



Fjrs.futa.edu.ng

FUTA Journal of Research in Sciences

ISSN: 2315 – 8239 (Print); E-ISSN: 2489 - 0413



FUTA Journal of Research in Sciences, Vol. 13 (2), October, 2017: 322-336

PREPARATION OF NITROGEN-PHOSPHORUS CO-DOPED ZINC OXIDE ACTIVATED CARBON COMPOSITE AND ITS APPLICATION FOR THE REMOVAL OF 4-NITROPHENOL

*O. T. OJEKUNLE, F. G. OKIBE, and E. D. PAUL

Department of Chemistry, Ahmadu Bello University, Zaria

*Corresponding Author: oladayoojekunle@gmail.com; Phone No:+2348060794639

ABSTRACT

Nitrogen-Phosphorus co-doped Zinc Oxide activated carbon (NPZAC) composite was prepared in this study. The prepared photocatalyst was characterized by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy. The removal of 4-Nitrophenol (4-NP); by the modified ZnO based catalyst was studied and the effects of operational parameters such as 4-NP initial concentration, catalyst loading, pH and irradiation time were studied using full factorial experimental design. The reusability of NPZAC was also investigated. The investigation revealed that doping increased the removal efficiency of the catalyst by a factor of 0.35 (35 %) while addition of activated carbon further increased it to a factor of 1.82 (182 %) under the same condition. The statistical analysis of the experimental results showed that some model terms were significant ($p < 0.05$) and the interactions plots revealed that catalyst loading was the most significant factor affecting the removal efficiency. This study revealed that optimum removal value of 100 % was achieved at low initial 4-NP concentration (10 mg/L), high catalyst loading (0.5 g), high pH (11) and long irradiation time (150 min). Also, the reusability test revealed that the composite can be used up to fifth cycles. Therefore, NPZAC can be used for the removal of 4-NP phenol pollutant.

Keywords: Photocatalytic removal, 4-Nitrophenol, Full factorial experimental design.

INTRODUCTION

4-Nitrophenol (4-NP) is one of the most used organic compounds in manufacturing industries for the production of pesticides, dyes, pharmaceutical products, plastics, and explosives. It is environmentally significant because it is a highly toxic, recalcitrant organic compound, and so, it has been classified as environmentally hazardous substance (Takahashi *et al.*, 1994;

Kashif and Feng, 2009; Smida and Jamoussi, 2012; Benhebal *et al.*, 2013). A large amount of 4-NP is released into the environment through industrial wastewater in industrially populated area, leading to the pollution of fresh water, sea water and ground water (Deka, 2016).

Most common physicochemical methods of removing 4-NP are not efficient enough to destroy the compound, they only transfer it from one

medium to another, thereby creating more remediation problem (Panda *et al.*, 2011; Rajamanickam and Shanti, 2016). Biological method is also hampered by high toxicity of the compound especially at high concentration (Yi *et al.*, 2006; Kulkarni and Chadhari, 2007).

The use of heterogeneous catalyst which is an advanced oxidation process (AOP) for the removal of 4-NP has achieved significant results, in that it can both degrade and mineralize the organic compounds to less toxic inorganic compounds (Sugiyama *et al.*, 2012; Rajamanickam and Shanti, 2016). TiO₂ has been widely reported to be the best catalyst for the removal of organic compounds in the presence of light. However, Zinc Oxide (ZnO) has also been reported to have great potential as well, and it has been suggested as an alternative to TiO₂ for the removal of some organic compounds (Velmurugan *et al.*, 2011; Abdollahi *et al.*, 2012). ZnO has large band gap energy, just like TiO₂ which reduces the chance of it being used in low energy spectrum (high wavelength) such as visible light source (Neppolian *et al.*, 1999; Shifu *et al.*, 2009; Gionco *et al.*, 2016). Fortunately, this problem can be overcome by doping the catalyst with either non-metallic or metallic elements or both. This often results in band gap narrowing, and enables its utilization under visible radiations (Ibhadon and Fitzpatrick, 2013; Welderfael *et al.*, 2013; Mondal and Sharma, 2014; Jain *et al.*, 2015; Lavand and Malghe, 2015; Abdullah *et al.*, 2016).

Other problems associated with the use of ZnO as a photocatalyst for the removal of organic compounds is the aggregation of particles in suspension due to the agglomeration nature of the compound and difficulty in separating the powder from solution after the completion of the process (El-Sheikh *et al.*, 2004). However, this problem can easily be overcome by using a good support such as activated carbon to form a composite. ZnO/Activated carbon composite also promote

fast adsorption on the activated carbon, followed by an efficient diffusion of pollutants from activated carbon to photoactive semiconductor where degradation will take place (Velasco *et al.*, 2010; Muthirulan *et al.*, 2013; Matos *et al.*, 2014; Sobana *et al.*, 2016).

In this study, ZnO was co-doped with nitrogen (N) and phosphorus (P); it was thereafter supported on activated carbon to form activated carbon composite. This was done to overcome the aforementioned challenges and also study the synergic effect of both doping and activated carbon support. The efficiency of the catalyst was then investigated by monitoring the removal of 4-NP through full factorial experimental design method.

MATERIALS AND METHOD

Reagents

All the chemicals for this study were of analytical grade and used in this experiment without further purification. 4-Nitrophenol (4-NP), zinc oxide (ZnO), ammonium dihydrogen phosphate (NH₄H₂PO₄), and commercial activated carbon (CAC) were supplied by BDH (United Kingdom). The tetraoxosulphate (IV) acid (H₂SO₄) purchased from Sigma Aldrich (Germany) and sodium hydroxide (NaOH) purchased from Fluka (US) were used to adjust the solutions' pH. Deionized water was used for preparation of the modified catalysts while distilled water was used for photocatalytic removal studies.

