Novel Immobilized Titanium dioxide onto Peanut shell-based activated Carbon for Advance Oxidation Process coupled with response surface models in organic wastewater treatment.

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By

Kingsley Safo

MSc. Research Student

Department of Chemical and Petrochemicals Engineering, Egypt-Japan University of Science and Technology (E-JUST), New Borg Al-Arab city, Alexandria, Egypt.

kingley.safo@ejust.edu.eg

Authors

Kingsley Safo
Mavis Berko
Hillarus Dela Gohoho

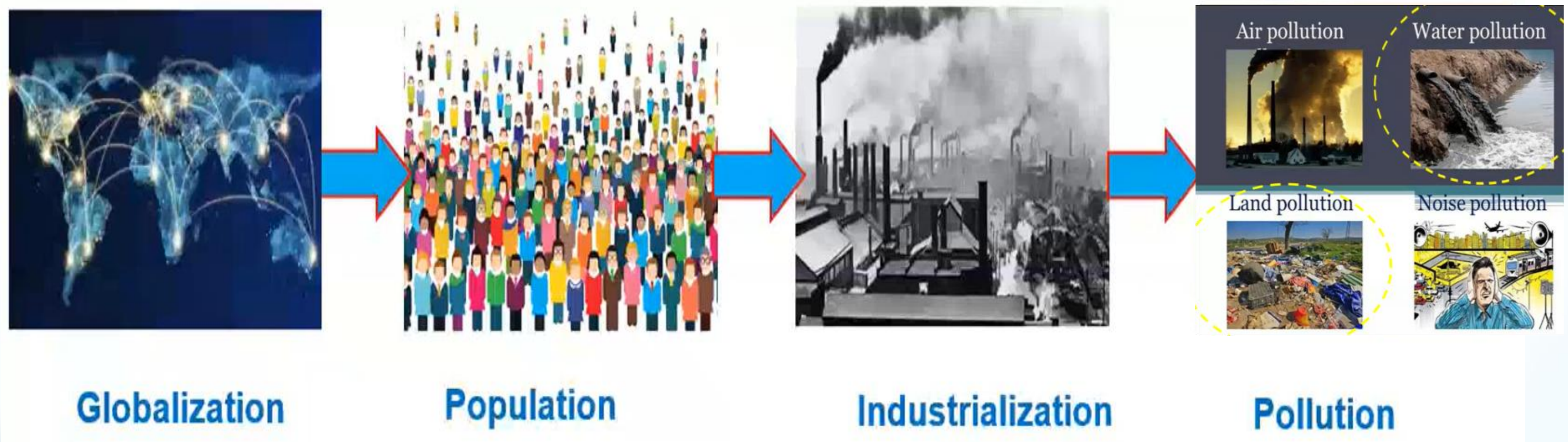
Presentation Outline

- ❖ **Introduction and Background**
- ❖ **Objective of the Study**
- ❖ **Experimental Works**
- ❖ **Results and Discussion**
- ❖ **Contribution of the Research Work to the World**

Introduction

The annual increase in the global population resulting in the high demand for clean and potable water for both domestic and industrial activities which conforms to Goal number 6 of the Sustainable development Goals (SDGs) by the United Nations.

Discharging of toxic and harmful substances in the water bodies and the environment endangers both human life and the ecosystem.



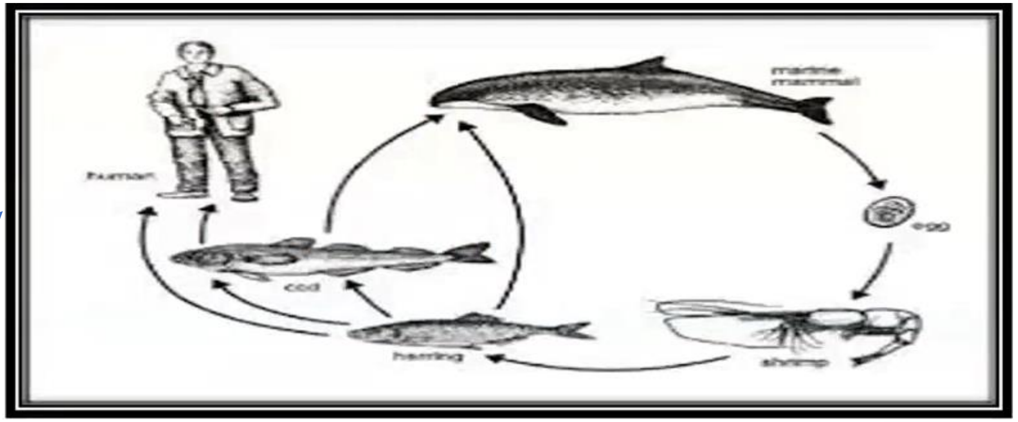
K. Safo, H. Noby, M. Matatoshi, and H. Naragino, "Statistical optimization modeling of organic dye photodegradation process using slag nanocomposite," *Res. Chem. Intermed.*, no. 0123456789, 2022, doi: 10.1007/s11164-022-04807-5.

Introduction Cont'd

- There are problems with waste disposal that arise before, during, and after industrial and agricultural processing.
- Several developing nations have poor waste management systems and generate enormous volumes of this kind of trash.
- Inadequate action to mitigate the resultant dangers might have disastrous consequences.
- Users of water and aquatic life may be placed at danger if these pollutants are washed into water sources.
- Yet, agricultural solid wastes are rich in carbon and might be used as a low-cost and easily accessible carbon adsorbent alternative.

H. D. Gohoho, H. Noby, J. I. Hayashi, and A. H. El-shazly, "Various acids functionalized polyaniline–peanut shell activated carbon composites for dye removal," *J. Mater. Cycles Waste Manag.*, vol. 24, no. 4, pp. 1508–1523, 2022, doi: 10.1007/s10163-022-01408-7.

Introduction Cont'd



T. Shindhal et al., "A critical review on advances in the practices and perspectives for the treatment of dye industry wastewater," Bioengineered, vol. 12, no. 1, pp. 70-87, 2021, doi: 10.1080/21655979.2020.1863034

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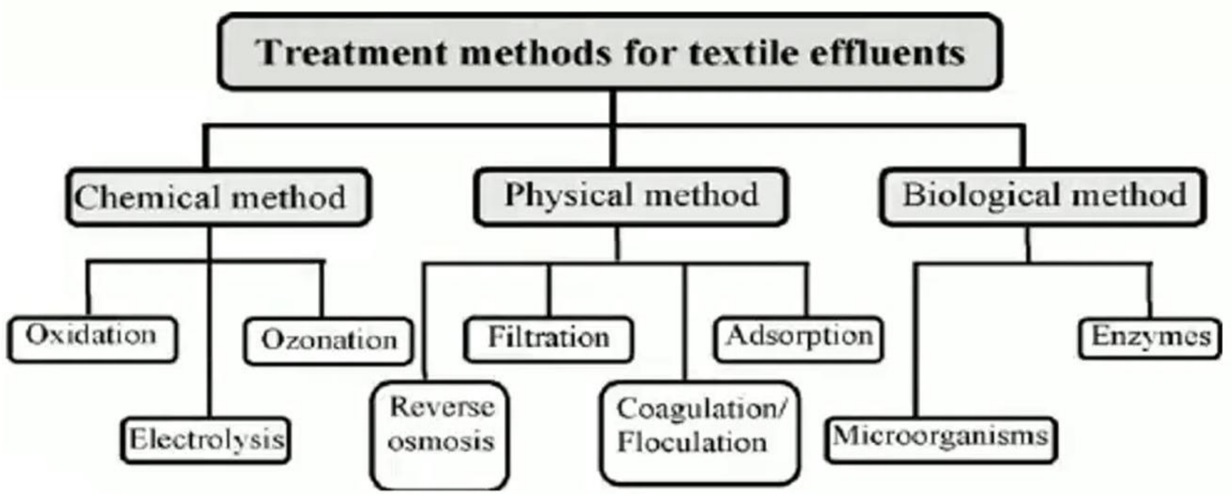

