International Journal of Applied and Physical Sciences
volume 10 pp. 15-21 doi: https://dx.doi.org/10.20469/ijaps.10.50002

# Preparation and Characterization of Chitosan Furfural Schiff Base in the Removal of Aqueous 2, 4- Dinitrophenol

**Iyobosa Gift Okunzuwa**
Chemistry Department
University of Benin
Benin, Nigeria.

**Omamoke O. E. Enaroseha***
Department of Physics
Delta State University
Abraka, Nigeria.

**Samuel Ikponmwosa Okunzuwa**
Physics Department
University of Benin
Benin, Nigeria.

**Omale S. Ojodale**
Chemistry Department
University of Benin
Benin, Nigeria.

**Obed Oyibo**
Department of Physics
Delta State University of Science and Technology
Ozoro, Nigeria.

***Abstract:*** Chitosan was prepared and coupled with Furfural. The resulting chitosan furfural Schiff base was characterized using Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Brunauer Emmett Teller (BET) analysis. It was observed that Chitosan furfural Schiff base shows characteristic absorption peaks at 3290.35cm$^{-1}$,, 1644.47cm$^{-1}$, 1552.69 cm$^{-1}$,, which confirms the stretching vibration attributed to OH and NH groups of chitosan, NH=C (Imine linkage) of the Schiff base and aromatic ring of the furfural respectively. The SEM analysis, showed a rough large pore surface, the BET analysis revealed a large surface area of 339.85 m$^2$/g, a pore diameter of 2.94nm, and a pore volume of 0.1194 cm$^3$,/g. The material was used to adsorb aqueous 2, 4- Dinitrophenol (2, 4-DNP). The results obtained were evaluated with Langmuir and Freundlich adsorption isotherm. The material data fitted best with Freundlich isotherm $R_2$ value of 0.9690 when compared to Langmuir isotherm $R_2$ value of 0.8560. This indicates that the material proved uptake onto heterogeneous adsorbent surfaces. The $R_2$ values are regarded as a measure of the best fit of experimental data on the isotherm model.

***Keywords:*** : *Chitosan furfural, schiff base, adsorption isotherm, freundlich, langmuir*

***Received:*** 25 January 2024; ***Accepted:*** 19 February 2024; ***Published:*** 20 April 2024

## I. INTRODUCTION

Polluted water has caused significant threat to the advancements in agriculture and industry [1]. These sectors release wastewater containing various harmful substances like metals, dyes, pharmaceuticals, herbicides, phenols, phosphates, and nitrates [2]. When these pollutants exceed safe levels, they pose a threat to organisms and the environment [3]; [4]; [5]. Therefore, it is crucial to eliminate these contaminants from wastewater. Numerous methods have been employed for treating water pollutants, including adsorption and ion bio – degradation [6]; [7].

Chitosan has demonstrated several promising biological properties such as antimicrobial, antitumor, and hemostatic effects, as well as the ability to accelerate wound healing [8]. Chitosan possesses outstanding bioavailability, biodegradability, adsorption capabilities, and is nontoxic. These attributes render it highly valuable for a wide range of applications across diverse fields, including wound healing, drug delivery, food packaging, dietary supplements, chelation therapy, pharmaceuticals, biomaterials, and more.p [9]; [10]; [11]. As a result of the OH and NH2 modification using sulfonation, [11], amination [12] carboxymethylation reactions [13] and Schiff bases

*Correspondence concerning this article should be addressed to Omamoke O. E. Enaroseha, Physics Department, Delta State University, Abraka, Nigeria. E-mail: enarosehaomamoke@gmail.com

[7]; [8]; [14]; [15]; [16]; [17]; [18]; [19]. Due to its harmful effects, there is a need to reduce its presence in the environment hence its adsorption using Schiff base.

Schiff bases contains azomethine group (-HC=N-). They are condensation products of ketones or aldehydes with primary amines. Over the years, many chemist has synthesized different Schiff bases, for example; [20] synthesized a Thiophene Schiff base which he used for corrosion inhibition of steel. [21] synthesized a Schiff base using 2-Aminopyridine and 2-Methoxybenzaldehyde which he used to form complex with Cobalt (II) and Nickel (II) for antimicrobial studies. [22] synthesized a Schiff base using chitosan with phenol and cyclodextrin groups, which they used for the adsorption of phenolic compounds. This work is consigned with the use of adsorption using chitosan furfural Schiff base (CF-SB) for the treatment of water containing different amounts of 2,4 – Dinitrophenol (2,4-DNP).

