed that the model terms were significant at 95% confidence level. Interactions plots revealed that irradiation time was the most significant factor affecting the degradation process. The cube plots of the interactions of the variables showed that an optimum degradation efficiency of 66.9% was achieved at 10mg/L initial PNP concentration, 0.5g catalyst loading, pH 7 and 150 minutes irradiation time.

Keywords: Nitrogen and Phosphorous co-doped ZnO, p-Nitrophenol, Photocatalytic degradation, Optimization, Factorial-design of experimental

Introduction

Over the years, great effort has been made to develop methods for removing recalcitrant organic pollutants from water. Some of the methods that have achieved significant success are adsorption (Hong *et al.*, 2009, Okibe *et al.*, 2016), solvent extraction (Shen *et al.*, 2006), membrane separation (Ghosh *et al.*, 2006), ozonation (Daneshvar *et al.*, 2007), and so on. However, these methods are not efficient enough to destroy organic pollutants; they only transfer them from one medium to another, thereby creating more remediation problem (Rajamanickam and Shanthi, 2016).

One of the methods of removing recalcitrant organic compounds that is currently gaining research ground is advanced oxidation processes (AOPs). AOPs are processes that use mainly hydroxyl radicals (˙OH) to destroy organic

and/or inorganic pollutants in water. They can proceed in the presence of oxidizing agents, appropriate radiation, and/or heterogeneous catalyst (Ibhadon and Fitzpatrick, 2013; Deng and Zhao, 2015). The use of heterogeneous catalysts in particular for degradation of recalcitrant pollutants in water in the presence of radiation has achieved a significant success.

Titanium (IV) oxide (TiO_2) has been widely reported to be the best photo-catalyst for the degradation of organic compounds but few other semiconductor materials have shown a great potential as well (Ibhadon & Fitzpatrick, 2013). One of such semiconductor materials is ZnO, and it has been suggested as a good alternative to TiO_2 due to its low cost, and availability (Velmurugan *et al*., 2011; Abdollahi *et al.*, 2012). However, similar to TiO_2, its photocatalytic activity is limited to UV region due to its wide band gap (3.37eV) and so cannot absorb significant amount of radiation beyond that region (Dijken *et al*., 1998; Neppolian *et al*., 1999; Shifu *et al*., 2009). One of the ways to enhance its use in high wavelength spectrum region such as the visible light is by doping it with metallic or non-metalic elements or both. Most researches carried out so far in this area have shown a better result in the presence of visible light due to doping of the catalyst (Yelcin *et al*., 2010; Rajamanikam and Shanti, 2012; Ma, et al., 2013; Yirga, 2013; Matos *et al.*, 2014; Lavand and Malghe, 2015; Gionco *et al.*, 2016).

In this study, the photocatalytic degradation of p-nitrophenol (PNP), a typical poisonous and recalcitrant pollutant (Daffri *et al.*, 2014; Deka*et al.*, 2016) was carried out by N, P-codoped ZnO (NPZ) in the presence of visible light was undertaken. The effects of the factors such as initial PNP concentration, catalyst loading , pH and irradiation time was investigated using full factorial experimental design in order to optimize the process. Statistical experimental design was used because it allows for the investigation of the interaction effects unlike the usual conventional method which does not give room for interaction effects evaluation (Brereton, 2007; Aljuboury, 2015, Okibe *et al.*, 2016). To the best of our knowledge, no report has been made as regards the degradation of PNP with NPZ and subsequent optimization with statistical experimental design.

Methdology

Reagents

All the chemicals for this study were analytical grade and used in this experiment without further purification.p-Nitrophenol (PNP), zinc oxide (ZnO), ammonium dihydrogen phosphate ($NH_4H_2PO_4$) supplied by BDH (United Kingdom). The tetraoxosulphate (VI) acid (H_2SO_4) purchased from Sigma Aldrich (Germany) and sodium hydroxide (NaOH) purchased from Fluka (US) were used to adjust the solutions' pH. Distilled water was used for photocatalytic degradation experiment.

Preparation of nitrogen-phosphorus codoped zinc oxide

N; P-codoped Zinc Oxide (NPZ) was prepared in a solvent free reaction

(Welderfael *et al.*, 2013). The doping agent, ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and ZnO were mixed in the following mass ratios: 0.25:10, 0.5:10, 0.75:20, 1:10, 2:10 and ground in mortar for 20 minutes each.The mixtures were calcined in a covered ceramic crucible at 400^0C for 3 hours in a furnace. The products were ground to fine powder and labelled NPZ accordingly. $NH_4H_2PO_4$/ZnO mixing ratios were as follows: NPZ-0.025 (0.25/10), NPZ-0.050 (0.5/10), NPZ-0.075 (0.75/10), NPZ-0.100 (1/10) and NPZ-0.200 (2/10). They were then used for photocatalytic degradation study in order to investigate the effect of the doping process on the photocatalytic activity of ZnO and to determine the best doped photo-catalyst. Undoped ZnO was also calcined at the same conditions to serve as control for the purpose of comparison.

Characterization Studies

Surface structures characterization of ZnO and NPZ was done by a Fourier Transform Infrared spectroscopy using Cary 630 FTIR, Agilent Technology equipment. The FTIR spectra were recorded between the wave numbers 650 and 4000 cm−1.The surface morphologies and pore structures of undoped ZnO and NPZ were examined using Phenom^{TM} (Pro-X) Scanning electron microscope (SEM) at 5000 magnification.