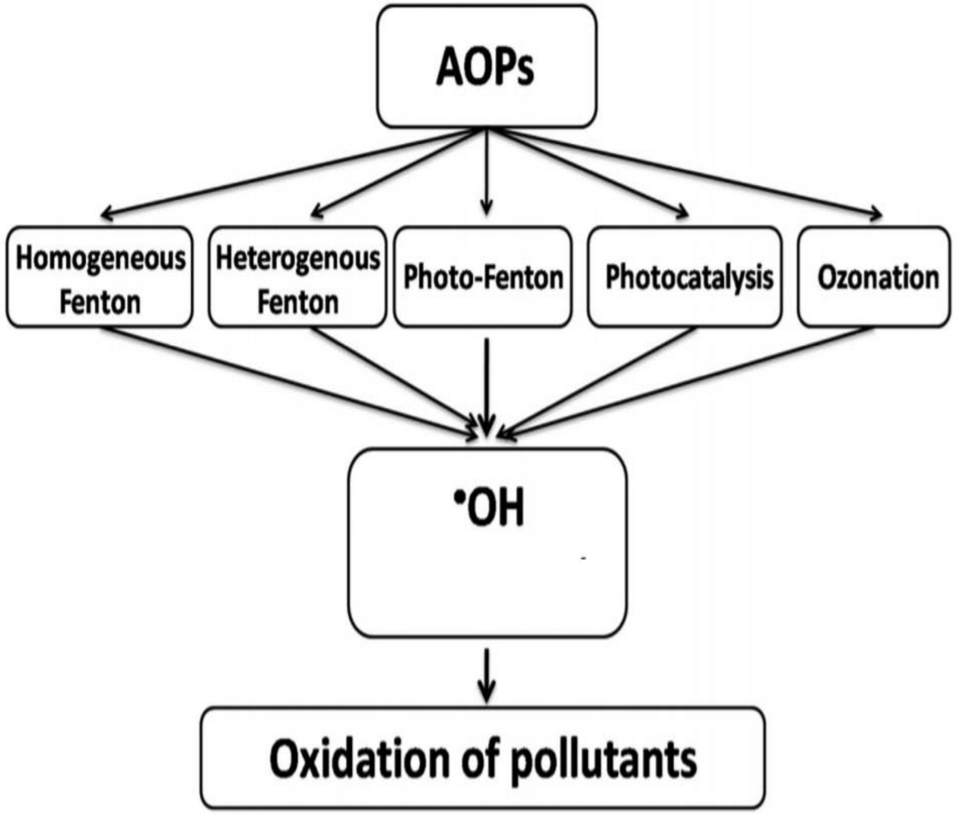

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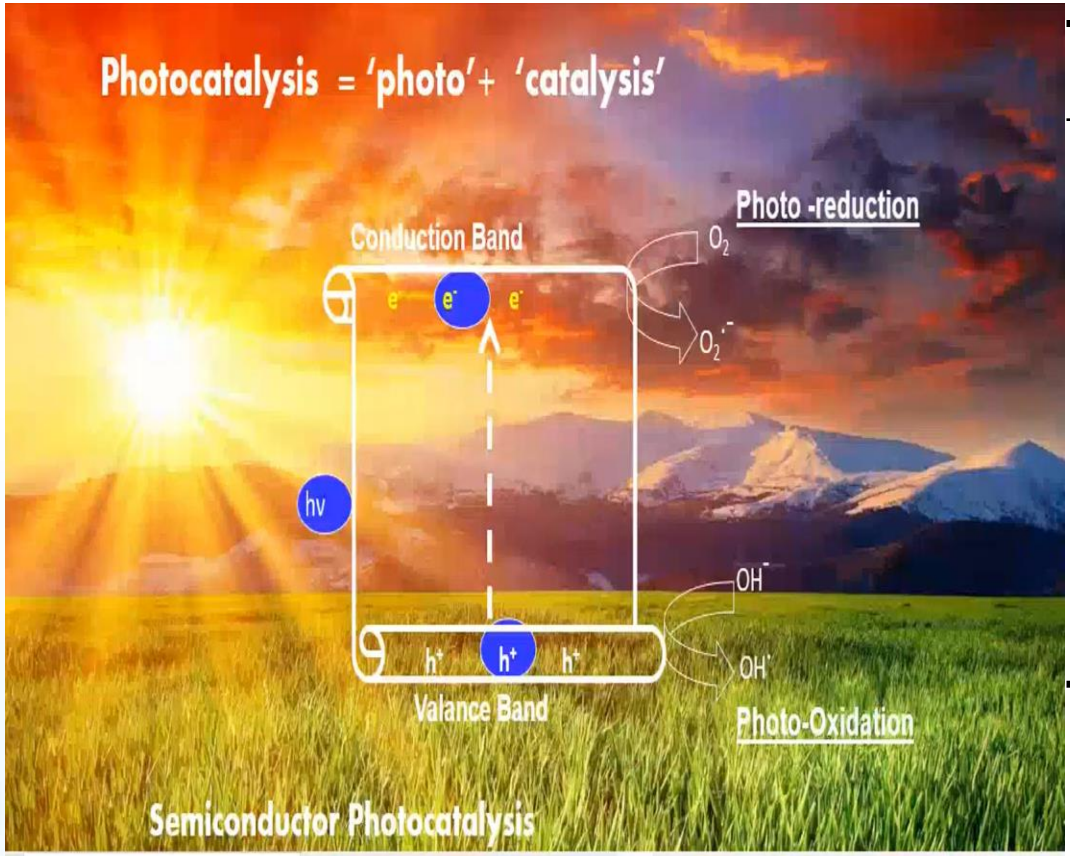
Introduction Cont'd

Photodegradation is a green chemical process that may be accomplished by using free solar light to break down contaminants into nonharmful compounds such as water and carbon dioxide



Photocatalyst	Bandgap (eV)	Photocatalyst	Bandgap (eV)
Diamond	5.4	SnO_2	3.8
Cubic ZnS	3.6	$SrTiO_3$	3.4
ZnO	3.3	TiO_2 (anatase)	3.2
α-Fe_2O_3	3.1	TiO_2 (rutile)	3.0
WO_3	2.8	CdS	2.4
Fe_2O_3	2.2	Cu_2O	2.1
CdSe	1.7	CdTe	1.4
WSe_2	1.2	Si	1.1

K. Safo, H. Noby, M. Matatoshi, H. Naragino, and A. H. El-Shazly, "Solvothermal Prepared Slag Nanocomposite as a Catalyst for Organic Dye Photodegradation," Key Eng. Mater., vol. 931, pp. 125–130, Sep. 2022, doi: 10.4028/p-u25360.

Introduction Cont'd

The need for modification of TiO_2

1. Due to its large Bandgap,

2. Is very expensive,

3. Take so much time for degradation under visible light,

4. Low reusability, Conventional TiO_2 powder catalysts present the disadvantages of agglomeration and of difficult separation of the final particle-fluid for the catalyst recycling

5 . Low photostability

Objective of the Study

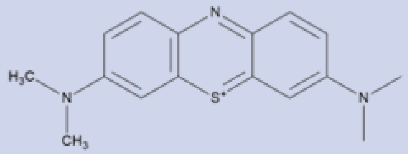
- To successfully convert agriculture waste (peanut shell) into activated carbon using the top-down approach (ACPNS)
- To immobilize TiO_2 nanoparticles onto the activated carbon at a mass ratio of 1:3.
- To successfully Characterize the prepared materials.
- To study the photodegradation ability of the Prepared photocatalyst on MB dye under a simulated solar photoreactor using the Box-Behnken Design Model in Response surface methodology (RSM).
- To evaluate the stability and reusability of the immobilized ACPNS-TiO_2
- To study the transformation product of the degradation process using LCMS

