Multidisciplinary Output Research For Actual and International Issue (MORFAI Journal) ISSN (e): 2808-6635
Volumes 5 No. 6 (2025)

METHYL RED ADSORPTION BY BIODEGRADABLE POLYCAPROLACTONE/RICE HUSK ASH/TiO2 NANOFILLER HYBRID BIONANOCOMPOSITES: SYNTHESIS AND CHARACTERIZATION

Armelia Yuniani[1], **Erna Frida**[2*], **Syahrul Humaidi**[3]
[1,2,3]Universitas Sumatera Utara
Corresponding E-mail: ernafridatarigan@usu.ac.id

Received : 20 May 2025
Revised : 29 May 2025
Accepted. : 15 June 2025
Published : 11 July 2025
DOI : https://doi.org/10.54443/morfai.v5i6.3470
Link Publish : https://radjapublika.com/index.php/MORFAI/article/view/3470

Abstract

The contamination of wastewater by synthetic dyes such as Methyl Red poses serious environmental and health risks, necessitating effective remediation methods. This study investigates the synthesis and characterization of hybrid bionanocomposites composed of polycaprolactone (PCL), rice husk ash (RHA), and titanium dioxide (TiO2) nanoparticles for the efficient degradation of Methyl Red (MR) dye. The composites were prepared using a co-precipitation method for the incorporation of nano-RHA and TiO2. Characterization of the bionanocomposites was conducted through scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and photodegradation tests. XRD analysis, using the Scherrer equation, revealed crystallite sizes ranging from 19.01 nm (composite S0) to 27.25 nm (composite S2). FTIR spectra showed characteristic absorption peaks corresponding to Ti–O (669.29 cm^{-1}), Si–O (970.19 cm^{-1}), and C–H (2960.73 cm^{-1}) bonds. The photodegradation results indicated a significant improvement in dye adsorption, with the highest degradation efficiency observed in composite S1, achieving 93.55% degradation after 45 hours of UV irradiation. The degradation efficiencies of S0, S1, and S2 were found to be 87.1%, 93.55%, and 25.81%, respectively, under the same conditions. The incorporation of TiO2 and RHA in PCL significantly enhanced its photocatalytic activity. This study demonstrates the potential of these bionanocomposites as sustainable materials for textile wastewater treatment

Keywords: ***Bionanocomposite, Polycaprolactone, Rice Husk Ash, Nano TiO2, Methyl Red***

INTRODUCTION

Access to clean water is a global challenge aggravated by rapid population growth and industrialization, leading to increased water pollution. Textile industries are major contributors to water contamination, discharging synthetic dyes such as Methyl Red (MR) that are toxic, carcinogenic, and resistant to biodegradation [1] MR's high solubility and color intensity even at low concentrations impair aquatic ecosystems and pose health hazards if untreated. Conventional wastewater treatment methods ion exchange, reverse osmosis, nanofiltration face limitations including high cost, complex operation, and energy consumption. Adsorption is a promising alternative due to its simplicity, cost-effectiveness, and ability to regenerate adsorbents [2]. Various adsorbents have been explored, including synthetic TiO2 nanoparticles known for photocatalytic degradation of dyes [3] and natural biomass wastes such as rice husk ash (RHA), which is rich in silica and offers a sustainable filler option [4].

Biopolymers like polycaprolactone (PCL) have gained attention for environmental applications due to their biodegradability and biocompatibility [5] However, pure PCL has limited adsorption capacity and mechanical properties, which can be enhanced by incorporating fillers such as RHA and TiO2 nanoparticles. RHA provides a porous structure and high surface area, while TiO2 adds photocatalytic activity, making the hybrid composite multifunctional for dye adsorption and degradation. This study aims to synthesize and characterize PCL-based hybrid bionanocomposites reinforced with nano RHA and TiO2 for efficient adsorption of Methyl Red. The composites are evaluated for structural, morphological, and adsorption performance to explore their feasibility as sustainable materials for textile wastewater treatment.