Photocatalytic Degradation Efficiency Study

An open glass tube of 1000ml capacity was used as the reaction vessel and 500W halogen light placed at a distance of 90cm above the reactor as visible light source. The system temperature was maintained at 30 ± 2^0C by the circulating water and was monitored with a laboratory thermometer. The study was carried out at 10mg/L initial PNP concentration, 0.2g catalyst loading, pH 5 and 120 minutes irradiation time.100ml of PNP solution and the photo-catalyst was irradiated and continuously aerated by an air pump to provide oxygen and for the complete mixing of the reaction solution. The solution was allowed to stay in the dark for 30 minutes with appropriate stirring prior to illumination to ensure pre-adsorption of the PNP on the catalyst. At an interval of 30 minutes or at the end of the reaction, 2-3ml of the sample was withdrawn and centrifuged to separate the catalyst particles. 2ml of the sample was suitably diluted, the pH modified to 4 in order to retain its phenolic structure, because PNP is highly pH dependent. UV-Visible absorbance was measured at 311nm. The degradation efficiency (DE) of the samples was calculated by the equation below.

$$DE\ \% = \frac{A_0 - A_X}{A_0} 100 \quad (1)$$

Where, A_0 and A are the UV–Vis absorption of initial PNP solution and sampled solution, respectively.

Full Factorial Experimental Design for the Photo-degradation of PNP

Four factors which are important variables in photocatalytic degradation process were selected to study the photocatalytic degradation of PNP in aqueous solution by NPZ-0.050. The variables investigated were coded as; PNP concentration (A), catalyst loading (B), pH (C) and irradiation

time (D). The photocatalytic process was investigated by varying these factors at two levels (2^4) high (+1) and low (-1) levels (Tables 1) to generate 35 experimental runs consisting of 16 experimental runs, their replicates and three centre points. Interactions between these factors were studied and optimized using the interaction and cube plots. Design expert software 6.0.6 was used to generate the experimental runs and for statistical analysis of photo degradation efficiency (%).

Results and Discussion

Surface Structure Characteristics of the Photo-catalysts

The FTIR Spectrum for the undoped ZnO presented in Figure 1 shows the major absorption peaks around 3500cm^{-1} and 685 cm^{-1}.

Table 1: Factors and levels used in the factorial design for photocatalytic Degradation of PNP by NPZ-0.5

Factors	Symbol	Low (-)	Centre (0)	High (+)
PNP Concentration (mg/L)	A	10	30	50
Catalyst Loading (g)	B	0.1	0.3	0.5
pH	C	3	7	11
Contact Time (min)	D	30	90	150

Table 2: Design matrix for the photocatalytic degradation of PNP by NPZ-0.05 using 2^4 full factorial and three central points

Std	Run	A: Initial PNP Conc. (mg/L)	B: Catalyst Loading (g)	C: pH	D: Contact Time (min)	Degradation Efficiency (%)
31	1	50.00	0.50	11.00	150.00	
28	2	50.00	0.10	11.00	150.00	
25	3	10.00	0.10	11.00	150.00	
26	4	10.00	0.10	11.00	150.00	
20	5	50.00	0.10	3.00	150.00	
33	6	30.00	0.30	7.00	90.00	
15	7	50.00	0.50	11.00	30.00	
8	8	50.00	0.50	3.00	30.00	
35	9	30.00	0.30	7.00	90.00	
19	10	50.00	0.10	3.00	150.00	
16	11	50.00	0.50	11.00	30.00	
27	12	50.00	0.10	11.00	150.0	
17	13	10.00	0.10	3.00	150.00	
3	14	50.00	0.10	3.00	30.00	
29	15	10.00	0.50	11.00	150.00	
1	16	10.00	0.10	3.00	30.00	
32	17	50.00	0.50	11.00	150.00	
12	18	50.00	0.10	11.00	30.00	
30	19	10.00	0.50	11.00	150.00	
4	20	50.00	0.10	3.00	30.00	
2	21	10.00	0.10	3.00	30.00	
6	22	10.00	0.50	3.00	30.00	
9	23	10.00	0.10	11.00	30.00	
18	24	10.00	0.10	3.00	150.00	
13	25	10.00	0.50	11.00	30.00	
21	26	10.00	0.50	3.00	150.00	
22	27	10.00	0.50	3.00	150.00	
7	28	50.00	0.50	3.00	30.00	

14	29	10.00	0.50	11.00	30.00
24	30	50.00	0.50	3.00	150.00
34	31	30.00	0.30	7.00	90.00
10	32	10.00	0.10	11.00	30.00
23	33	50.00	0.50	3.00	150.00
11	34	50.00	0.10	11.00	30.00
5	35	10.00	0.50	3.00	30.00