Experimental Work

1. The agriculture waste (peanut shell) in Egypt was used in this study

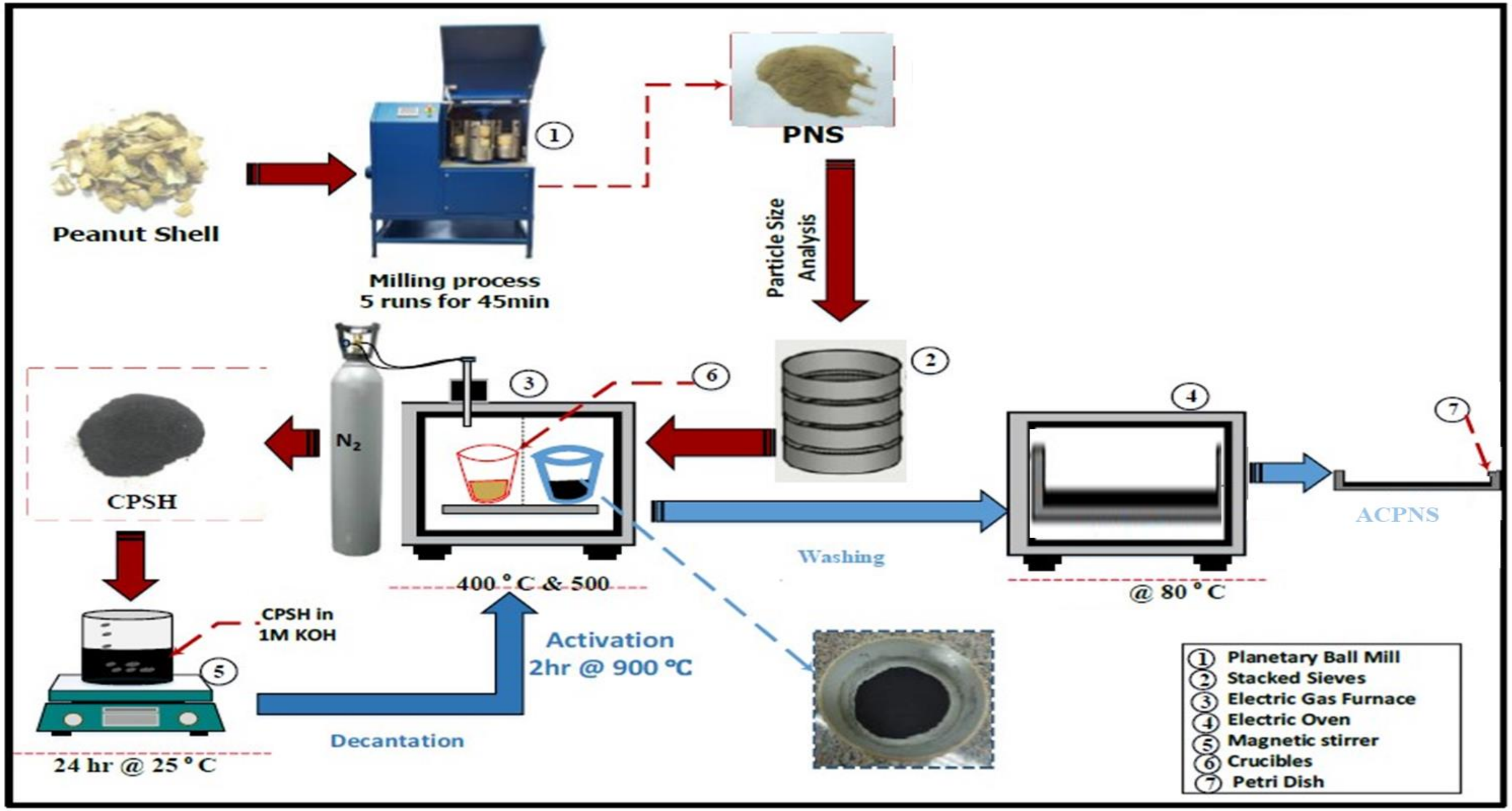
2. KOH, NaOH, and HCl, purchased from Fisher Scientific Company UK was used for the research

3. Methylene Blue (MB) dye with the characteristics below is used for these studies

Pollutant	Molecular Formula	λ_{max} (nm)	Molar Weight	Molecular Structure
Methylene Blue (MB) dye	$C_{16}H_{18}ClN_3S$	663	319.85	

Experimental Work Cont'd

❖ **Synthesis of the Activated Carbon Peanut Shell (ACPNS)**



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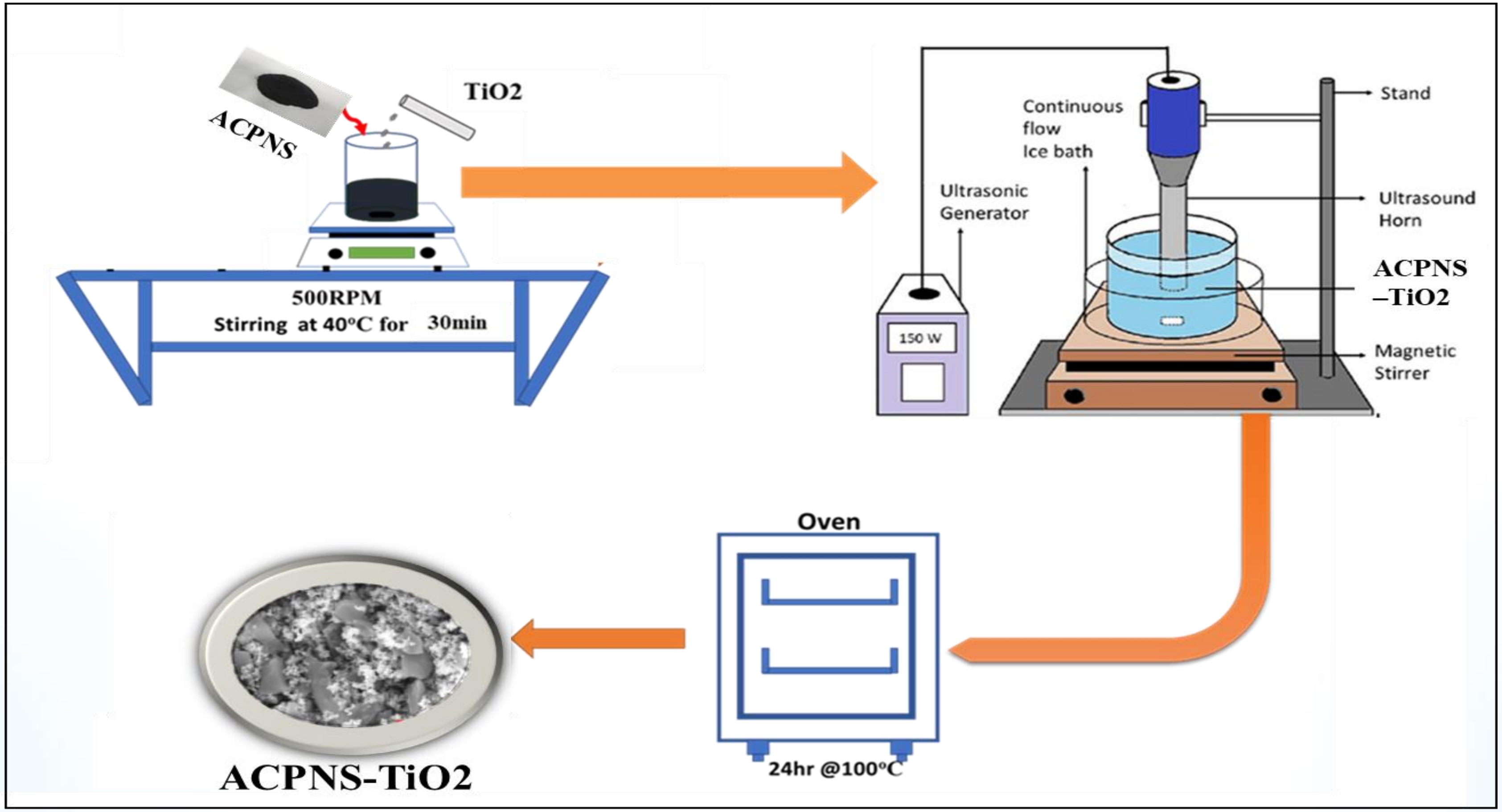
Experimental Work Cont'd

❖ **Synthesis of the ACPNS-TiO2**



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Experimental Work Cont'd

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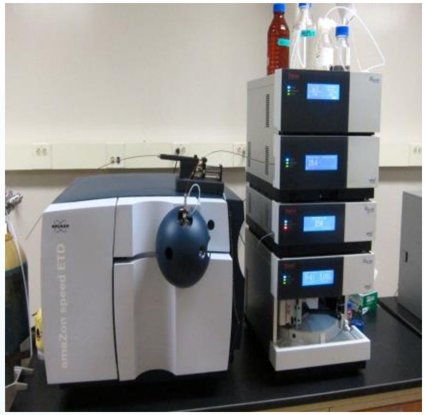
❖ **Characterization of the prepared Materials**