Publish by **Radja Publika**

MATERIALS AND METHOD

Materials

This research utilized rice husk ash (RHA) as the primary precursor for bionanocomposite synthesis, obtained from the rice milling factory PT. Jampalan Baru, located in Desa Jampalan Km. 10, Simpang Empat, Kab. Asahan. Additional materials included Polycaprolactone (PCL, CAPA-6800), Titanium Dioxide nanoparticles (synthesized in the NRE Lab) , chloroform (Merck) as the solvent, hydrochloric acid (HCl, 2M, Merck) to remove inorganic components from the rice husk ash, sodium hydroxide (NaOH, 2.5M, Merck) for extracting silica oxide, and methyl red (Merck) for the adsorption test.

Methods

1. Preparation of Rice Husk Ash Nanoparticles Using Ball Milling and Co-Precipitation Method
   The rice husk ash preparation began by washing the rice husks with deionized water and hydrochloric acid (HCl) solution to remove any impurities. The husks were then sun-dried before being oven-dried at 60°C for 5 hours. After drying, the husks were calcined in a furnace at 800°C for 6 hours to obtain rice husk ash. The resulting ash was then processed using a ball mill at 300 rpm for 1 hour to break it down further. The milled ash was sieved using a 200 mesh sieve to obtain a particle size of 74 µm.
2. Synthesis of Nano Rice Husk Ash Using Co-Precipitation Method
   In the next stage, the synthesized rice husk ash was dissolved in a 2M HCl solution at a 1:3 ratio. The solution was stirred and heated using a magnetic stirrer at 70°C for 1 hour at 400 rpm. After the reaction, the mixture was filtered. The rice husk ash was then dissolved in a 2.5M NaOH solution, maintaining the same ratio of rice husk ash to solution, and heated with continuous stirring for 1 hour. The resulting solution was filtered and washed with deionized water until the pH reached neutral (pH 7). The filtered material was dried at 70°C for 4 hours in an oven, then ground using a mortar. The dried material was sieved and characterized using a Particle Size Analyzer (PSA).
3. Preparation of Bionanocomposite
   To synthesize the bionanocomposite, nano rice husk ash was used as a filler in combination with nano TiO_2 and Polycaprolactone (PCL). Fourthty grams of PCL (CAPA-6800) were placed in a beaker and melted using a magnetic stirrer at 70°C. Chloroform (60 mL) was added as a compatibilizer. Nano rice husk ash was incorporated into the PCL solution in varying proportions, as shown in Table 1. The mixture was stirred at 200 rpm for 45 minutes to ensure uniform dispersion. After drying, the bionanocomposite was characterized using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray (EDX), X-ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR).

Table 1. Bionanocomposite Composition

Sample Code	PCL (g)	$nTiO_2$ (g)	nRHA (g)	$CaCl_2$ (g)
S0	50	0	0	1
S1	40	0	10	1
S2	40	2.5	7.5	1

4. Photodegradation of Methyl Red
   For the adsorption test, Methyl Red was dissolved in distilled water to prepare a 500 ppm solution. One gram of each bionanocomposite sample (S0 to S2) was added to the Methyl Red solution in 200 mL glass bottles. The dye adsorption was monitored over a period of 45 hours. At 5-hour

intervals, 10 mL of the solution was removed for analysis using a UV-Vis spectrophotometer to measure changes in absorbance and determine the adsorption rate.