Experimental Methods

Preparation of Nitrogen-Phosphorus Co-doped ZnO-Activated Carbon Composite (NPZAC)

Nitrogen-phosphorus co-doped ZnO-activated carbon (NPZAC) composite was prepared in two stages, viz; preparation of nitrogen-phosphorus co-doped ZnO (NPZ) through a solvent free reaction and subsequent wet incipient

impregnation of NPZ with activated carbon to form NPZAC composite (Welderfael *et al.*, 2013; Matos *et al.*, 2014). The doping agent, ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and ZnO were mixed in mass ratio (w/w) 0.5:10 and ground in mortar for 20 min each. The mixture was calcined in a covered ceramic crucible at $400\text{ }^\circ\text{C}$ for 3 h in a furnace, to allow for deposition of nitrogen and phosphorus vapour on the ZnO particles. Thereafter, activated carbon (AC) and NPZ were mixed using 20 mL deionised water in mass ratio 1.5:10 and the slurry formed was vigorously stirred with magnetic stirrer for 20 min at room temperature. The resultant composite was filtered and dried for 2 h at $100\text{ }^\circ\text{C}$ in oven. The product obtained was ground into fine powder and labeled NPZAC. Undoped ZnO was also calcined at the same conditions to serve as control for the purpose of comparison.

Characterization Studies

Undoped ZnO and NPZAC were characterized by Fourier Transform Infrared spectroscopy (Cary 630 FTIR, Agilent Technology) in order to study the chemical characteristics of the modified catalysts. The FTIR spectra were recorded between the wave numbers 650 and 4000 cm^{-1} . The surface morphologies of undoped ZnO and NPZAC were examined using PhenomTM (Pro-X) Scanning electron microscope (SEM).

Photocatalytic Removal Efficiency Studies

The photocatalytic activities of undoped ZnO, nitrogen-phosphorus co-doped ZnO (NPZ) and NPZAC composites were studied by monitoring the removal of 4-NP. This was done in order to investigate the effects of the doping process and activated carbon support on the photocatalytic activity of ZnO.

An open glass tube of 1000 mL capacity was used as the reaction vessel and 500W halogen light placed at a distance of 90 cm above the reactor as the light source. The system temperature was maintained at $30\pm 2\text{ }^\circ\text{C}$ by the circulating water and

was monitored with a laboratory thermometer. The study was carried out at 10 mg/L initial 4-NP concentration, 0.2 g catalyst loading, pH 5 and 60 min irradiation time. The conditions were selected based on the previous studies carried out by Modirshahla *et al.* (2009) and Udom *et al.* (2014). 100 mL of 4-NP solution and the photocatalyst 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 min with appropriate stirring prior to illumination to ensure pre-adsorption of the 4-NP on the catalyst. At the completion of reaction time, 2 mL of the sample was withdrawn and centrifuged to separate the catalyst particles. The pH of the solution was modified to 4 in order to retain its phenolic structure, because 4-NP is highly pH dependent and its UV-Visible absorbance was measured at 311 nm. The removal efficiency (RE) of the samples was calculated by equation 1.

$$\text{RE}\% = \frac{A_0 - A_1}{A_0} \times 100 \quad 1$$

Where, A_0 and A_1 are the UV-Vis absorption of initial and final 4-NP solution, respectively.

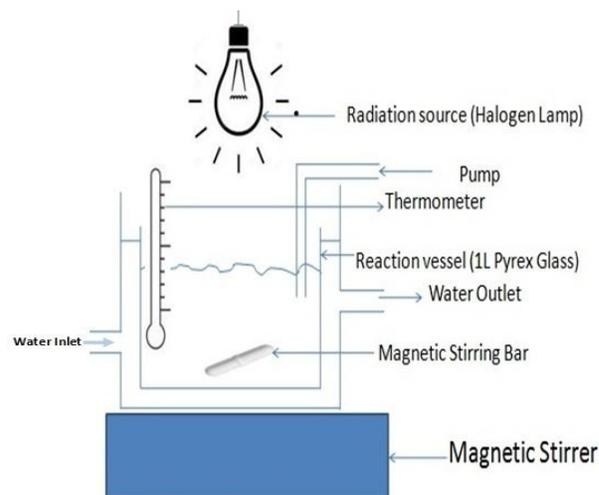


Figure 1: Schematic diagram of the laboratory scale photo reactor used for the study

Full Factorial Experimental Design for the Removal of 4-NP by NPZAC

Four factors were selected to study the removal efficiency of NPZAC composite using full factorial experimental design. Statistical experimental design was used because it allows for the investigation of the interaction effects unlike the conventional method which does not give room for interaction effects study. The variables investigated were coded as; initial 4-NP 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 (Table 1) to generate 35 experimental runs consisting of 16 experimental runs, their duplicates and three centre points. Interactions between these factors were studied using the two variables interaction plot and cube plot (three variables interaction plot). Design expert software 6.0.6 was used to generate the experimental runs, carried out the statistical analysis of removal efficiency and generate the model equation for the studies.

Table 1: Factors and levels used in the factorial design for photocatalytic removal of 4-NP by NPZAC

Factors	Symbol	Low (-)	Centre (0)	High (+)
4-NP 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

Determination of the Reusability of NPAZC

The reusability of NPZAC composite was studied using the following optimized conditions from the full factorial experimental design results: 10 mg/L initial 4-NP concentration, pH 11, 0.5 g catalyst dosage and 150 min contact time. The photocatalyst was separated from the reaction mixture through centrifugation and filtration at the end of each experiment. The recovered photocatalyst particles were washed four times with deionized water, dried at 90 °C in oven and reused again. The procedure was again repeated four times which gave a total of five cycles.

RESULTS AND DISCUSSION

Chemical Structure Characteristics of the Photocatalysts

Presented in Figure 2 is the Spectrum for the undoped ZnO. It shows the major absorption peaks around 3500 cm^{-1} and 685 cm^{-1} . The peak around 3500 cm^{-1} corresponds to the O-H stretching of water molecule which indicates that small amount of water molecule was adsorbed on the surface of the photocatalyst particles. The peaks around 685 cm^{-1} can be attributed to absorption of Zn-O bonds in ZnO (Faal and Farnaneh, 2006). Figure 3 is the FTIR spectrum of NPZAC photocatalyst. The absorption spectrum shows major absorption band at 1051.1 cm^{-1} , 984.0 cm^{-1} , and 943.0 cm^{-1} . The peaks at 1051.1 cm^{-1} , could be attributed to P-O stretching vibration (Stuart, 2004, Shao *et al.*, 2009), while the peaks at 984 and 943 cm^{-1} may be assigned to Zn≡N (Stuart, 2004). This shows a successful doping of phosphorus and nitrogen atoms into ZnO photocatalyst particles.