1. TEM & EDX

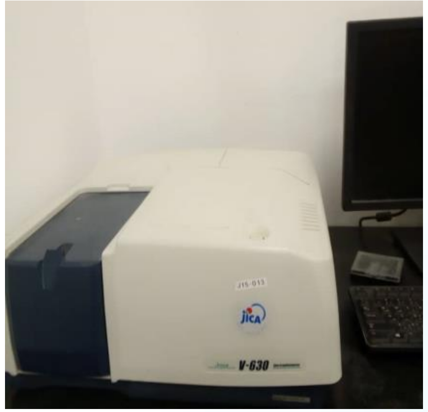
2. SEM

3. FTIR



4. LCMS

5. XRD



6. UV-Vis MS

Experimental Work Cont'd

❖ Response Surface Methodology for Optimization Study

1. RSM was used to optimize the photodegradation of MB wastewater using BBD with three operating variables: A; ACPNS-TiO2 dosage, B; pH, C; MB concentration

Factors			Levels		
Name	unit	Label	Lowest value -1	Median value 0	Highest Value +1
ACPNS-TiO_2 dosage	mg/L	A	10	35	60
pH		B	2	7	12
MB Concentration	ppm	C	10	30	50

Experimental Work Cont'd

❖ **Response Surface Methodology for Optimization Study Cont'd**

2. The optimization method was carried out using a quadratic Equation below as depicted from the three independent variables

$$Y(\%) = b_0 + \sum_{I=1}^{k} b_I X_I + \sum_{I=1}^{k} b_{II} X_I^2 + \sum_{I=1}^{k-1} \sum_{J=2}^{k} b_{IJ} X_I X_J + \varepsilon \quad \text{.........(1)}$$

Where Y (%) denotes the degradation efficiency, the response variable in the Equation, ε unidentified error constant, b is a set of regression coefficients normally known as constant, and k represents the number of independent variables

Experimental Work Cont'd

❖ **Response Surface Methodology for Optimization Study Cont'd**

3. To calculate the number of experimental runs, the equation below is used

$$TNE = K^2 + K + RCp \quad \text{.........................(2)}$$

Where K is the number of factors, RCp is the replicated number of the center point, and

TNE is the total number of experiments

Experimental Work Cont'd

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❖ Photocatalytic Test

The test was done based on the matrix parameters from the response surface methodology, at varying pH from 2-12 and MB concentration of 10-50ppm under the simulated Solar photo rector at 60 mins reaction time