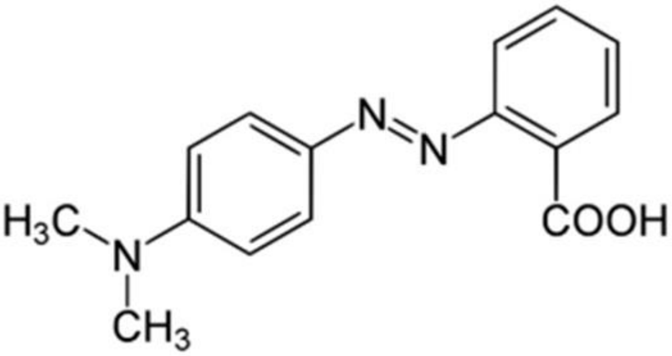


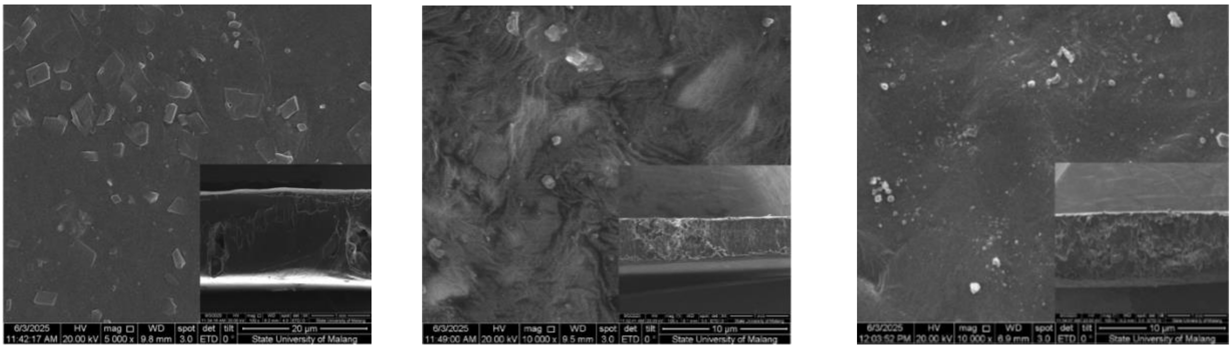
Figure 2.1. Chemical structure of Methyl Red dye

5. Biodegradation test
   The biodegradation of the PCL bionanocomposite was tested by burying the samples in soil enriched with EM4 bioactivator, which enhances decomposition, and with a pH of 6-7. The samples were buried for 1 month and weighed every 10 days to observe the degradation process. The percentage of mass loss was calculated using the formula:
   $$Mass\ loss\ (\%) = \frac{m_0 - m_t}{m_0} \times 100\%$$
   This formula is used to quantify the degradation of polymers or materials by microorganisms under controlled test conditions.

RESULTS AND DISCUSSION

Morphological and Elemental Characterization (SEM-EDX)

SEM images of samples S0, S1, and S2 revealed distinct differences in morphology. The pure PCL matrix in S0 showed a smooth surface with no significant agglomeration of particles (Figure 3.1). In contrast, the addition of nano-RHA in S1 led to a more porous structure with better particle dispersion, contributing to an increased surface area, which is crucial for dye adsorption. In S2, while TiO2 was added alongside RHA, a slight agglomeration of particles was observed, indicating less effective particle dispersion than in S1.



(a) S0 (b)S1 (c)S2

Figure 3.1. Morphology and Cross-section of Nanocomposite

EDX analysis (Tables 3.1–3.3) confirmed the successful incorporation of carbon (C), oxygen (O), and silicon (Si) in all samples. Sample S1 exhibited a higher concentration of Si (3.07 wt%), indicating improved integration of rice husk ash (RHA) into the PCL matrix, which likely contributed to the enhanced surface area and increased dye adsorption capacity.

OPEN ACCESS

Table 3.1 Percentage content of Bionanocomposite Sample S0

Element	Weight %	Atomic %
C	78.30	82.78
O	21.70	17.22

Table 3.2 Percentage content of Bionanocomposite Sample S1

Element	Weight %	Atomic %
C	73.71	79.86
O	22.88	18.60
Si	3.07	1.42
Cl	0.16	0.06
Ca	0.18	0.06

Table 3.3 Percentage content of Bionanocomposite Sample S2

Element	Weight %	Atomic %
C	77.47	82.55
O	21.06	16.84
Si	0.99	0.45
Cl	0.17	0.06
Ca	0.14	0.04
Ti	0.18	0.05

X-Ray Diffraction (XRD) Analysis

The incorporation of rice husk ash (RHA) into the polycaprolactone (PCL) matrix, as demonstrated in sample S1, significantly enhanced the structural properties of the bionanocomposites. The EDX analysis (Tables 3.1–3.3) revealed a higher silicon (Si) content in S1 (3.07 wt%), suggesting that the RHA was effectively integrated into the PCL matrix. This higher Si concentration correlates with an increase in the composite's surface area, which is a critical factor for improving dye adsorption capacity. RHA, being a rich source of silica, provides additional surface sites that facilitate the adsorption of pollutants like Methyl Red. The high surface area of RHA, combined with its inherent porosity, contributes to enhanced interaction between the dye molecules and the composite, promoting more efficient adsorption. This result aligns with previous studies, which have shown that silica-based materials enhance the adsorption capacity of polymers in wastewater treatment applications [6].