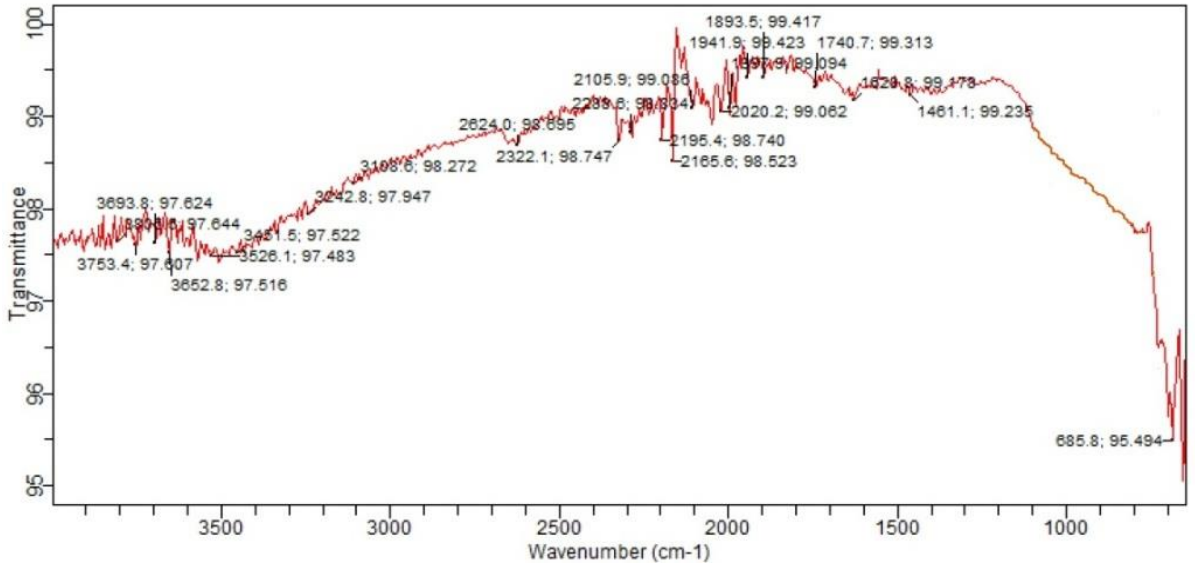


Figure 1: FTIR Spectra of undoped ZnO

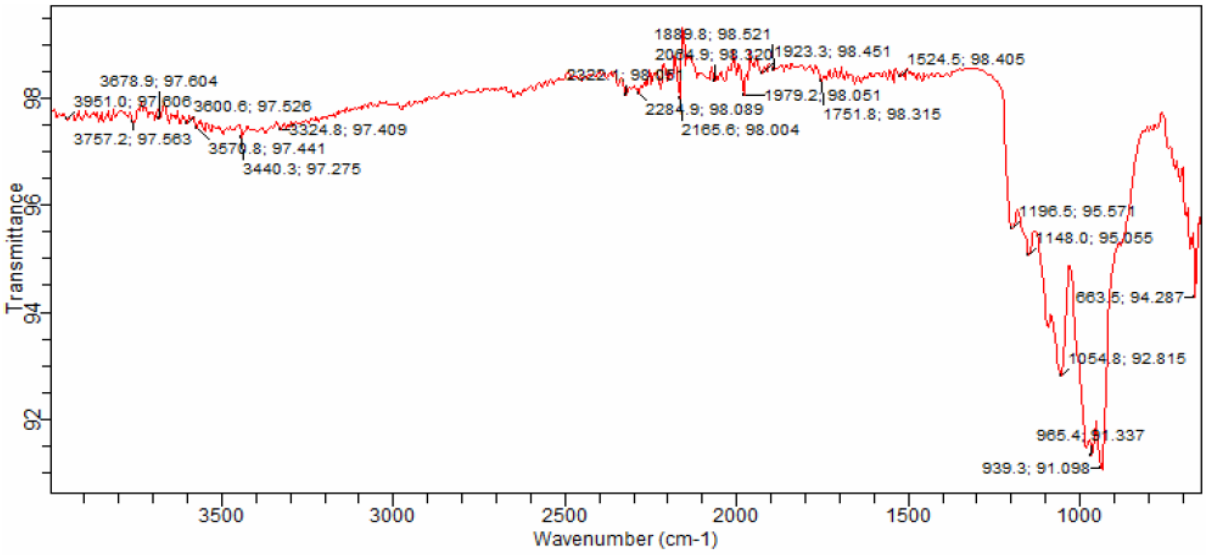


Figure 2: FTIR Spectra of NPZ

The broad peak around 3500cm^{-1} corresponds to the O-H stretching of water molecule. This shows the presence of small amount of water molecule adsorbed on the surface of the photo-catalyst

particles. The peaks around 685 cm^{-1} may be attributed to Zn-O bending vibration (Faal and Farnaneh, 2006).

Presented in Figure 2 is the FTIR spectrum of NPZ-0.050. The absorption spectrum shows the major absorption peaks at 1196.5cm^{-1}, 1148.0cm^{-1}, 1054.8cm^{-1}, 965.4cm^{-1} and 939.3cm^{-1}. The peaks at 1196.5cm^{-1}, 1148.0cm^{-1} and 1054.8cm^{-1} may be attributed to P-O stretching vibration, suggesting the possible introduction of phosphorus into the ZnO particles (Stauart, 2007, Shao *et al.,* 2009). The peaks at 965.4 and 939.3 cm^{-1} may be attributed to Zn≡N stretching suggesting the introduction of nitrogen into the ZnO particles (Stuart, 2007). These results confirm the successful doping of ZnO particles with nitrogen and phosphorus atoms.