## II. MATERIALS AND METHODS

### A. *Materials*

Chitosan, Fufural (C5H8O2), Sodium chloride (NaOH), Acetic acid (CH3COOH), Ethanol (CH3CH2OH) where procured ed from Pyrex Chemicals, Ugbowo – Nigeria. They were used without further purification.

### B. *Synthesis of Chitosan furfural Schiff Base (CF-SB)[8]*

The synthesis of Chitosan furfural Schiff base (CF-SB) as proposed by [8]. Chitosan 1 g was dissolved in acetic acid 50 mL of 2%, this was stirred using a magnetic stirrer. Then we added Ethanol 10 mL containing furfural 0.125 mL slowly under stirring to form a homogenous mix. Using a magnetic stirrer the solutions were stirrd for 6 hrs at a temperature of 50$^o$C. The formation of a deep yellow gel signals the formation of the chitosan fufural schiff base (CF-SB). The resulting solution was then added to excess of sodium hydroxide 5% solution to form a precipitate, this was filtered and the resulting precipitate washed using Ethanol and Water, then dried at 60$^o$C.

### C. *Characterization of Chitosan Furfural Schiff Base*

The Material was analyzed with FTIR of model Cary 630. The surface morphology of the compound was examined using TESCAN Vega Model scanning electron microscope (SEM). Porosity and surface area of CF-SB was analyzed using BET of model nova 4200e, USA. The of phenol concentration in liquid samples was measured using Shimadzu UV-2600, USA.

### D. *Adsorption Experiment[23]*

The adsorption experiment was carried out by modifying the method proposed by [23]. 2, 4 – Dinitrophenol stock solution was prepared by dissolving 2, 4 – Dinitrophenol 1 g in distilled water 1 L. The batch adsorption was carried out with different initial concentration of 2, 4-DNP from 10-50ppm, and was conducted at different times (every 5 mins in 1 hour). For a typical experiment, The prepared chitosan furfural Schiff base 1 g was added to the prepared solution 10 mL.

### E. *Adsorption Isotherm*

We used (1) to determined the adsorption capacity of CF-SB at dierent times (qt)

$q_t = \frac{v(c_0 - c_t)}{m}$....(1)

where V (L) is the 2, 4 – Dinitrophenol solution volume, $C_o$ (mg $L^{-1}$) is the initial concentration. The adsorption capacity of the Schiff base at equilibrium (qe) was determined from Equation 2 [24]; [25].;

$q_e = \frac{v(c_0 - c_e)}{m}$.....(2)

Langmuir and Freundlich isotherm models are expressed by Equation 3 and 4:

$q_e = \frac{q_0 k_l c_e}{1 + k_l c_e q_e}$......(3)

The langmuir equation can be linearized to plot a graph. The values of qo and kl can be determined by plotting the graph of Ce/qe versus Ce.

$q_e = k_f \, [c_e]^{\frac{1}{n}}$......(4)

where $k_f$ and 1/n are the Freundlich constant and adsorption intensities respectively, the equation can be linearized in logarithmic form to plot a graph of log qe versus Ce using experimental data. The slope and intercept gives the value of $k_f$ and 1/n respectively.

## III. RESULTS AND DISCUSSION

### A. *Synthesis of Chitosan furfural Schiff base*

The coupling of furfural molecules with chitosan are present in the Figure below.