Furthermore, the enhanced photocatalytic activity observed in sample S1 can be attributed to the optimal dispersion of nanoparticles, which was facilitated by the RHA filler. Studies have indicated that the uniform distribution of nanoparticles within the polymer matrix is crucial for maximizing photocatalytic performance, as it improves the interaction between the dye molecules and the active sites on the composite surface [7]. In sample S2, which incorporated both TiO_2 and RHA, a lower degradation efficiency was observed, suggesting that the TiO_2 particles were not as well dispersed as in S1. This agglomeration of TiO_2 particles can hinder the photocatalytic process by reducing the available active sites for dye degradation. These findings highlight the importance of controlling the dispersion of nanoparticles within the composite to optimize both adsorption and photocatalytic efficiency, thus enhancing the overall efficacy of the bionanocomposite for environmental remediation purposes.

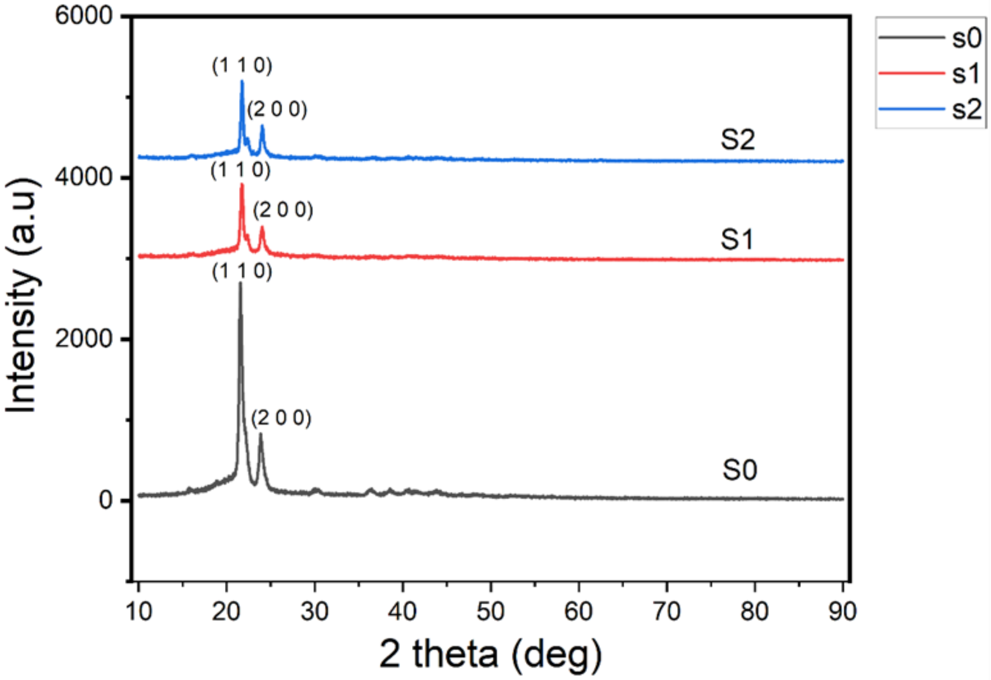


Figure 3.3 Diffractograms of Bionanocomposite

Photo-degradation Of MR dye analysis

The photodegradation efficiency of the composites was evaluated by measuring the discoloration of Methyl Red dye over 45 hours of UV irradiation. The highest degradation efficiency was achieved by sample S1 (93.55%), which contains only SiO2. This suggests that the RHA component plays a crucial role in enhancing photocatalytic activity. In comparison, sample S2, which contains both RHA and TiO2, showed a degradation efficiency of only 25.81%, indicating that the TiO2 content might not have been uniformly distributed within the matrix, limiting its photocatalytic effectiveness. Sample S0, which contains only PCL, exhibited a degradation efficiency of 87.1%. These results suggest that while RHA significantly enhances the degradation efficiency, the addition of TiO2 must be optimized for effective dye removal.