Surface Morphologies of the photo-catalysts

Presented in Figure 3 is the Scanning Electron Micrograph (SEM) of undoped ZnO. The surface morphology showed that it has a rough surface but relatively poor pore structure. Also, the photo-catalyst particles are highly agglomerated a factor which could lead to decrease in the efficiency of the photo-catalyst. The increase in the level of roughness and decrease in the level of agglomeration of the photo-catalyst particles shown in the SEM of NPZ-0.050(Figure 4) show that the doping process had effect on the morphology of the photo-catalyst particles. The result shows a better pore structure with relatively large pore holes. This suggests that the NPZ will perform better than undoped ZnO during photocatalytic processes.

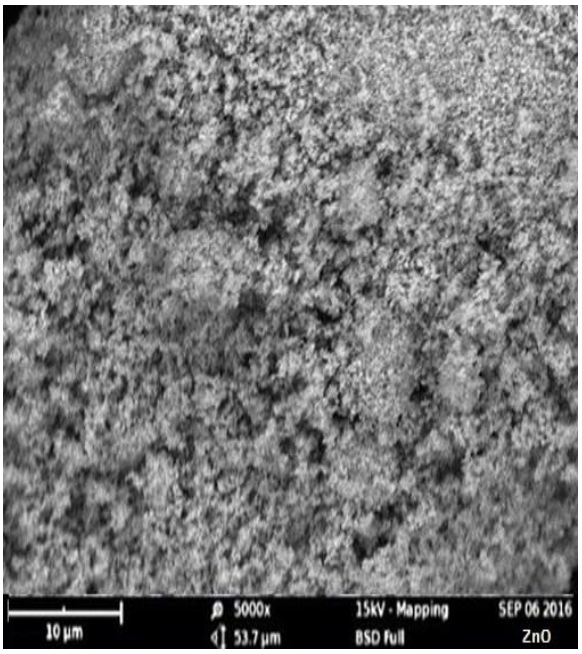


Figure 3: Scanning electron micrograph of Undoped ZnO

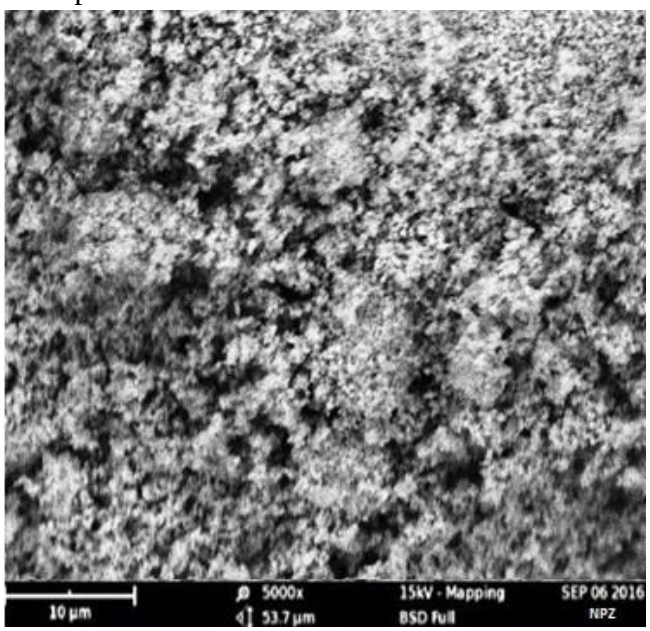


Figure 4: Scanning electron micrograph of NPZ

Effect of Doping on Photocatalytic Degradation Efficiency of ZnO

Shown in Figure 5 are the results of the photocatalytic activities of the doped catalyst under visible light irradiation for

120 minutes. No obvious PNP degradation was observed in the absence of a catalyst, suggesting that the photolysis of PNP by the light was negligible. The photo degradation efficiency of PNP with undoped ZnO gave only 32.40% while 56.30% was observe for NPZ-0.050 after 120minutes of irradiation time, representing 73.8% improvement in the photocatalytic activity of ZnO. Therefore, the visible light photocatalytic activity of ZnO increases with N and P co-doping. The positive influence of the doped N and P atoms on the visible light photo-activity of ZnO could be attributed to band-gap narrowing by the doping process. The band gap narrowing may have resulted due to the replacement of oxygen in ZnO by N and P, which might have led to the shifting in absorption edge of ZnO to the lower energy region (higher wavelength) (Mohamed and Aazan, 2013; Yirga, 2013). The influence of the variation of the amount of N and P content on the photo-activity of ZnO as the mass ratio of the dopant increases can also be seen in Figure 5. The results show that the photocatalytic activity of NPZ depends on the amount of N and P present as determined by the amount of the dopant used. The photocatalytic activity increases as the dopant ratio increases from 0.025 to 0.050 where the highest degradation value of approximately 56% after 120 minutes of irradiation was recorded but began to decrease beyond that. This may be due to the decrease in the free active site of ZnO available for degradation beyond 0.050 doping ratio and as such, the efficiency of the degradation starts to decrease. This result is in agreement with the similar work some scholars who have investigated the doping of ZnO with different dopants ratio (Mohamed and Aazan 2013; Jain *et al.,* 2015).

Degradation Efficiency and Analysis of Variance for the Photocatalytic Degradation of PNP by NPZ-0.050

Presented in Table 3 are the degradation efficiency results of the experimental runs obtained by varying the selected factors affecting the photocatalytic degradation process. The results show that the experimental run fifteen (15) gave the highest degradation efficiency value of 74.60% and the least value of 12.30% for the sixteenth run. The analysis of variance (ANOVA) values are presented in Table 4.2. From the results of the ANOVA, model F-value of 68.87 implies that the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AB, AC, AD and BD are significant model terms. A mean of 28.13, standard deviation of 2.99, R^2 0.9760 and R^2_{adj} 0.9559 were obtained at 95% confidence limit. The model equation that defines each of the responses obtained in the factorial design for the degradation of PNP by NPZ is given by Equation 2.