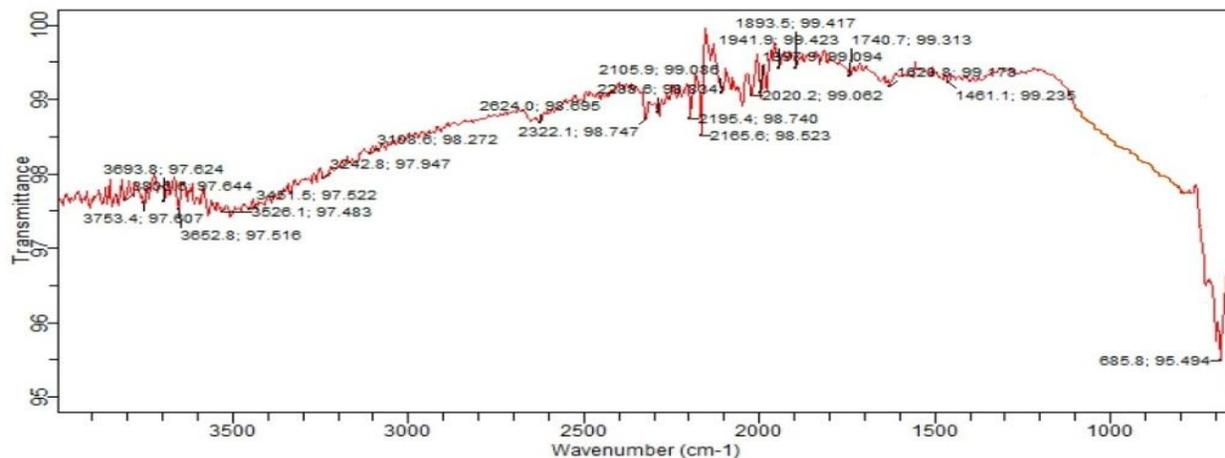


Figure 2: FTIR Spectrum of undoped ZnO

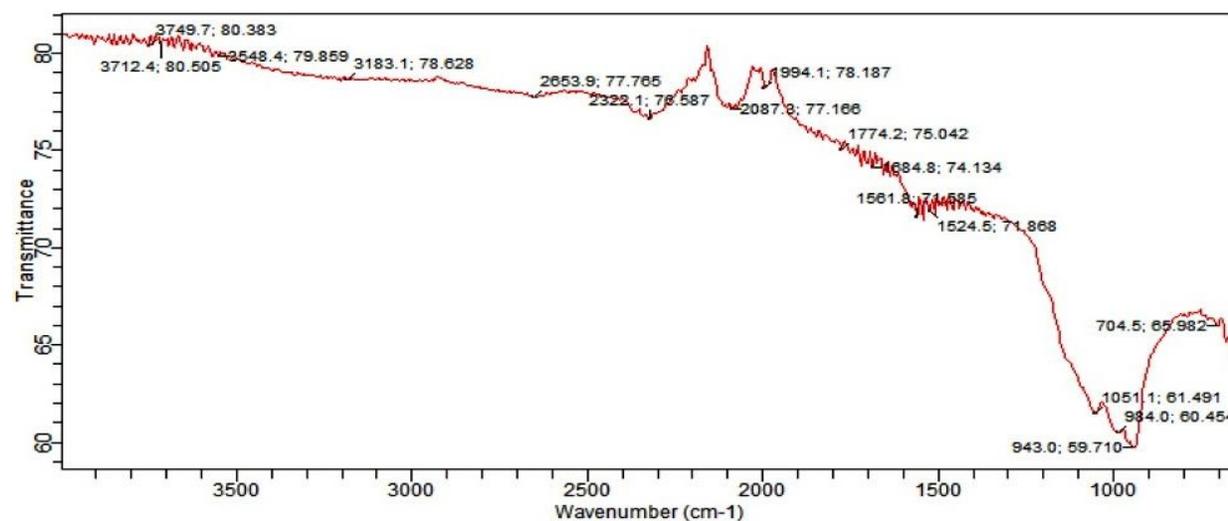


Figure 3: FTIR Spectrum of NPZAC

Surface Morphologies of the photocatalysts

Shown in Figure 4 is the SEM result of undoped ZnO. The surface morphology showed that it has a rough surface and highly agglomerated. Also, the photocatalyst particles are highly agglomerated a factor which could lead to decrease in the efficiency of the photocatalyst. Figure 5 shows the scanning electron micrograph of NPZAC. The result showed that NPZAC has a rough surface

texture but with reduced level of agglomeration. A significant reduction in the level of agglomeration was also observed due to the addition of activated carbon. The observation is in agreement with the results obtained by Muthirulan *et al.* (2013) and Sobana and Swaminathan (2007) who reported a similar improvement in the surface morphology of ZnO after addition of activated carbon.

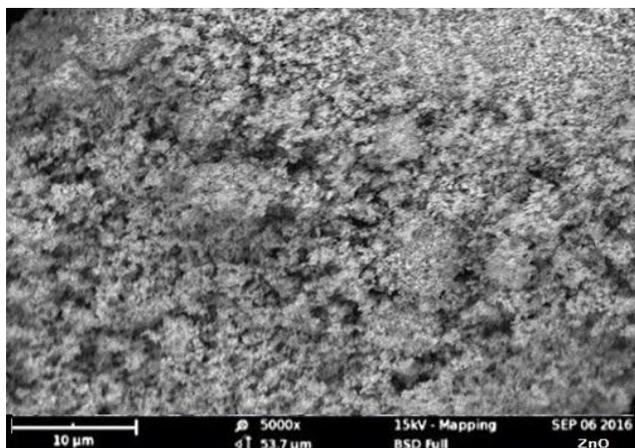


Figure 4: Scanning electron micrograph of undoped ZnO

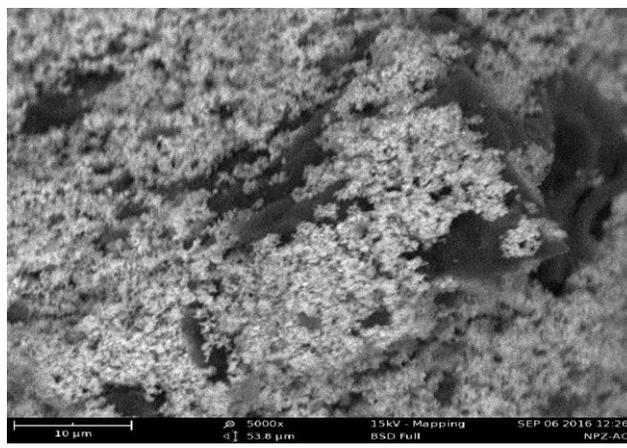


Figure 5: Scanning electron micrograph of NPZAC

Synergistic Effect of Doping and Activated Carbon Support on Photocatalytic Removal Efficiency of ZnO