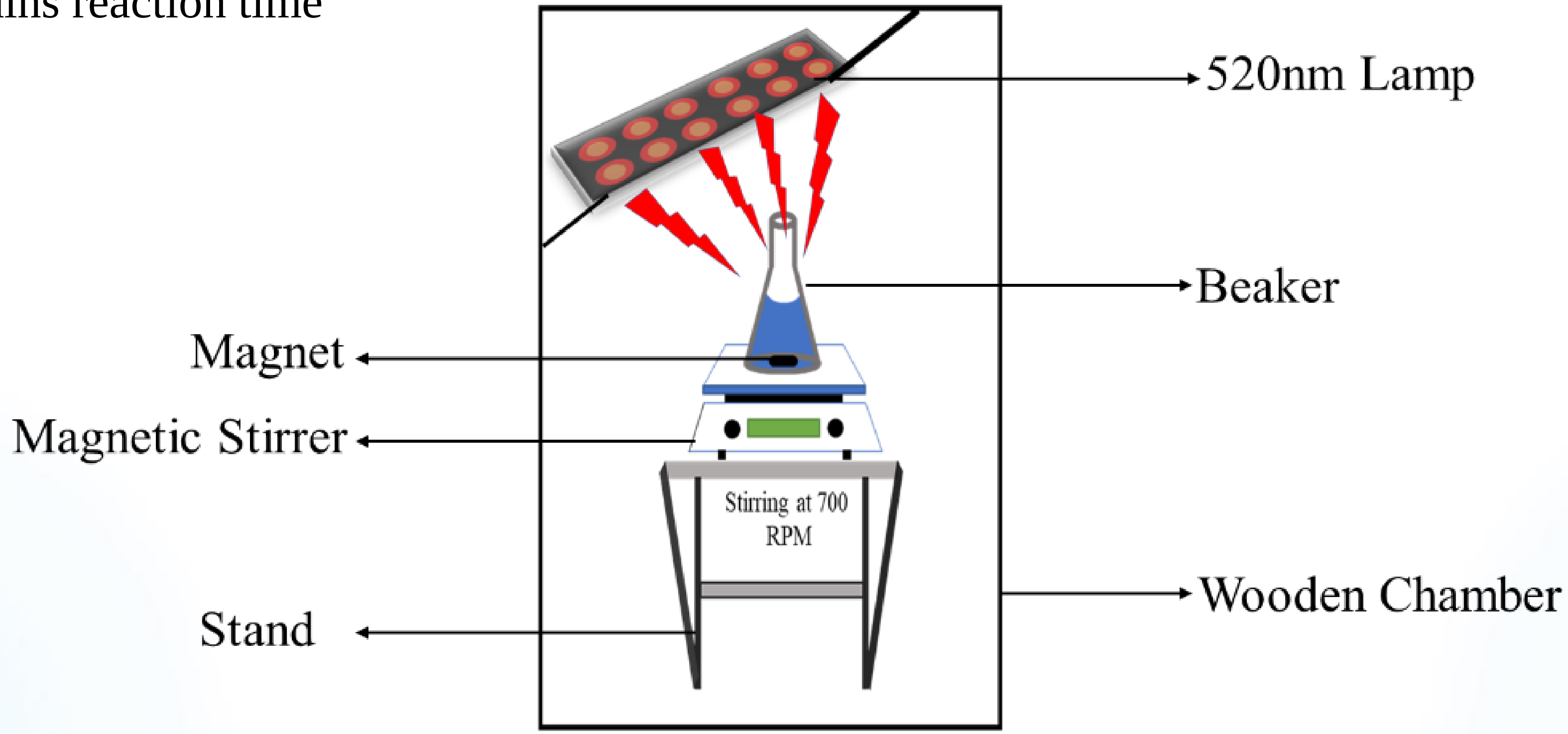


Fig 1. Simulated solar Photo Reactor

Results and Discussion

3.1 Characterization of ACPNS and ACPNS-TiO2

SEM

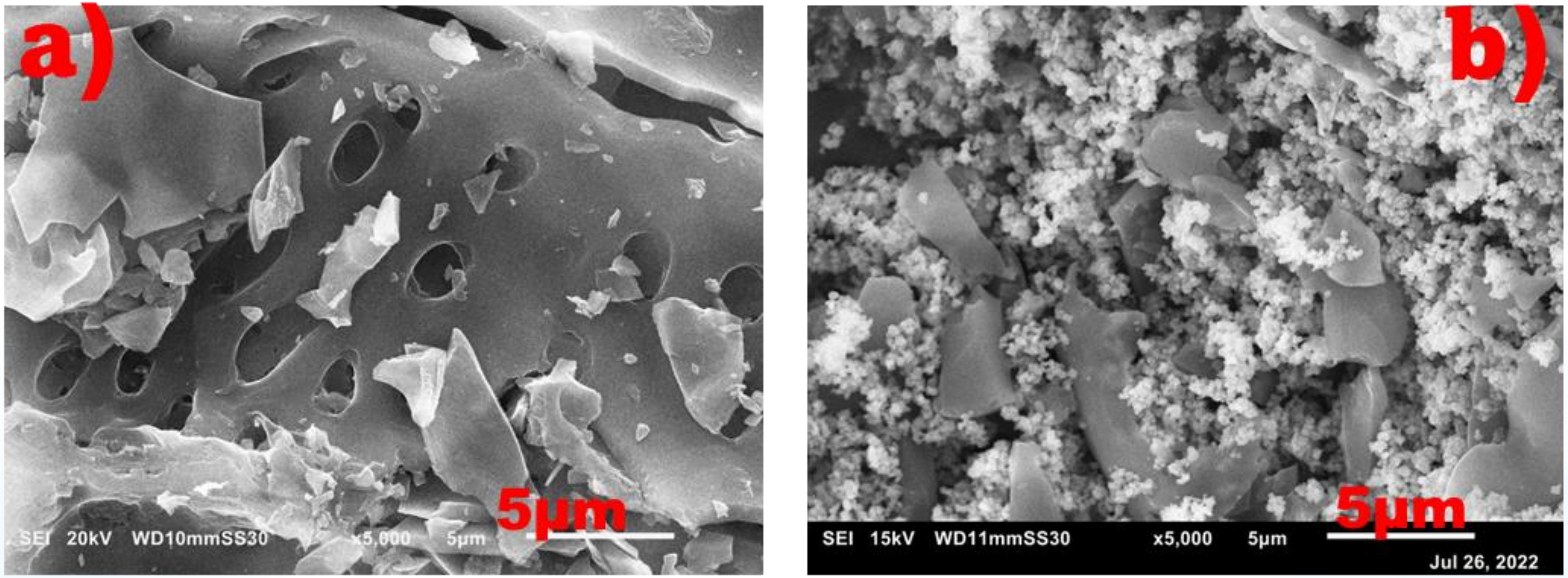
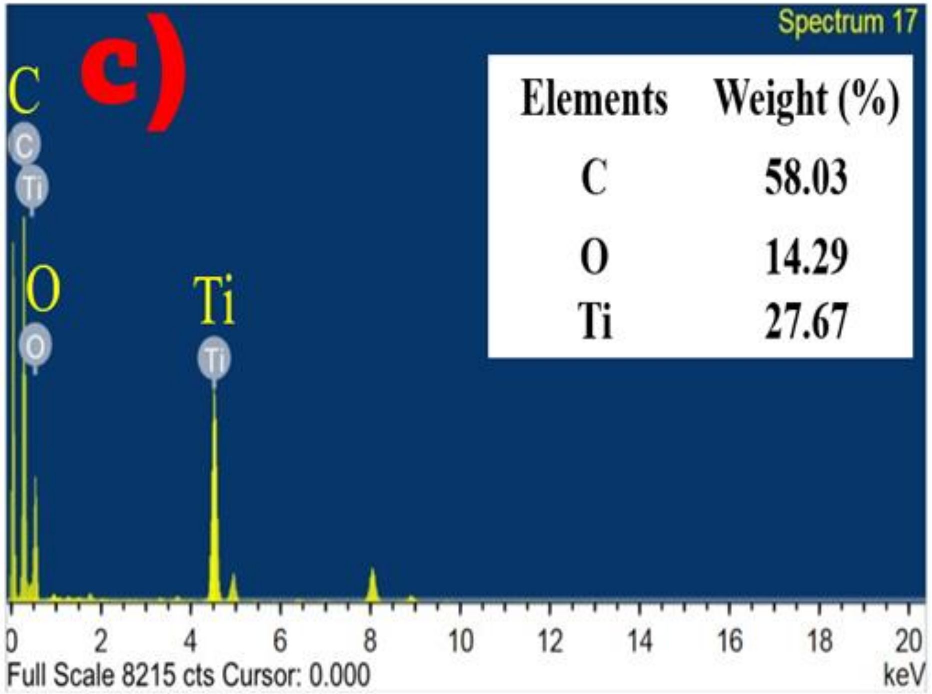