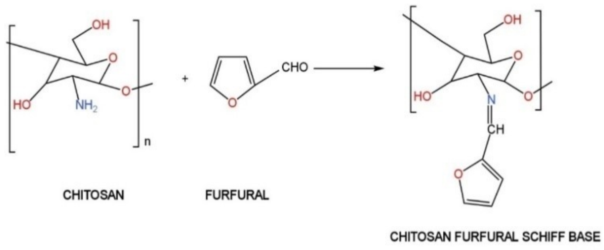


Fig. 1. Scheme of Chitosan furfural Schiff base

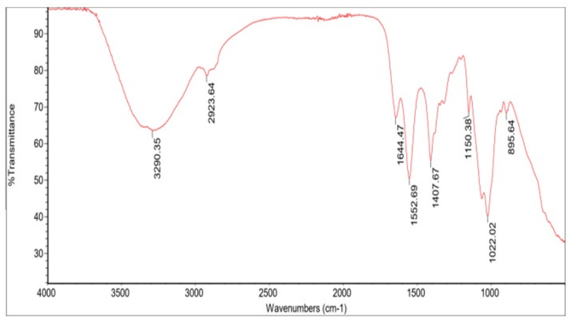


Fig. 2. FTIR spectroscopy of Chitosan furfural SB

The spectrum of CF-SB in Fig 2 exhibits main characteristic strong broad band at 3290.35cm$^{-1}$ [7]. FTIR result also revealed clearly the interaction which was formed allying chitosan matrix and furfural through the emergence of new Imine linkage established by the crest at 1644.5cm$^{-1}$. Also crests at 1552.69, 1150.38, 1022.02 cm$^{-1}$ signals the presence of the C=C aromatic ring, C-O ether stretch, and C-O stretch of primary alcohol in –CHO, of furfural.

### B. *Sem Analysis*

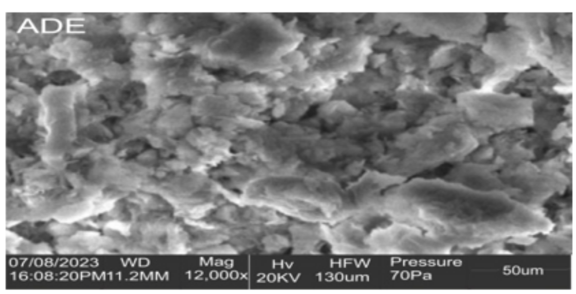


Fig. 3. SEM image of CF-SB.

In order to visualize the external morphology of the synthesized CF-SB, scanning electron microscopy analysis was carried out. Figure 3 above shows the SEM result of the chitosan furfural Schiff base. The surface morphology is rough with various pores indicating the porous nature of the material due to the coupling of furfural to chitosan matrix. Similar rough images were observed in 3-ethoxy-4-hydroxybenzylidene chitosan Schiff base [26]

### C. *Bet Analysis*

Table 1 BET surface area, Pore volume and Pore diameter

TABLE 1
BET SURFACE AREA, PORE VOLUME AND PORE DIAMETER

| Material | Surface Area($m^2$/g) | Pore Volume ($cm^3$/g) | Pore diameter (nm) |
|---|---|---|---|
| CF-SB | 339.85 | 0.194 | 2.94 |

The specific surface area of a material measures how much surface area is available per unit mass. The synthesized material has a significantly higher specific surface area (339.85 $m^2$/g). This suggests that the material has a larger exposed surface area, which can be indicative of a material with more pores, finer particles, or a more intricate structure. Higher specific surface area can be desirable for applications such as adsorption, catalysis, and filtration, as it provides more active sites for chemical reactions or adsorption processes. Pore volume indicates the total volume of pores within the material. CF-SB has a high pore volume (0.194$cm^3$/g). A higher pore volume suggests that the sample contains a greater volume of open spaces or pores within its structure, which could be related to its larger specific surface area. Pore volume is important in applications where materials need to hold or store liquids or gases, such as in adsorbents for gas separation or storage. The average pore diameter gives you an idea of the size of the pores within the material. The synthesized sample has a slightly larger average pore diameter (2.94 nm). A larger average pore diameter in the sample could indicate a somewhat coarser pore structure. The average pore diameter is crucial for applications where the size of the molecules or particles being adsorbed or transported is important. It can affect the selectivity and efficiency of the material. The BET result above is in line with that obtained from Ni (II)-Vanillin-Schiff base [27]; [28]; [29]; [30]; [31].

### D. *Effect of Initial Concentration*

TABLE 2
EFFECT OF INITIAL CONCENTRATION ON ADSORPTION

| Initial Conc. ($C_o$) | $C_e$ | Amount Absorbed | % Removal | $q_e$ (mg/g) | $C_e/q_e$ | Log $C_e$ | Log $q_e$ |
|---|---|---|---|---|---|---|---|
| 10 | 3.729 | 6.271 | 62.71 | 0.0627 | 59.47 | 0.572 | -1.203 |
| 20 | 7.119 | 12.881 | 64.405 | 0.12881 | 55.28 | 0.852 | -0.89 |
| 30 | 10.169 | 19.831 | 66.103 | 0.198 | 51.36 | 1.007 | -0.703 |
| 40 | 11.525 | 28.475 | 71.188 | 0.285 | 40.44 | 1.062 | -0.545 |
| 50 | 12.881 | 37.119 | 74.238 | 0.371 | 34.72 | 1.11 | -0.431 |