Degradation Efficiency(%)= +28.84-9.05A + 5.81B +1.42C + 10.45D-3.70AB - 1.72AC -6.22AD + 0.75B C + 1.89BD +0.097 C D - 0.57A BC - 1.00 ABD - 0.22ACD - 0.87BCD -0.059ABCD

Shown in Figure 6 is the normal probability plot of PNP degradation

efficiency using NPZ photocatalyst. This was necessary to confirm that the assumptions from the ANOVA are met. The distribution of the residual is normal giving rise to a straight line, indicating that the assumptions from ANOVA are met and the statistical model is reliable (Mansouriieh *et al*., 2015). The predicted vs actual plot shown in Figure 7 shows that the points were randomly scattered and the actual values were very close to the predicted values, which further confirms the reliability of the model.

Interaction Effect of Two Variables on the Photocatalytic Degradation of PNP by NPZ-0.050

Initial PNP Concentration and Catalyst Loading: The interaction effect of initial PNP concentration and catalyst loading dosage on the degradation process is presented in Figure 7a.

Table 3: Design matrix and response for the photocatalytic degradation of PNP by NPZ-0.050

Std	Run	A: Initial PNP Conc. (mg/L)	B: Catalyst Loading (g)	C: pH	D: Contact Time (min)	Degradation Efficiency (%)
31	1	50.00	0.50	11.00	150.00	28.10
28	2	50.00	0.10	11.00	150.00	23.10
25	3	10.00	0.10	11.00	150.00	45.60
26	4	10.00	0.10	11.00	150.00	44.60
20	5	50.00	0.10	3.00	150.00	20.90
33	6	30.00	0.30	7.00	90.00	35.33
15	7	50.00	0.50	11.00	30.00	15.80
8	8	50.00	0.50	3.00	30.00	12.90
35	9	30.00	0.30	7.00	90.00	32.50
19	10	50.00	0.10	3.00	150.00	20.50
16	11	50.00	0.50	11.00	30.00	19.60
27	12	50.00	0.10	11.00	150.0	19.60
17	13	10.00	0.10	3.00	150.00	38.20
3	14	50.00	0.10	3.00	30.00	18.80
29	15	10.00	0.50	11.00	150.00	74.60
1	16	10.00	0.10	3.00	30.00	12.30
32	17	50.00	0.50	11.00	150.00	23.60
12	18	50.00	0.10	11.00	30.00	13.04
30	19	10.00	0.50	11.00	150.00	67.20
4	20	50.00	0.10	3.00	30.00	12.50
2	21	10.00	0.10	3.00	30.00	15.50
6	22	10.00	0.50	3.00	30.00	21.80
9	23	10.00	0.10	11.00	30.00	16.80
18	24	10.00	0.10	3.00	150.00	40.20
13	25	10.00	0.50	11.00	30.00	37.00
21	26	10.00	0.50	3.00	150.00	66.00
22	27	10.00	0.50	3.00	150.00	60.00
7	28	50.00	0.50	3.00	30.00	18.80
14	29	10.00	0.50	11.00	30.00	28.60
24	30	50.00	0.50	3.00	150.00	28.80
34	31	30.00	0.30	7.00	90.00	33.73
10	32	10.00	0.10	11.00	30.00	13.80
23	33	50.00	0.50	3.00	150.00	27.60
11	34	50.00	0.10	11.00	30.00	13.06
5	35	10.00	0.50	3.00	30.00	24.00

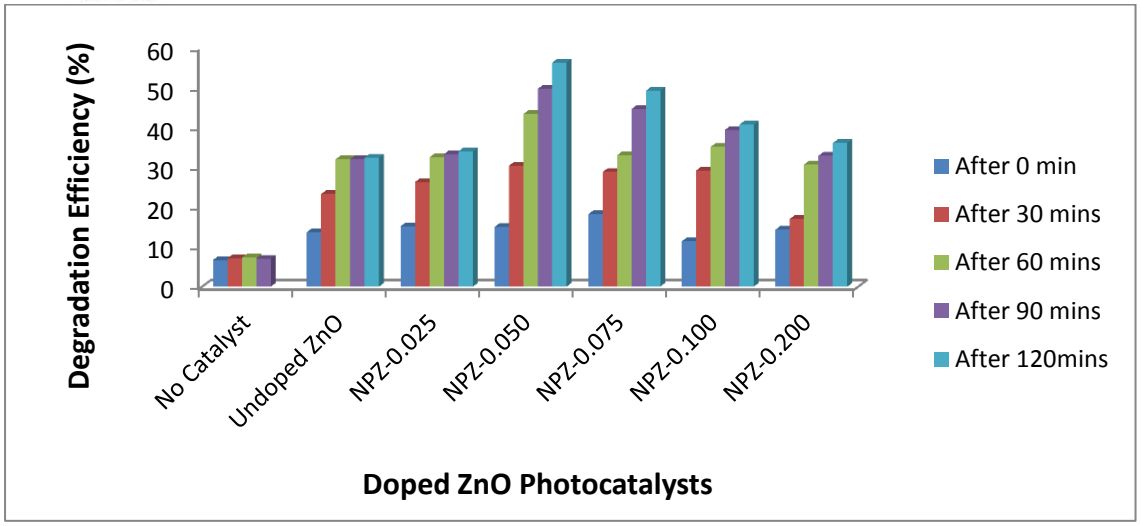


Figure 5: Effect of N, P-codoping on the photocatalytic efficiency of ZnO at 10mg/L initial PNP conc, 0.2g catalyst loading, and pH 5