The results of the photocatalytic removal study are shown in Figure 6. The results showed that removal efficiencies 32.00 % and 43.40 % were achieved for undoped ZnO and NPZ respectively at 10 mg/L initial PNP concentration, 0.2 g catalyst loading, pH 5 and 60 min contact time respectively, indicating a positive effect of doping on the ZnO. Also, the results show that the removal efficiency of ZnO increased the more with the addition of AC. This implies that NPZAC has a better photocatalytic activity than undoped ZnO and NPZ. This improvement was due to the increase in the number of active site afforded by the addition of AC.

Comparative analysis of the results shows that codoping ZnO with N and P is capable of increasing the removal efficiency of ZnO by a factor of 0.35(35 %) while inclusion of AC support to form NPZAC-0.15 composite, will increase it further by a factor of 1.82 (182 %). Overall, the results reveal that the synergistic effect of both doping and activated carbon support caused an increase in the removal efficiency of ZnO for 4-NP from 32 % to over 90 %.

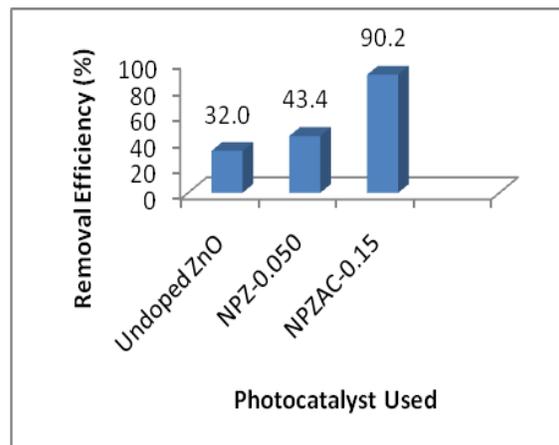


Figure 6: Effect of doping and activated carbon support on the efficiency of ZnO photocatalyst

The Removal Efficiency under Variable Conditions

The response or removal efficiency of 4-NP by NPZAC under variable conditions is presented in Table 3. The results showed that experimental run ten (10) and its Replicate, run twenty four (24) produced the highest removal efficiency value of 100.00% and the least value of 33.50% at run 18. This revealed that 4-NP was completely removed by NPZAC at 10 mg/L initial 4-NP concentration, 0.50 g catalyst loading, pH 11 and 150 minute irradiation time.

Table 3: Design matrix and responses for the photocatalytic removal of 4-NP by NPZAC

Std	Run	A: Initial PNP Conc. (mg/L)	B: Catalyst Loading (g)	C: Ph	D: Contact Time (min)	Removal Efficiency (%)
12	1	50.00	0.10	11.00	30.00	45.70
8	2	50.00	0.50	3.00	30.00	83.70
27	3	50.00	0.10	11.00	150.00	58.12
15	4	50.00	0.50	11.00	30.00	94.88
3	5	50.00	0.10	3.00	30.00	35.50
21	6	10.00	0.50	3.00	150.00	97.20
14	7	10.00	0.50	11.00	30.00	96.50
6	8	10.00	0.50	3.00	30.00	94.10
19	9	50.00	0.10	3.00	150.00	44.80
29	10	10.00	0.50	11.00	150.00	100.00
31	11	50.00	0.50	11.00	150.00	97.00
32	12	50.00	0.50	11.00	150.00	96.74
26	13	10.00	0.10	11.00	150.00	91.80
18	14	10.00	0.10	3.00	150.00	91.70
13	15	10.00	0.50	11.00	30.00	95.60
10	16	10.00	0.10	11.00	30.00	85.40
16	17	50.00	0.50	11.00	30.00	82.60
4	18	50.00	0.10	3.00	30.00	33.50
35	19	30.00	0.30	7.00	90.00	97.73
22	20	10.00	0.50	3.00	150.00	97.10
5	21	10.00	0.50	3.00	30.00	94.20
24	22	50.00	0.50	3.00	150.00	93.40
28	23	50.00	0.10	11.00	150.00	58.70
30	24	10.00	0.50	11.00	150.00	100.00
17	25	10.00	0.10	3.00	150.00	90.50
11	26	50.00	0.10	11.00	30.00	36.90
20	27	50.00	0.10	3.00	150.00	44.90
25	28	10.00	0.10	11.00	150.00	91.50
7	29	50.00	0.50	3.00	30.00	82.60
23	30	50.00	0.50	3.00	150.00	93.82
1	31	10.00	0.10	3.00	30.00	81.30
9	32	10.00	0.10	11.00	30.00	84.00
34	33	30.00	0.30	7.00	90.00	97.97
2	34	10.00	0.10	3.00	30.00	81.00
33	35	30.00	0.30	7.00	90.00	97.60

ANOVA and Model Equation for photocatalytic removal of 4-NP by NPZAC

The ANOVA results for the removal of 4-NP by NPZAC is presented in Table 4. It shows the model terms which are the four variables and their combinations (interactions). Values of "Prob > F" less than 0.0500 indicate that the model terms are

significant. In this case A, B, C, D, AB, AC, AD, BC, BD, ABC, ABD, BCD are significant model terms. Table 4 also showed the ANOVA result of the overall Model (Model F-value of 2655.46). This 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.