Fig 2. (a) ACPNS and (b) ACPNS-TiO2

Results and Discussion

3.3 Characterization ; ACPNS-TiO2

EDX and TEM



Elements	Weight (%)
C	58.03
O	14.29
Ti	27.67

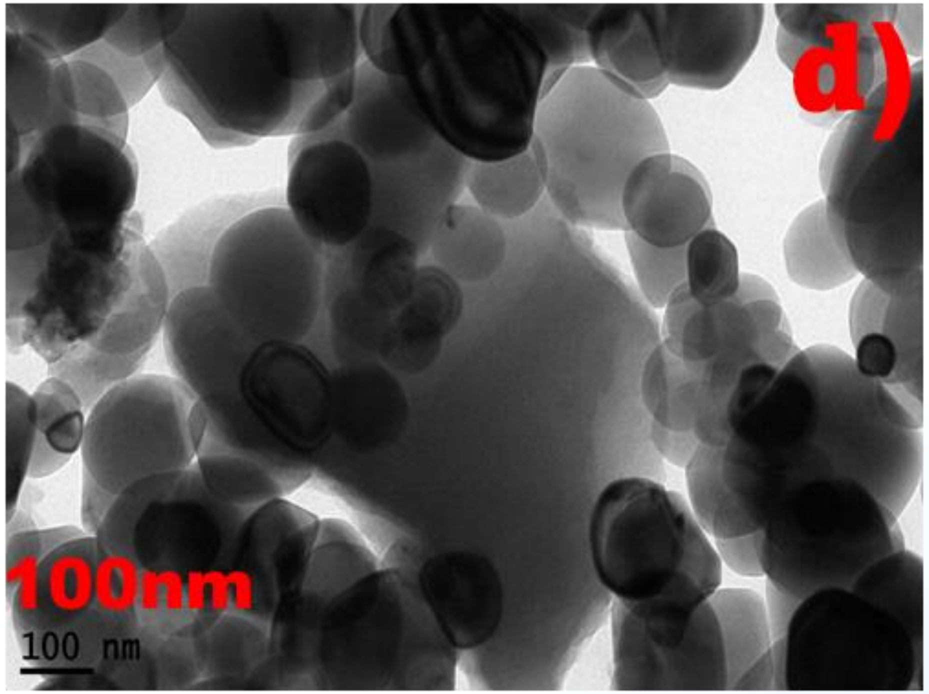


Fig 3. (a) EDX and (b) TEM images of ACPNS-TiO2

Results and Discussion

1.3 Characterization ;

FTIR and XRD

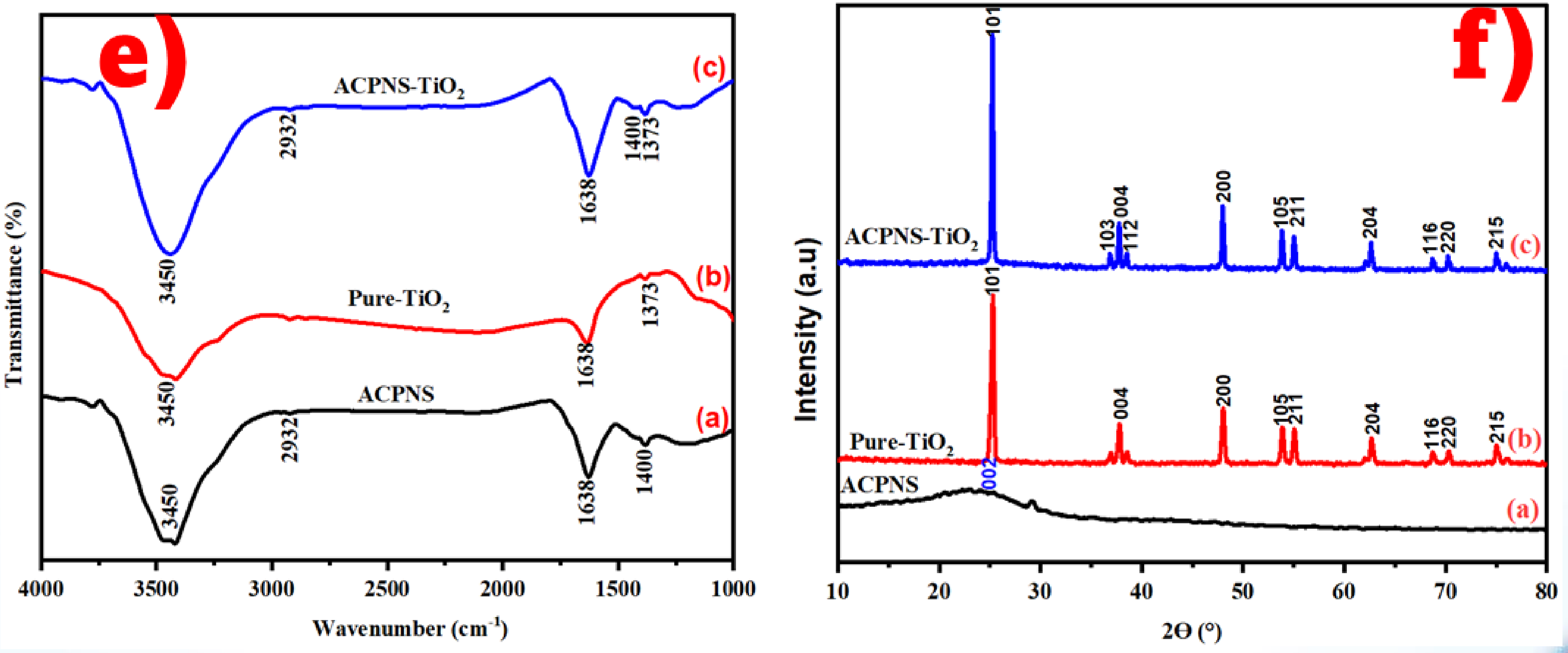


Fig 4. (a) FTIR and (b) XRD images

Results and Discussion

3.4 Experimental Design and Result of the Response Surface Methodology (RSM) Study

Box-Behnken design matrix result for MB degradation efficiency(%) with experimental and predicted values

$$Y(\%) = 79.71+11.60A+13.18B-10.56C-0.13AB-2.78AC-2.72BC-4.76A^2-8.70B^2-10.17C^2$$

Run	Factors (Actual Values)			Degradation Efficiency (%)	
	A(mg/L)	B	C (ppm)	Experimental	Predicted
1	35	12	10	89.56	87.30
2	35	2	50	37.56	39.82
3	10	2	30	43.67	41.34
4	35	7	30	79.87	79.71
5	35	12	50	60.45	60.74
6	35	2	10	55.78	55.49
7	35	7	30	78.45	79.71
8	10	7	50	45.33	45.40
9	60	7	50	65.65	63.03
10	35	7	30	80.22	79.71
11	60	7	10	89.78	89.71
12	35	7	30	78.56	79.71
13	10	7	10	58.34	60.96
14	10	12	30	68.32	67.96
15	35	7	30	81.44	79.71
16	60	2	30	64.43	64.79
17	60	12	30	88.56	90.89

Operating Conditions:
17 Run at 60 mins.

Results and Discussion

3.5 Experimental Design and Result of the Response Surface Methodology (RSM) Study

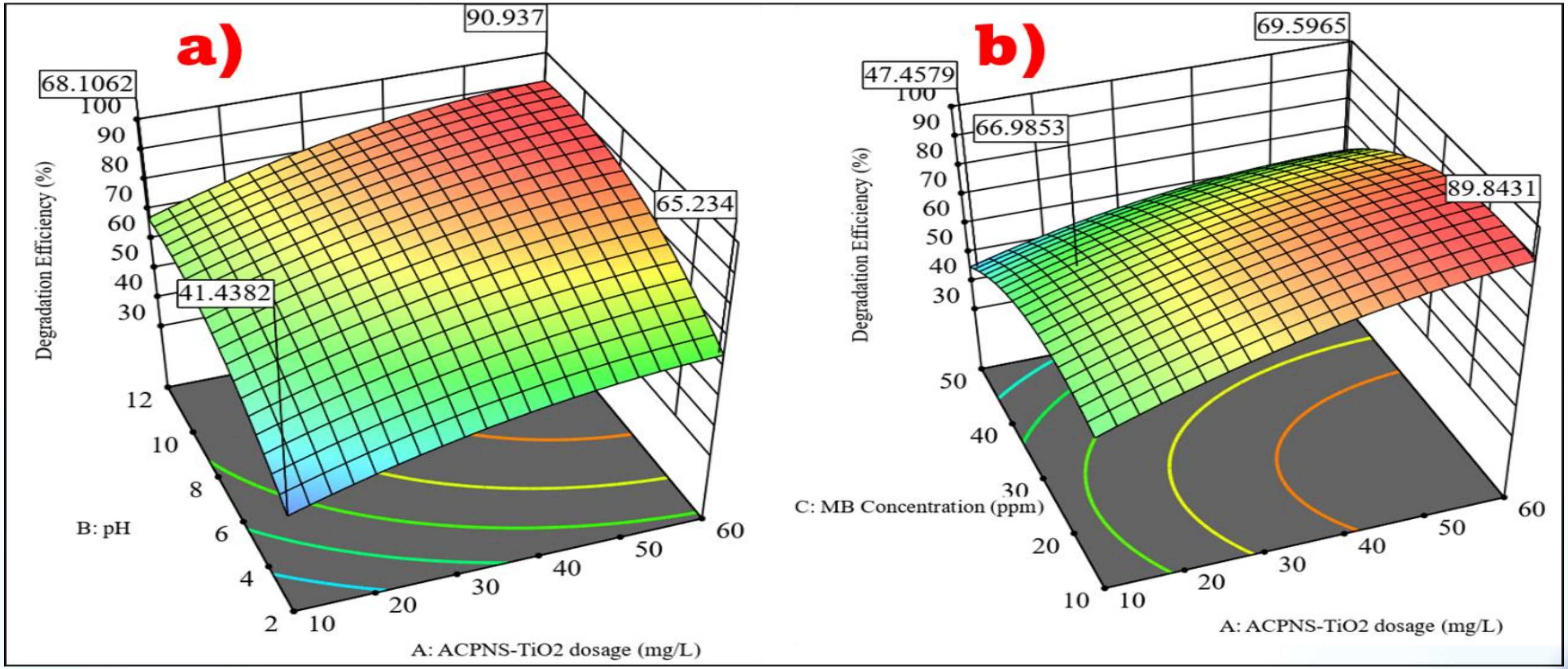
1.2 (ANOVA) Analysis of Variance

Source	Sum of Squares	df	Mean Square	F-Value	P-Value
Model	4356.71	9	484.08	81.81	< 0.0001
A-ACPNS-TiO_2 dosage	1075.55	1	1075.55	181.76	< 0.0001
B-pH	1389.96	1	1389.96	234.89	< 0.0001
C-MB Concentration	891.90	1	891.90	150.72	< 0.0001
AB	0.0676	1	0.0676	0.0114	0.9179
AC	30.91	1	30.91	5.22	0.0562
BC	29.65	1	29.65	5.01	0.0602
A^2	95.51	1	95.51	16.14	0.0051
B^2	318.71	1	318.71	53.86	0.0002
C^2	435.51	1	435.51	73.60	< 0.0001
Residual	41.42	7	5.92		
Lack of Fit	35.23	3	11.74	7.59	0.0
Pure Error	6.19	4	1.55		