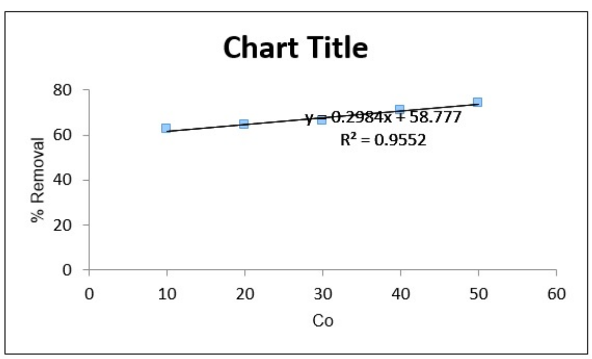


Fig. 4. Graph of % removal as a function of initial concentration Co

Table 2 shows the effect initial 2, 4 – Dinitrophenol concentration on it adsorption on CF-SB. From the Table, the graph of % removal against initial concentration was plotted in Fig 4. It was observed from the graph and Table that the 2, 4 – Dinitrophenol percentage removal increased gradually with increase in 2, 4 – Dinitrophenol initial concentration, the percentage increased from 62.71% to 74.238%. The phenomenon was attributed to increase in the number of active sites on the surface of the adsorbent. At high concentration the available sites of the adsorbent increases. The behavior results from the competitive diffusion process of the ions through the pores of the adsorbent.

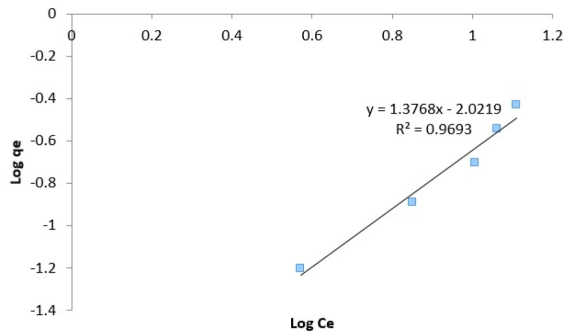


Fig. 5. Langmuir isotherm of 2,4 – Dinitrophenol on CF-SB

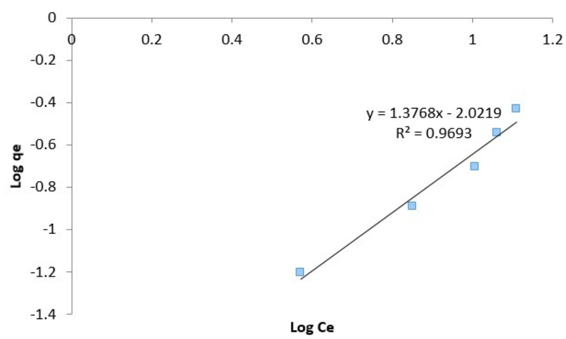


Fig. 6. Freundlich isotherm of 2, 4 – Dinitrophenol on CF-SB

The rate of adsorption of 2, 4 – Dinitrophenol unto CF-SB can be studied using Langmuir (Fig 5) and Freundlich (Fig 6) isotherm models, upon comparism Freundlich isotherm with $R^2$ value of 0.9690 was found to fit better to the adsorption data compared to the Langmuir isotherm model with $R^2$ value of 0.8560. Thus the freundlich isotherm is more suitably used to describe the relationship between the amounts of 2, 4 – Dinitrophenol adsorbed by CF-SB, although langmuir isotherm can also be used for this purpose.

TABLE 3
FITTING PARAMETERS FOR ISOTHERM MODEL

| Isotherm | Langmuir | Freundlich |
|---|---|---|
| K | -2.606 | 1.3738 |
| $q_e$ | 71.129 | - |
| 1/n | - | 2.0219 |
| $R^2$ | 0.856 | 0.969 |

## IV. CONCLUSION

Chitosan furfural Schiff base was synthesized using appropriate methodology and this was characterized using FTIR, SEM and BET. FTIR result, confirm the presence of CF-SB characteristic absorption peaks at 3290.35cm$^{-1}$, 1644.47cm$^{-1}$, 1552.69 cm$^{-1}$, which confirms the stretching vibration attributed to OH and NH groups of chitosan, NH=C (Imine linkage) of the Schiff base and aromatic ring of the furfural respectively. The BET result shows that the compound has a large surface area, pore size and pore diameter, hence it is suitable for use in the adsorbing of liquid or gaseous samples. Also through the SEM analysis, it was found that the compound appeared rough with large pore surface, thereby allowing substances to bind to its surface. It was also found out through the adsorption experiment that CF-SB is a good adsorbent for the removal of aqueous 2, 4 – Dinitrophenol and this study has demonstrated the application of Chitosan furfural Schiff base.