In fitting the multivariate model, the most obvious choice for a mathematical description of the experimental data was factorial model because it involves multivariate analysis showing the

interaction among the variables. The full factorial model equation relating the significant model terms with one another obtained by the analysis of the experimental data for the removal of 4-NP by NPZAC is given by equation 2

$$\text{Removal Efficiency (\%)} = +80.24 - 11.75A + 13.06B + 2.78C + 3.96D + 8.22AB + 1.68AC + 0.98AD - 1.49BC - 0.36BD - 0.26CD - 1.58ABC + 0.88ABD + 0.49BCD \text{ -----(2)}$$

The diagnostic checks revealed that runs 1, 4, 17 and 26 were marked as outlier and so, they were excluded from the analysis. Figure 7a shows the normal probability plot of the removal efficiency of NPZAC photocatalyst. This was done to confirm the accuracy of the statistical model. The result shows that the residual points distribution

were normal giving rise to a straight line plot, which confirms the reliability of the model terms (Mansouriieh *et al.*, 2015). Shown in Figure 7b is the predicted vs actual plot. The plot 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

Table 4:ANOVA for the factorial model for the catalytic removal of 4-NP by NPZAC

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remarks
Model	11166.80	13	858.98	2655.46	<0.0001	Significant
A	2209.94	1	2209.94	6831.78	< 0.0001	
B	2730.59	1	2730.59	8441.30	< 0.0001	
C	123.99	1	123.99	383.30	< 0.0001	
D	251.38	1	251.38	777.12	< 0.0001	
AB	1081.09	1	1081.09	3342.08	< 0.0001	
AC	45.02	1	45.02	139.19	< 0.0001	
AD	15.44	1	15.44	47.75	< 0.0001	
BC	35.70	1	35.70	110.36	< 0.0001	
BD	2.09	1	2.09	6.45	0.0218	
CD	1.05	1	1.05	3.25	0.0904	
ABC	39.69	1	39.69	122.70	< 0.0001	
ABD	12.46	1	12.46	38.52	< 0.0001	
BCD	3.90	1	3.90	12.06	0.0031	
Curvature	775.93	1	775.93	2398.71	< 0.0001	
Pure Error	5.18	16	0.32			
Cor Total	11947.91	30				significant

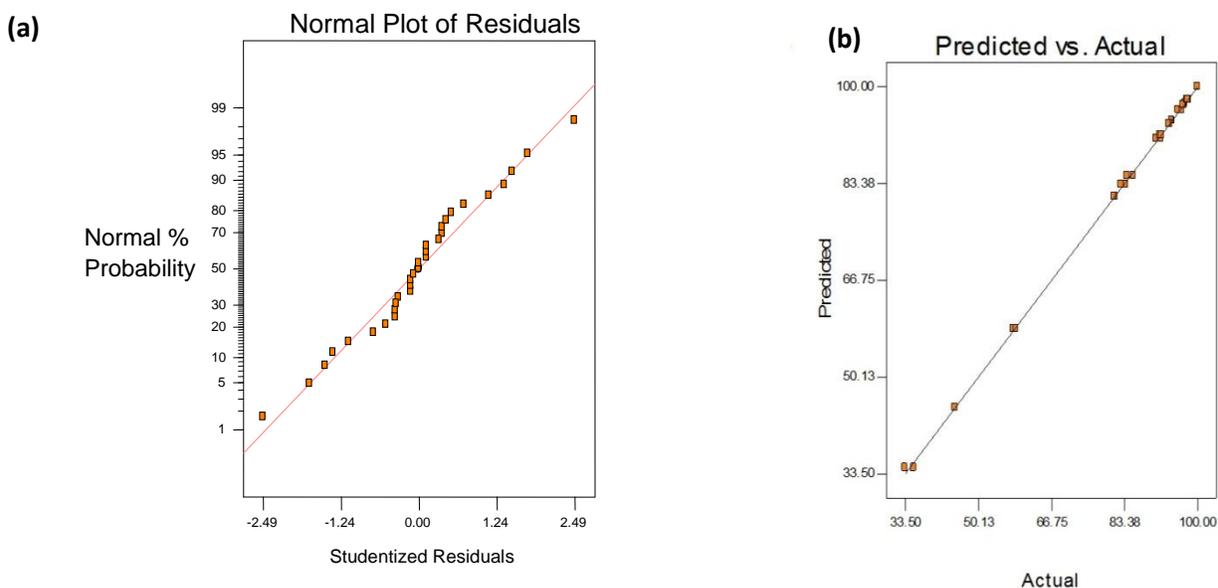


Figure 7: Diagnostic plots: (a). Normal distribution plot

(b) Predicted value vs. actual value

Effect of the interaction of variables on the removal of 4-NP by NPZAC

A) Initial PNP Concentration and Catalyst Loading: Presented in Figure 8 is the interaction plot showing the interaction effect of initial 4-NP concentration and the catalyst loading on the removal efficiency of NPZAC for 4-NP. The result showed that the interaction of both variables had effect on the removal efficiency. An increase in catalyst loading produced a corresponding increase in removal efficiency while an increase in initial 4-NP concentration resulted in a decrease in removal efficiency. This implies that if initial 4-NP concentration and catalyst loading were the only factor affecting the removal process, then catalyst loading would be the most critical factor. Approximately 97 % removal efficiency was achieved at pH 7, 90 min contact time, 0.50 g catalyst loading and 10 mg/L initial 4-NP concentration.

(B) Catalyst Loading and Solution's pH: Figure 9 is the interaction plot showing the effect of catalyst loading and pH on removal efficiency of NPZAC for 4-NP. The effect of change in pH was very small while increase in catalyst loading produced a significant change. A removal efficiency of 94.60% was achieved at 0.50 g catalyst loading, pH 11, 30 mg/L initial 4-NP concentration and 90 min contact time. By implication, if catalyst loading and pH were the only parameters affecting the removal process, then, catalyst loading would still be the most critical factor.

(C) Catalyst Loading and Irradiation Time: The interaction plot showing the effect of catalyst loading and contact time on the removal efficiency of NPZAC for 4-NP is shown in Figure 10. The result obtained shows that the interaction between the two factors produced a significant increase in the removal efficiency. However, the result showed that increase catalyst loading produced the most

significant effect on the removal process which further confirmed it as the most critical factor in the process. The highest removal efficiency for

this interaction was 96.91 % at 0.50 g catalyst dosage, 150 min contact time, pH 7 and 30 mg/L initial 4-NP concentration.