ANOVA-result for degradation quadratic models

Results and Discussion

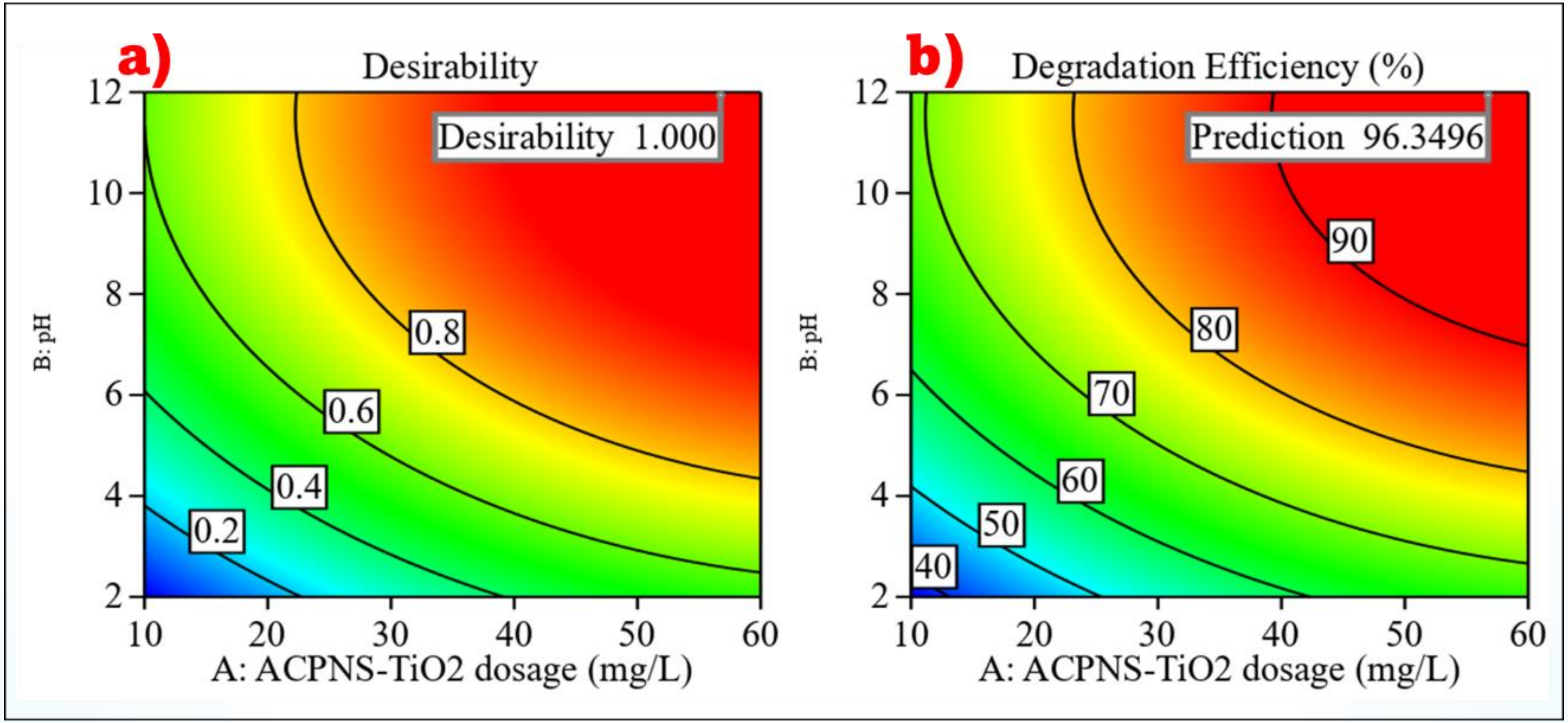
3.6 Effect of ACPNS-TiO2 Dosage (A), B, pH and MB concentration (C) on MB degradation



(a) 3D surface plot, of ACPNS-TiO2 and pH and (b) 3D surface plot og ACPNS0TiO2 and MB Concentration at 60 mins reaction time

Results and Discussion

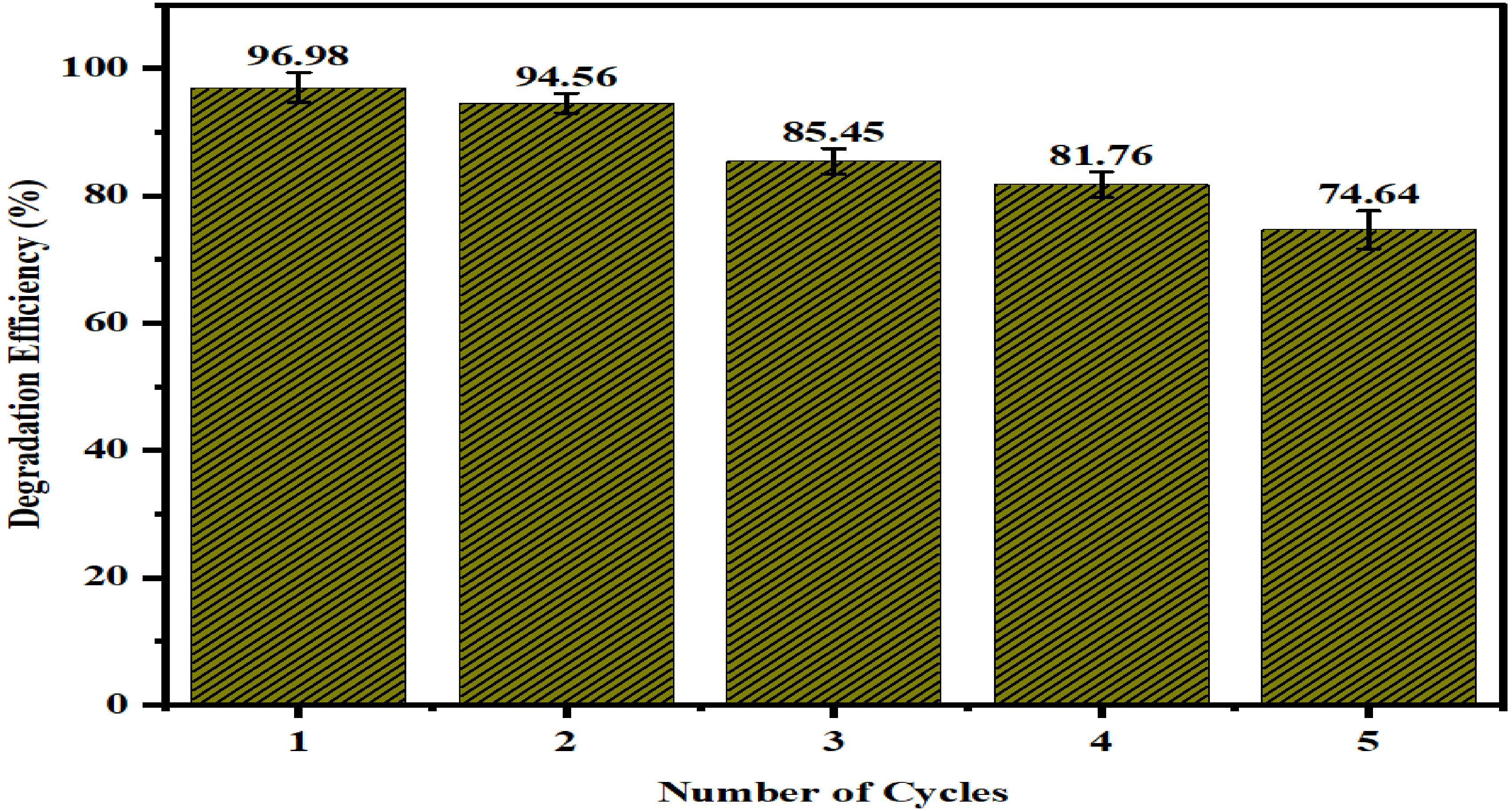
3.7 Numerical Process Optimization



Optimum operating values were pH of 11.9, ACPNS-TiO_2 dosage of 56.75mg/L, and MB concentration of 20.77ppm, time of 60mins with photodegradation efficiency of 96.34%.