## V. DECLARATION OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## REFERENCES


[1] L. Zhang, Y. Zeng, and Z. Cheng, "Removal of heavy metal ions using chitosan and modified chitosan: A review," *Journal of Molecular Liquids*, vol. 214, pp. 175–191, 2016.

[2] D. H. K. Reddy and S.-M. Lee, "Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions," *Advances in colloid and interface science*, vol. 201, pp. 68–93, 2013.

[3] A. Bhatnagar and M. Sillanpää, "Applications of chitin-and chitosan-derivatives for the detoxification of water and wastewater—a short review," *Advances in colloid and Interface science*, vol. 152, no. 1-2, pp. 26–38, 2009.

[4] U. O. Aigbe, K. E. Ukhurebor, R. B. Onyancha, B. Okundaye, E. Aigbe, K. Obodo, E. O. Omamoke, L. L. Noto, A. O. Osibote, and H. I. Atagana, "Activated biosorbents for the removal of metals from aqueous solutions," in *Adsorption Applications for Environmental Sustainability*. IOP Publishing Bristol, UK, 2023, pp. 3–1.

[5] U. O. Aigbe, R. B. Onyancha, K. E. Ukhurebor, B. Okundaye, E. Aigbe, O. O. Enaroseha, K. Obodo, O. A. Osibote, A. El Nemr, L. L. Noto *et al.*, "Utility of magnetic nanomaterials for theranostic nanomedicine," in *Magnetic Nanomaterials: Synthesis, Characterization and Applications*. Springer, 2023, pp. 47–86.

[6] S. Sarode, P. Upadhyay, M. A. Khosa, T. Mak, A. Shakir, S. Song, and A. Ullah, "Overview of wastewater treatment methods with special focus on biopolymer chitin-chitosan," *International journal of biological macromolecules*, vol. 121, pp. 1086–1100, 2019.

[7] N. Q. Haj, M. O. Mohammed, and L. E. Mohammood, "Synthesis and biological evaluation of three new chitosan schiff base derivatives," *ACS omega*, vol. 5, no. 23, pp. 13 948–13 954, 2020.

[8] T. M. Tamer, M. A. Hassan, A. M. Omer, W. M. Baset, M. E. Hassan, M. E. El-Shafeey, and M. S. M. Eldin, "Synthesis, characterization and antimicrobial evaluation of two aromatic chitosan schiff base derivatives," *Process Biochemistry*, vol. 51, no. 10, pp. 1721–1730, 2016.

[9] M. Gallo, D. Naviglio, A. A. Caruso, and L. Ferrara, "Applications of chitosan as a functional food," in *Novel approaches of nanotechnology in food*. Elsevier, 2016, pp. 425–464.

[10] G. I. Okunzuwa, O. O. Enaroseha, and S. I. Okunzuwa, "Synthesis and characterization of fe (iii) chitosan nanoparticles n-benzaldehyde schiff base for biomedical application," *Chemical Papers*, vol. 78, no. 5, pp. 3253–3260, 2024.

[11] S.-P. Rwei and C.-C. Lien, "Synthesis and viscoelastic characterization of sulfonated chitosan solutions," *Colloid and Polymer Science*, vol. 292, pp. 785–795, 2014.

[12] H. A. Afshar and A. Ghaee, "Preparation of aminated chitosan/alginate scaffold containing halloysite nanotubes with improved cell attachment," *Carbohydrate polymers*, vol. 151, pp. 1120–1131, 2016.

[13] A. L. Bukzem, R. Signini, D. M. Dos Santos, L. M. Lião, and D. P. R. Ascheri, "Optimization of carboxymethyl chitosan synthesis using response surface methodology and desirability function," *International journal of biological macromolecules*, vol. 85, pp. 615–624, 2016.

[14] S.-N. Wu and H.-D. Chang, "Diethyl pyrocarbonate, a histidine-modifying agent, directly stimulates activity of atp-sensitive potassium channels in pituitary gh3 cells," *Biochemical pharmacology*, vol. 71, no. 5, pp. 615–623, 2006.

[15] H. Hoydonckx, W. Van Rhijn, W. Van Rhijn, D. De Vos, and P. Jacobs, "Furfural and derivatives," *Ullmann's encyclopedia of industrial chemistry*, 2000.