(D) Interaction Effect of Three Variables on the Photocatalytic Removal of 4-NP by NPZAC

Shown in Figure 11 is the cube plot for the effect of interaction of the most significant factors (initial 4-NP concentration, catalyst loading and contact time) for the removal of 4-NP by NPZAC-0.15 photocatalyst. The results showed that for the interaction of these three variables at pH 7, a removal efficiency of 98.57 % was achieved at 10

mg/L initial 4-NP concentration, 0.5 g catalyst loading, and 150 min catalyst loading (A-, B+, D+). A closer look at the interaction shows that increase in the catalyst loading have the strongest influence among the factors while increase in contact time is also capable of enhancing it further.

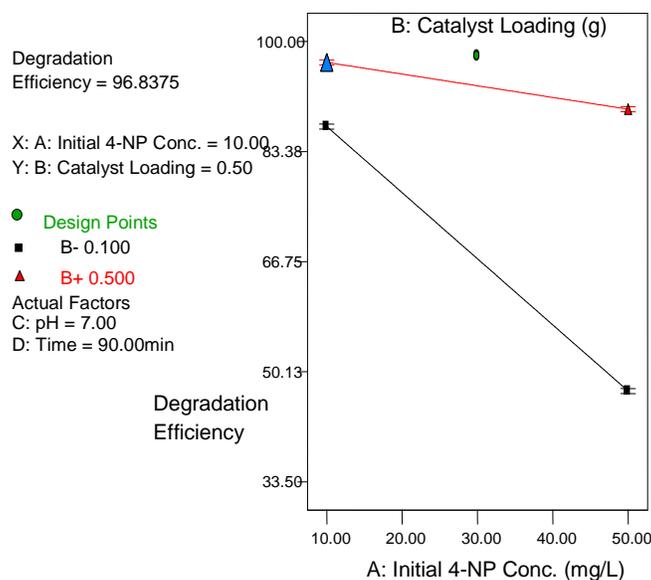


Figure 8: Interaction effect of initial 4-NP concentration and catalyst loading on the removal of efficiency of NPZAC

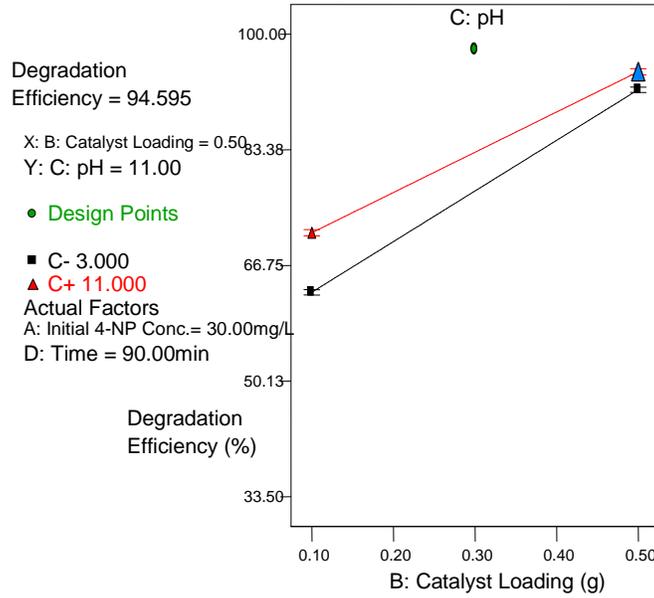


Figure 9: Interaction effect of Initial 4-NP concentration and pH on the removal of efficiency of NPZAC

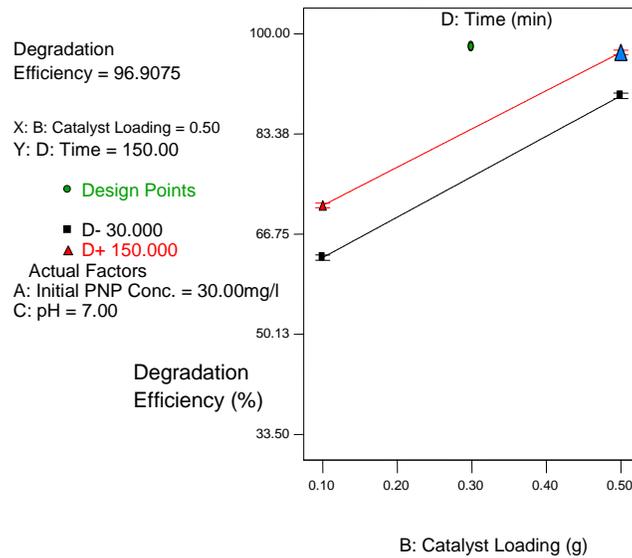


Figure 10: Interaction effect of catalyst loading and irradiation time on the removal of efficiency of NPZAC

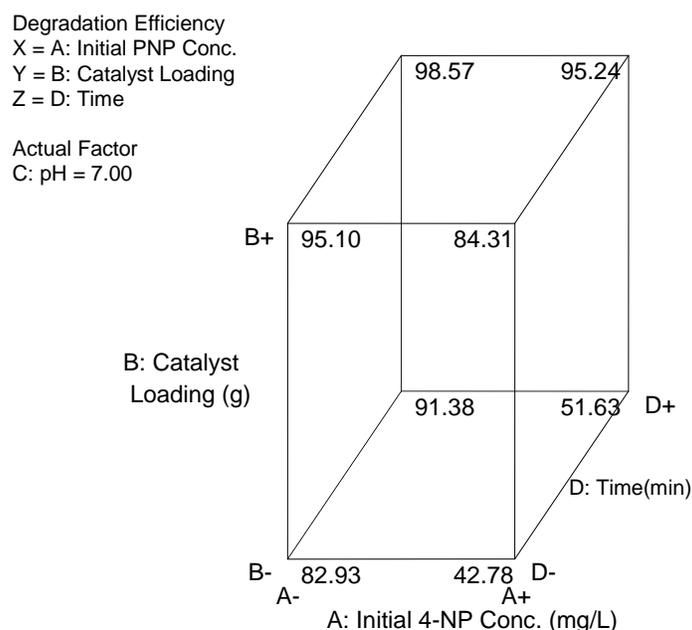


Figure 11: Interaction effect of initial concentration, catalyst loading and time on the removal efficiency of 4-NP by NPZAC.