Table 4: ANOVA for the factorial model for the catalytic degradation of PNP by NPZ-0.050

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remarks
Model	9226.03	15	615.07	68.87	<0.0001	significant
A	2619.07	1	2619.07	293.28	< 0.0001	
B	1079.96	1	1079.96	120.93	< 0.0001	
C	64.13	1	64.13	7.18	0.0153	
D	3492.39	1	3492.39	391.07	< 0.0001	
AB	438.82	1	438.82	49.14	< 0.0001	
AC	94.88	1	94.88	10.62	0.0044	
AD	1236.29	1	1236.29	138.44	< 0.0001	
BC	17.85	1	17.85	2.00	0.1745	
BD	114.38	1	114.38	12.81	0.0021	
CD	0.30	1	0.30	0.034	0.8566	
ABC	10.24	1	10.24	1.15	0.2985	
ABD	31.80	1	31.80	3.56	0.0754	
ACD	1.49	1	1.49	0.17	0.6880	
BCD	24.33	1	24.33	2.72	0.1162	
ABCD	0.11	1	0.11	0.013	0.9118	
Curvature	68.92	1	68.92	7.72	0.0124	significant
Pure Error	160.75	18	8.93			
Cor Total	9455.70	34				

Std dev	2.99	R^2	0.9829
Mean	29.27	R^2 adj	0.9686
C.V.	10.21	CL	95%

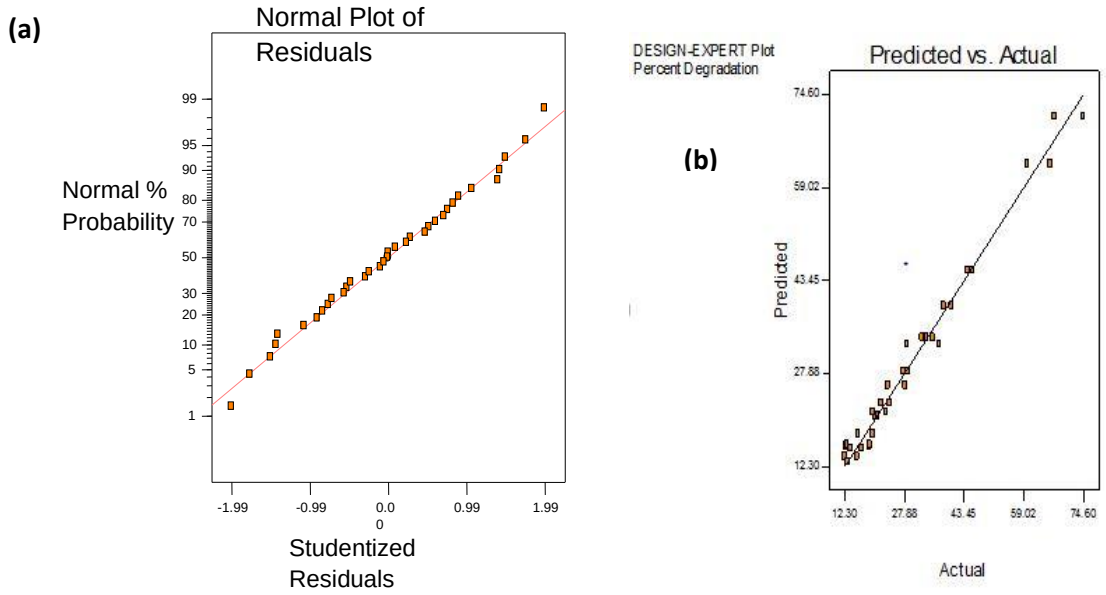


Figure 6: Diagnostic plots. (a) Normal distribution p lot. (b) Predicted value vs actual value plot

The results show that the effect of the interaction was significant and that an increase in catalyst loading produced a corresponding increase in degradation efficiency while an increase in initial PNP concentration resulted in a decrease in degradation efficiency. With an initial PNP concentration of 10mg/L, catalyst loading of 0.5g at pH 7 and 90 minutes irradiation time, 47.4% degradation efficiency was achieved.This implies that if initial PNP concentration and catalyst laoding were the only factor affecting the degradation process, then catalyst loading would be the most critical factor.Also, it can be observed that with a catalyst loading of 0.5g, the degradation profile is above the factorial model design point, while at 0.1g it is below the factorial model design point.

Catalyst Loading and Solution's pH:

The effect of the interaction between catalyst loading and pHon degradation efficiency of NPZ-0.050 is shown in Figure 7b. The results show that the effect of the interaction was very small (insignificant) and that the little effect was noticeable at high pH (basic medium) and high catalyst laoding.The optimum degradation efficiency of 36.8% can be achieved at 0.50g catalyst loading, pH 11, 30mg/L initial PNP concentration and 90 minutes contact time. The result shows that, catalyst loading had a stronger effect on the degradation efficiency than pH and if catalyst loading and the solution's pH were to be the only factors affecting the degradation process, catalyst dosage would be the most critical factor which should be given more attention.