Results and Discussion

3.8 Reusability of the ACPNS-TiO2

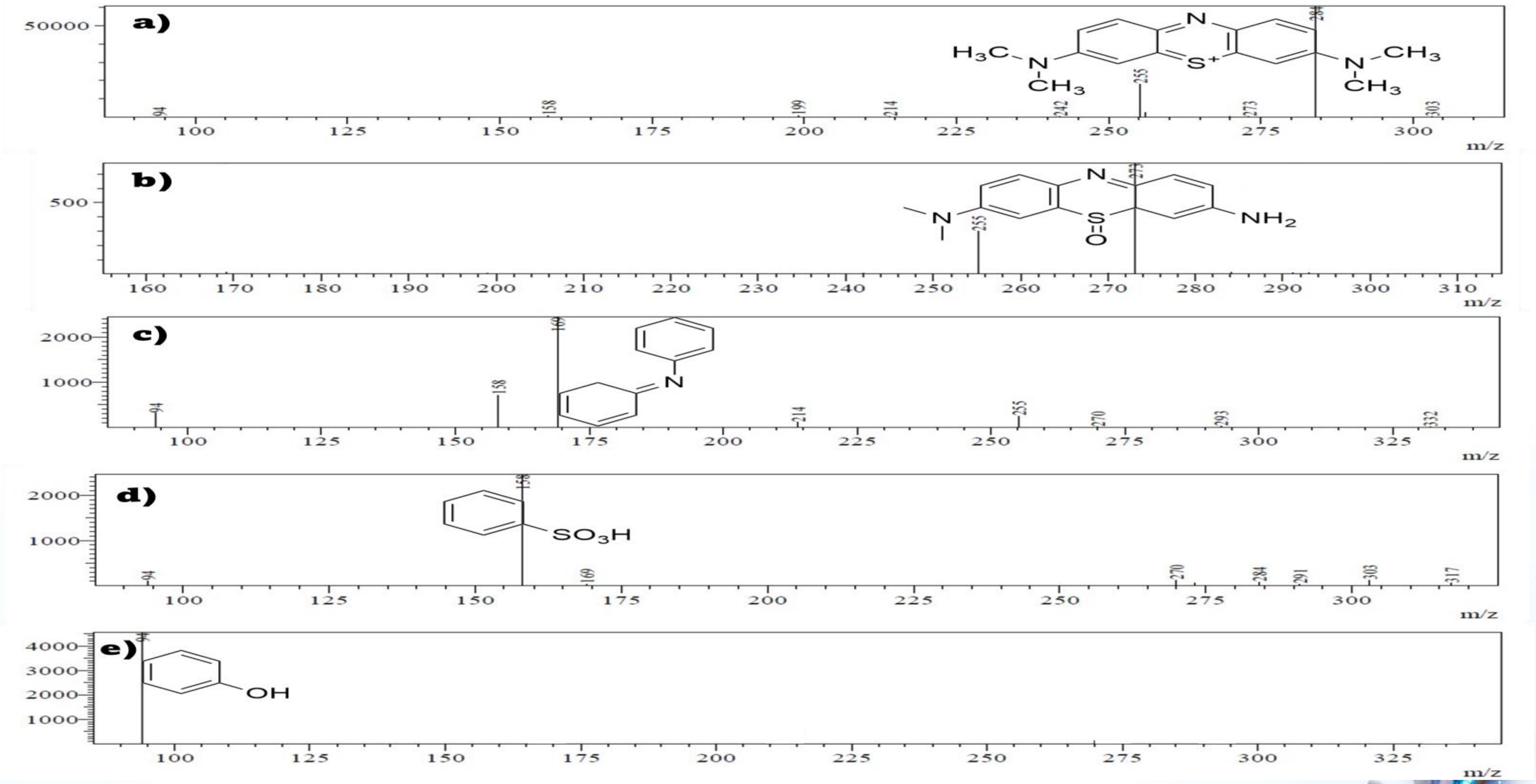


The reusability performance of ACPNS-TiO2 at the optimum conditions

Results and Discussion

3.9 Chromatographical analysis of degradation intermediate of MB using LCMS

Figure S 1. (a, b, c, d, and e). The Mass spectrometry peaks (m/z) of generated reaction intermediate during the photodegradation of MB dye.



Results and Discussion

3.9 Chromatographical analysis of degradation pathway of MB using LCMS

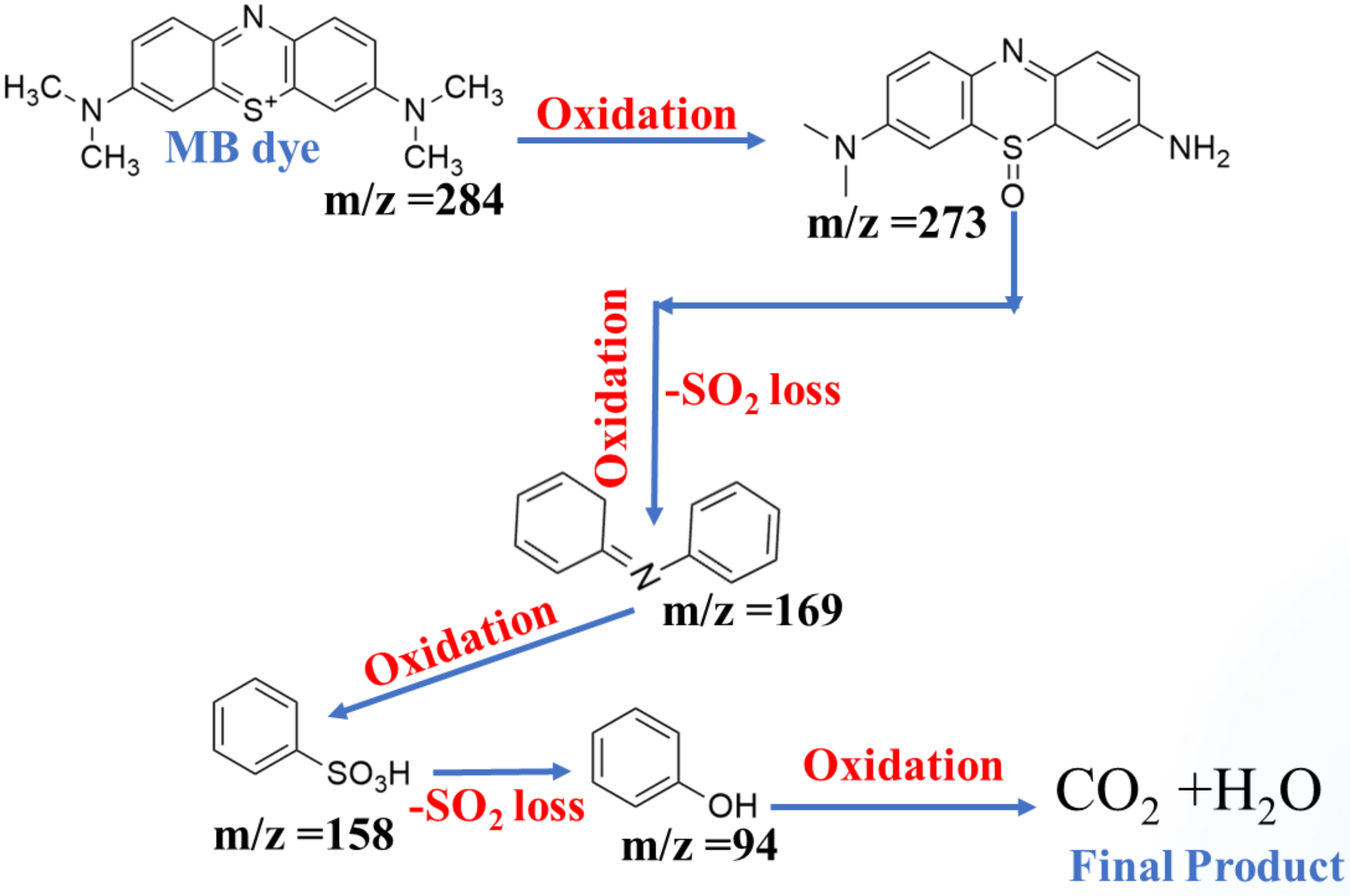


Figure S 2. Identified transformation products and proposed photodegradation pathway of MB dye using ACPNS -TiO_2 nanocomposite catalyst.

Conclusion

- In this work, raw agriculture waste was successfully synthesized, activated, and TiO2 immobilized for photodegradation of MB dye.
- Characterization of the produced materials was achieved for SEM, FTIR, TEM, EDX, and XRD.
- The result demonstrated that the produced catalyst is in a nanoform with stable immobilization structures comprised of different crystalline peaks.
- The degradation efficiency of ACPNS-TiO2 was studied, and we achieved almost a complete degradation of MB molecules after 60mins irradiation time.
- The photodegradation was optimized using response surface models where we attained 96.34% degradation efficiency at a pH of 11.9, ACPNS-TiO2 dosage of 56.75mg/L, MB concentration of 20.77ppm and a Time of 60mins.
- The MB degradation efficiency in five repeating cycles at the optimum parameters was 96.98%, 94.56%, 85.45%, 81.76%, and 74.64%, respectively.
- The degradation transformation product was achieved using LCMS which shows a complete degradation without any intermediate left

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Contribution of the Research Work

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This research will address two important environmental issues that affect numerous nations and the whole planet.

- ❖ The first is to reduce the massive volume of Agriculture waste that has been causing environmental problems for years.
- ❖ Second, it will aid in the resolution of water contamination issues.

The following aims in sustainable development goals will be met by these studies

Goal Number 3. Good health and well-being

Goal number 6. Clean water and sanitation

Goal Number 14. Life below water

Goal Number 15. Life on land

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