Reusability of the NPZAC Photocatalyst

Presented in Figure 12 are the results of the removal of 4-NP using 10 mg/L initial PNP concentration, 0.5 g catalyst dosage, pH 11 and 150 min contact time carried out five times using the NPZAC catalyst recovered from the preceding experiments. The results of the analysis showed that there was no appreciable decrease in the photocatalyst activity of NPZAC for all the cycles. This indicates that NPZAC prepared in this work is reusable. The study could not go beyond the fifth cycle because the amount of catalyst at that level became so small, thereby making the study for more cycles difficult.

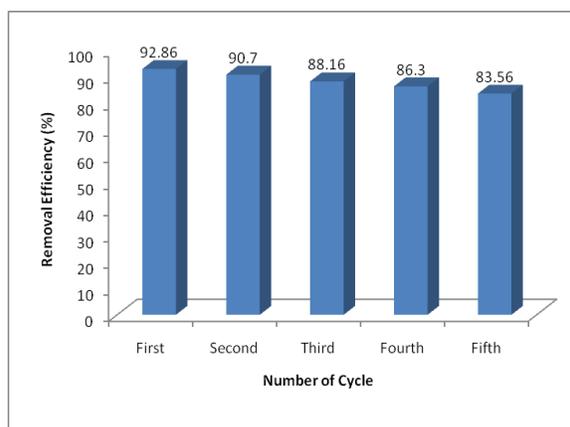


Figure 12: The Reusability Potential of NPZAC composite obtained at 50 mg/L initial 4-NP concentration, 0.5 g catalyst loading, pH 11 and 150 min contact time

CONCLUSION

Nitrogen-phosphorus co-doped ZnO-activated carbon was successfully prepared, characterized and used for removal of 4-NP. The study revealed

that the doping process increased the photocatalytic activity of ZnO by a factor of 0.35 (35 %) and addition of activated carbon support increased it further to a factor of 1.82 (182 %). This showed that there was a positive synergistic effect of doping and activated carbon support on the photocatalytic activity of ZnO. The results of the statistical experimental design using full factorial model at two levels and four factors revealed that catalyst loading is the most critical factor affecting the removal efficiency of NPZAC. This study also revealed that the optimum removal value of 100 % was achieved at low initial 4-NP concentration (10 mg/l), high catalyst loading (0.5 g), high pH (11) and long irradiation time (150 min). Finally, the reusability test revealed that NPZAC is reusable even up to five times.

REFERENCES

- Abdollahi, Y., Abdullah, A. H., Zainal, H., and Yusof, N. A.** (2012). Photocatalytic Degradation of *p*-Cresol by Zinc Oxide under UV Irradiation. *International Journal of Molecular Science*, 13, 302-315; doi:10.3390/ijms13010302
- Abdullah, A.M., Al-Thani, N.J., Tawbi, K., and Al-Kandari, H.** (2016). Carbon/nitrogen-doped TiO₂: New synthesis route, characterization and application for phenol degradation. *Arabian Journal of Chemistry*, 9, 229–237. doi: 10.1016/j.arabjc.2015.04.027
- Benhebal, H., Chaib, M., Salmon, T., Geens, J., Leonard, A., Lambert, S.D., and Heinrichs, B.** (2013). Photocatalytic Degradation of Phenol and Benzoic Acid Using Zinc Oxide Powders prepared by sol-gel process. *Alexandria Engineering Journal*, (52), 517-523. doi: 10.1016/j.aej.2013.04.005
- Deka, P., Bhattacharjee, D., Sarmah, P., and Bhardi, P.** (2016). Catalytic reduction of water contaminant “4-nitrophenol” over manganese oxide supported Ni nonparticles. In F. Kurisu (Ed), *Trends in Asian water environmental, science and technology*. New delhi: Capital Publishing Company.
- El-Sheikh A.H., Newman A. P., Al-Daffaee, H., Phull, S., Cresswell, N., and York, S.** (2004). Deposition of anatase on the surface of activated carbon. *Surface Coat Technology*, 187(2–3), 284–92. doi: 10.1016/j.surfcoat.2004.03.012
- Faal H. N. and Farzaneh, F.** (2006). Synthesis of ZnO nanocrystals with hexagonal (wurtzite) structure in water using microwave irradiation. *Journal of Science, Islamic Republic of Iran*, 17(3), 231-234.
- Gionco, C., Fabbria, D., Calza, P., and Paganini, M.C.** (2016). Synthesis, characterization, and photocatalytic tests of N-doped zinc oxide: a new interesting photocatalyst. *Journal of Nanomaterials*, 1-8. doi: 10.1155/2016/4129864
- Ibhadon, A.O., and Fitzpatrick, P.** (2013). Heterogeneous photocatalysis: recent advance and applications. *Catalysis*, 3, 189-218; doi:10.3390/catal3010189
- Jain, A.K. Sharma, S., and Ameta, R.** (2015). Enhanced photocatalytic activity of N, S-doped titania for degradation of Amaranath. *Merit Research Journal of Environmental Science and Toxicology*, 3(2), 025-030,
- Kashif, N., and Feng, O.** (2009.) Effect of various additives on photocatalytic degradation of 4- nitrophenol. *E-Journal of Chemistry*, 6(S1), S422-S428. doi:10.1155/2009/248548
- Kulkarni, M., and Chaudhari, A.** (2007). Microbial remediation of nitro-aromatic compounds: An overview, *Journal of Environmental Management*, 85(2), 496-512. doi: 10.1016/j.jenvman.2007.06.009
- Lavand, A. B., and Malghe, Y. S.** (2015). Synthesis, characterization and visible light photocatalytic activity of nitrogen-doped zinc oxide nanospheres. *Journal of Asian Ceramic*