Table 3.6 Parameters of Photodegradation Reaction of Bionanocomposite

Sample	Degradation Efficiency 45 hours (%)
S0	87,1
S1	93,55
S2	25,81

CONCLUSION

The results demonstrate that PCL-based bionanocomposites reinforced with rice husk ash and TiO2 nanoparticles are promising materials for the photocatalytic degradation of Methyl Red. Among the tested samples, S1, which contains only RHA, achieved the highest degradation efficiency of 93.55%. XRD and FTIR analyses confirm that the addition of RHA and TiO2 does not disrupt the PCL structure, and the physical interactions between the components enhance the material's photocatalytic properties. These findings suggest that these bionanocomposites are viable, sustainable solutions for the removal of textile dyes from wastewater, with the potential for further optimization to improve TiO2 dispersion and efficiency.

Acknowledgments

The authors would like to express to thank to the Integrated Research Lab and Pharmacy Research Center Lab at Universitas Sumatera Utara, and the Mineral and Materials Central Lab at Universitas Negeri Malang for their invaluable support and resources throughout this research. Special thanks are given to the supervisors and laboratory personnel for their expert guidance and technical assistance. The authors also appreciate the contributions and constructive feedback from colleagues during the preparation of this manuscript. Finally, the authors acknowledge the constant support, encouragement, and prayers from family members and close friends, without which the successful completion of this research would not have been possible.

REFERENCES

[1] Kumari, H., Sonia, Suman, Ranga, R., Chahal, S.,Devi, & Parmar, R. (2023). A Review on Photocatalysis Used For Wastewater Treatment: Dye Degradation. Water, Air, & Soil Pollution, 234(6), 349.

[2] Akter, M., Bhattacharjee, M., Dhar, A. K., Rahman, F. B. A., Haque, S., Rashid, T. U., & Kabir, S. F. (2021). Cellulose-based hydrogels for wastewater treatment: A concise review. Gels, 7(1), 30.

[3] Thahir, R., Wahab, A. W., Nafie, N. la, & Raya, I. (2019). Synthesis and Characterization of TiO2 Nanoparticle as Adsorbent on The Treatment of Methylene Blue Dye Pollutant. Jurnal Rekayasa Kimia & Lingkungan, 14(1), 19–27.

[4] Sulaiman (2025). Sekam Padi, Abu Sekam Padi, dan Aplikasinya. Dalam: Jawaid, M., Parmar, B. (eds) Biomassa Sekam Padi. Bahan dan Teknologi Berkelanjutan. Springer, Singapura. https://doi.org/10.1007/978-981-96-1082-2_3.

[5] Zhang, H., Pap, S., Taggart, M. A., Boyd, K. G., James, N. A., & Gibb, S. W. (2020). A review of the potential utilisation of plastic waste as adsorbent for removal of hazardous priority contaminants from aqueous environments. In Environmental Pollution (Vol. 258). Elsevier Ltd. https://doi.org/10.1016/j.envpol.2019.113698

[6] Costa, J., & Paranhos, C. (2019). Evaluation of rice husk ash in adsorption of Remazol Red dye from aqueous media. SN Applied Sciences, 1, 1-8. https://doi.org/10.1007/S42452-019-0436-1.

[7] Du, T., Cui, M., Chao, Y., Xiao, Y., Ren, Z., An, Y., & Meng, C. (2022). Persiapan dan sifat fotokatalitik nanopartikel samarium vanadat yang sangat terdispersi yang didukung pada komposit H-mordenit dengan metode bebas templat. Jurnal Fotokimia dan Fotobiologi A: Kimia . https://doi.org/10.1016/j.jphotochem.2022.114207.