[16] M. L. Granados and D. M. Alonso, *Furfural: an entry point of lignocellulose in biorefineries to produce renewable chemicals, polymers, and biofuels*. World Scientific, 2018, vol. 2.

[17] P. Shea, J. Weber, and M. Overcash, "Biological activities of 2, 4-dinitrophenol in plant-soil systems," in *Residue Reviews: Residues of Pesticides and Other Contaminants in the Total Environment*. Springer, 1983, pp. 1–41.

[18] N. Al-Mutairi, "2, 4-dinitrophenol adsorption by date seeds: Effect of physico-chemical environment and regeneration study," *Desalination*, vol. 250, no. 3, pp. 892–901, 2010.

[19] J. Grundlingh, P. I. Dargan, M. El-Zanfaly, and D. M. Wood, "2, 4-dinitrophenol (dnp): a weight loss agent with significant acute toxicity and risk of death," *Journal of medical toxicology*, vol. 7, pp. 205–212, 2011.

[20] D. Daoud, T. Douadi, S. Issaadi, and S. Chafaa, "Adsorption and corrosion inhibition of new synthesized thiophene schiff base on mild steel x52 in hcl and h2so4 solutions," *Corrosion science*, vol. 79, pp. 50–58, 2014.

[21] U. Sani and S. Iliyasu, "Synthesis, characterization and antimicrobial studies on schiff base derived from 2-aminopyridine and 2-methoxybenzaldehyde and its cobalt (ii) and nickel (ii) complexes," *Bayero Journal of Pure and Applied Sciences*, vol. 11, no. 1, pp. 214–219, 2018.

[22] L.-C. Zhou, X.-G. Meng, J.-W. Fu, Y.-C. Yang, P. Yang, and C. Mi, "Highly efficient adsorption of chlorophenols onto chemically modified chitosan," *Applied Surface Science*, vol. 292, pp. 735–741, 2014.

[23] L. Yu, D. P. Gamliel, B. Markunas, and J. A. Valla, "A promising solution for food waste: preparing activated carbons for phenol removal from water streams," *ACS omega*, vol. 6, no. 13, pp. 8870–8883, 2021.

[24] Y. Tang, Y. Zhao, T. Lin, Y. Li, R. Zhou, and Y. Peng, "Adsorption performance and mechanism of methylene blue by h3po4-modified corn stalks," *Journal of Environmental Chemical Engineering*, vol. 7, no. 6, p. 103398, 2019.

[25] M. Anbia and S. E. Moradi, "Adsorption of naphthalene-derived compounds from water by chemically oxidized nanoporous carbon," *Chemical Engineering Journal*, vol. 148, no. 2-3, pp. 452–458, 2009.

[26] A. Foroughnia, A. D. Khalaji, E. Kolvari, and N. Koukabi, "Synthesis of new chitosan schiff base and its fe2o3 nanocomposite: Evaluation of methyl orange removal and antibacterial activity," *International Journal of Biological Macromolecules*, vol. 177, pp. 83–91, 2021.

[27] M. Nikoorazm, A. Ghorbani-Choghamarani, and M. Khanmoradi, "Synthesis and characterization of ni (ii)–vanillin–schiff base–mcm-41 composite as an efficient and reusable nanocatalyst for multicomponent reactions," *RSC advances*, vol. 6, no. 61, pp. 56 549–56 561, 2016.

[28] I. M. Ezeh, O. O. Enaroseha, G. K. Agbajor, and F. I. Achuba, "Effect of titanium oxide (tio2) on natural dyes for the fabrication of dye-sensitized solar cells," *Engineering Proceedings*, vol. 63, no. 1, p. 25, 2024.

[29] O. Enaroseha, J. S. Apanapudor, and O. Oyebola, "Rate equation analysis of the 2.9 $\mu$m holmium-doped potassium lead bromide (ho: Kpb 2 br 5) transition for diode laser application." 2023.

[30] O. Ojegu and O. Omamoke, "Optical properties of the anatase phase of titanium dioxide thin films prepared by electrostatic spray deposition," *Nigerian Journal of Science and Environment*, vol. 18, no. 2, 2020.

[31] B. O. Ogo, O. O. Enaroseha, O. O. Robert, E. O. Ojegu, I. L. Ikhioya, A. Ekpekpo, and O. Osiele, "Fabrication of dye-sensitized solar cells using nitrogen doped carbon quantum dots and organic dye extracted from purple cabbage," *BW Academic Journal*, 2024.