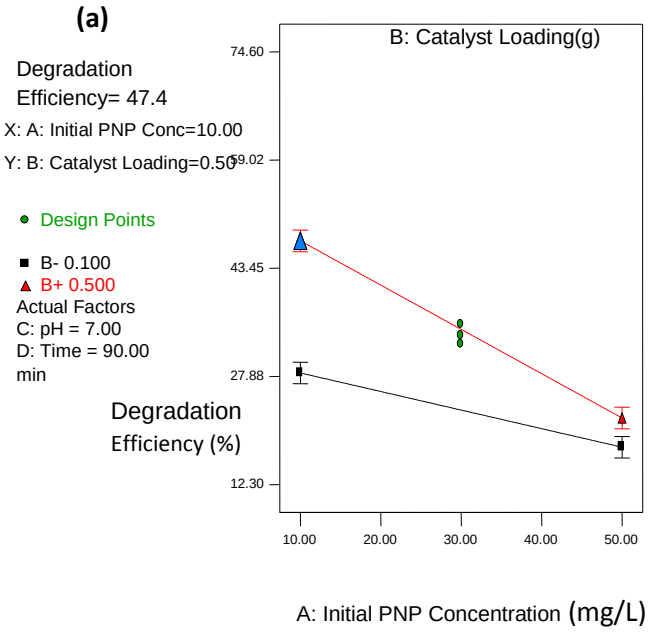
Catalyst loading and Irradiation Time:

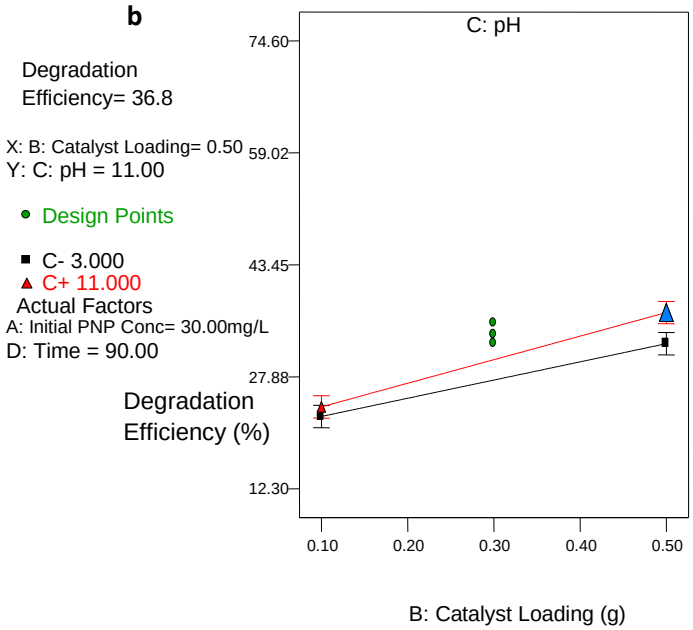
The interaction plot showing the effect of catalyst loading and contact time on the degradation efficiency of NPZ-0.050 for PNP is shown in Figure 7c. The results show that the interaction between the two factors produced a significant increase in the degradation efficeincy. Also, it can be

seen from Figure 8 that increase in irradiation time had a profound effect on the removal efficiency while increase in catalyst loading though resulted in increase in degradation efficiency, had a lesser effect than irradiation time. The optimum degradation efficiency for this interaction was 47.0% at 0.50g catalyst dosage, 150 minutes contact time, pH 7 and 30mg/L initial PNP concentration. This implies that if catalyst laoding and irradiation time were the only factor affecting the degradation process, then irradaition time would be the most critical factor.

Interaction Effect of Three Variables on the Photocatalytic Degradation of PNP by NPZ-0.050

Initial PNP Concentration, Catalyst Loading and Solution's pH: The cube plot for the effect of interaction of initial PNP concentration, catalyst loading and pH on the degradation of PNP by NPZ-0.050 is shown in Figure 8a. The results show that for the interaction of these three variables at 90 minutes contact time, the degration efficiencies were very high at the points where catalyst loading was high (B+). Also, it can be observed from the results that higher pH (basic medium) had a small postive effect on the process but the effect was insignificant at high initial PNP concentration. The highest value of 51.85% was achieved at 10mg/L initial PNP concentration, 0.5g catalyst loading, and pH 11 (A-, B+, C+) and the least value of 17.20% at high initial PNP concentration, low catalyst loading and Low pH (A+, B-, C+).