- Societies 3 (2015) 305–310. Doi: 10.1016/j.jascr.2015.06.002
- Mansouriieh, N., Sohrabi, M. R., and Khosravi, M.** (2015). Optimization of profenofos organophosphorus pesticide degradation by zero-valent bimetallic nanoparticles using response surface methodology. *Arabian Journal of Chemistry*, article in press.
- Matos, J., Montan, R., Rivers, E., Velasco, J., and Ledezma, G.** (2014). Photocatalytic activity of ZnO-Biochar hybrid composites. *Urasian Chemico-Technology Journal* 16:293-297. doi: 10.18321/ectj16
- Modirshahla, N., Behnajady, M. A., Jangi, O., and Mohammad, R.** (2009). Investigation of the Efficiency of ZnO Photocatalyst in the Removal of p-Nitrophenol from Contaminated Water. *Iran. Journal of Chemical Engineering*, 28(1), 49-55.
- Mondal, K., and Sharma, A.** (2014). Photocatalytic oxidation of pollutant dyes in wastewater by TiO₂ and ZnO nano-materials – A mini-review. In A. Misra, J. R. Bellare (Eds), *Nanoscience & Technology for Mankind* (pp.36-72). Allahabad: The National Academy of Sciences India (NASI).
- Muthirulan, P., Meenakshisundaram, M., and Kannan, N.** (2013). Beneficial role of ZnO photocatalyst supported with porous activated carbon for the mineralization of Alizarin Cyanin Green dye in aqueous solution. *Journal of Advanced research*, 4(6), 479-484. doi: 10.1016/j.jare.2012.08.005
- Neppolian, B., Sakthivel, S., Palanichamy, M., Banumathi, A., and Murugesan, V.** (1999). Degradation of Textile Dye by Solar Light Using TiO₂ and ZnO photocatalysts. *Journal of Environmental Science*, 34 (9), 18-29. doi: 10.1080/10934529909376931
- Panda, N., Sahoo, H., and Mohapatra, S.** (2011). Decolorization of methyl orange using fenton-like mesoporous Fe₂O₃-SiO₂ composite. *Journal of Hazardous Material*. 185: 359–365. doi:10.1016/j.cej.2012.02.077
- Rajamanickam, D., and Shanthi, M.**, (2012). Photocatalytic degradation of an organic pollutant by zinc oxide – solar process. *Arabian Journal of Chemistry*, 9(2), S1858–S1868. doi: 10.1016/j.arabjc.2012.05.006
- Shao, G., Wang, F., Ren, T., Liu, Y., and Yuan, Y.** (2009). Hierarchical mesoporous phosphorus and nitrogen doped titania materials: Synthesis, characterization and visible-light photocatalytic activity. *Applied Catalysis B: Environmental*, 92(1-2), 61–67. doi:10.1016/j.apcatb.2009.07.024
- Shifu, C., Wei, Z., Sujuan, Z., and Wei, L.** (2009) Preparation, characterization and photocatalytic activity of N-containing ZnO powder. *Chemical Engineering Journal* (148), 263–269. doi: 10.1016/j.cej.2008.08.039
- Smida, H., and Jamoussi, B.** (2012). Degradation of Nitroaromatic Pollutant by TiO₂/Zinc Phthalocyanine: Study of the influencing factors. *Journal of applied Chemistry*, 2(3): 11-17. Retrieved from <http://iosrjournals.org/iosr-jac/papers/vol2-issue3/C0231117.pdf?id=3048>
- Sobana, N., and Swaminathan, M.** (2007). Combination effect of ZnO and activated carbon for solar assisted photocatalytic degradation of Direct Blue 53. *Solar Energy Materials and Solar Cells*, 91, 727–734. doi:10.1016/j.solmat.2006.12.013
- Sobana, N., Thirumalai, K., and Swaminathan, M.**, (2016). Kinetics of solar light assisted degradation of Direct Red 23 on activated carbon-loaded zinc oxide and influence of operational parameters. *Canadian Chemical Transactions* 2(1), 77-89. doi:10.13179/canchemtrans.2016.04.01.0258
- Stuart, B.** (2004). *Infrared spectroscopy: fundamentals and applications*. Retrieved

from

<http://www.kinetics.nsc.ru/chichinin/books/spectroscopy/Stuart04.pdf>

Sugiyama, M., Salehi, Z., Tokumura, M., Kawase, Y. (2012). Photocatalytic degradation of p-nitrophenol by zinc oxide particles. *Water Science Technology*, 65(10), 1882-1886. doi: 10.2166/wst.2012.080

Takahashi, N., Nakai, T., Satoh, Y., and Katoh, Y. (1994). Variation of biodegradability of nitrogenous organic compounds by ozonation. *Journal of water resources*, 28(11), 1563-1570. doi:10.1016/0043-1354(94)90223-2

Udom, I. Myers, P. D. Ram, M. K. Hepp, A. F., Archibong, A. F., Stefanakos, E. K. and Goswami. D. Y. (2014). Optimization of Photocatalytic Degradation of Phenol Using Simple Photocatalytic Reactor. *American Journal of Analytical Chemistry*, 5, 743-750. Doi: 10.4236/ajac.2014.511083

Velasco, L. F., Parra, J. B., and Ania, C.O. (2010). Role of activated carbon features on the photocatalytic degradation of phenol. *Journal of Applied Surface Science*, 256 (17), 5254–5258. doi: 10.1016/j.apsusc.2009.12.113

Velmurugan, R., and Swaminathan, M. (2011). An efficient nanostructured ZnO for dye sensitized degradation of Reactive Red 120 dye under solar light. *Solar Energy Mater Sol Cells* 95, 942–50. doi: 10.1016/j.solmat.2010.11.029

Welderfael, T., Yadav, O. P., Taddesse, A. M., and Kaushal, J. (2013). synthesis, characterisation and photocatalytic activities of Ag-N-codoped ZnO nanoparticles for degradation of Methyl Red. *Chemical Society of Ethiopia*, 27(2), 221-232. doi:10.4314/bcse.v27i2.7.

Yi, S., Zhuang, W.Q., Wu, B., Tay, S.T., and Tay, J.H. (2006). Biodegradation of p-nitrophenol by aerobic granules in a sequencing batch reactor. *Journal of Environmental Science Technololy*, 40(7), 2396–2401. Available from <https://www.ncbi.nlm.nih.gov/pubmed/16646480>