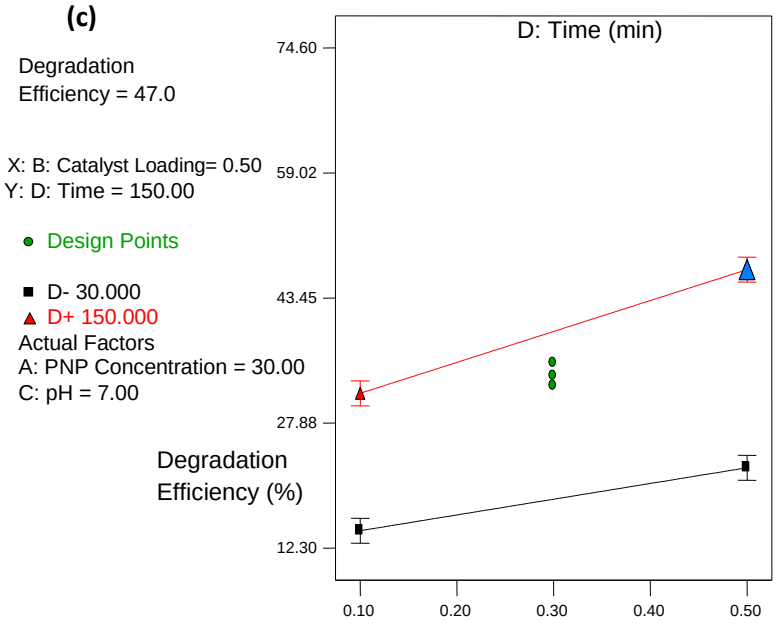


Figure 7: Interaction effect of two variables on the photocatalytic degradation process: (a) initial PNP concentration and catalyst loading (B) Initial PNP concentration and pH (c) catalyst loading and irradiation time.

This shows that high catalyst dosage was the most inflencing factor in this interaction.

Initial PNP Concentration, catalyst Loading and Irradiation Time: Shown in

Figure 8b is the cube plot for the effect of interaction of initial PNP concentration, catalyst loading and contact time for the degradation of PNP by NPZ-0.050 photocatalyst. The interaction is similar to that observe in Figure 9 (A, B, C) but with an improvement at all point where irradiation time was high (D+). The results show that for the interaction of these three variables at pH 7, optimum degradation efficeincy of 66.95% was achieved at 10mg/L initial PNP concentration, 0.5g catalyst loading, and 150 minutes catalyst loading (A-, B+, D+). A closer look at the interaction shows that increase in irradiation time has the strongest influence among the factors.

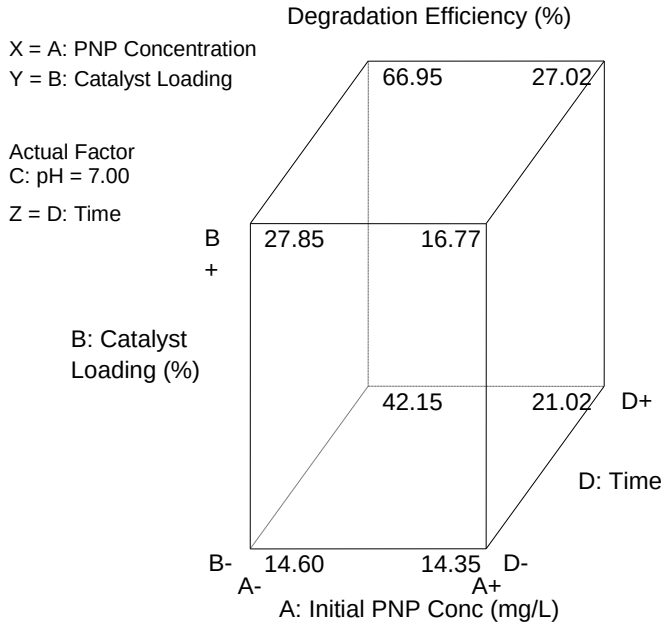
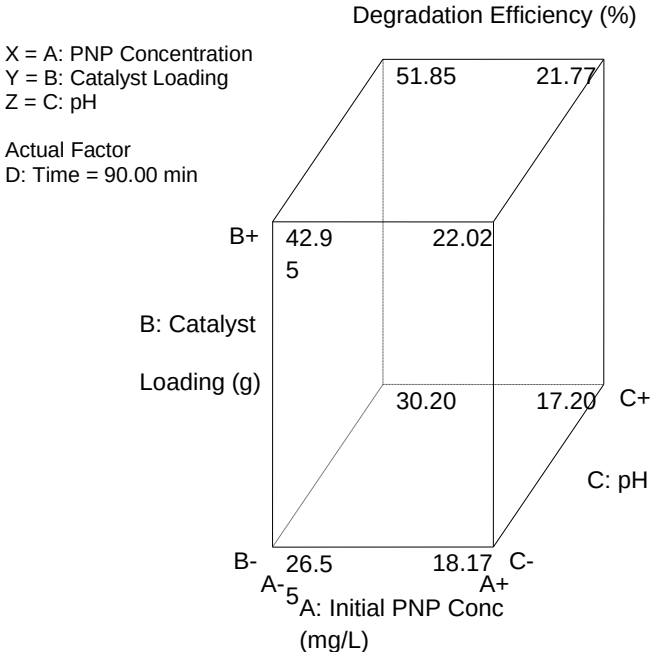


Figure 8: Interaction effect of three variables (a) initial PNP concentration, catalyst loading, and pH (b) initial PNP concentration, catalyst loading and irradiation time.



Conclusion

Nitrogen-phosphorus co-doped ZnO was successfully prepared through a simple solvent free reaction and the prepared material showed an improved pore structure. The photocatalytic activity of NPZ was higher than that of ZnO as revealed by the photocatalytic degradation of p-nitrophenol under visible light, confirming the positive effect of doping on photocatalytic activity of ZnO. The statistical analysis results showed that the model developed from experimental data to optimize the parameters were significant. The statistical optimization of the degradation process revealed that the major factor affecting the degradation process is irradiation time. The degradation efficiency of 66.95% was achieved at 10mg/L initial PNP

concentration, 0.5 catalyst loading, pH 7 and 150 minutes irradiation time.

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