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Synthesis of Bentonite-TiO_2 Bionanocomposite for Photodegradation of Used Lubricating Oil

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Abstract

Used lubricating oil waste contains heavy metal components which, if they enter the water, will block light. Used lubricants include toxic and hazardous waste (Hazmat) so they need further processing before being reused or thrown away, because they are dangerous for human health and the environment. This research aims to determine the ability or effectiveness of the Bentonite-TiO_2 composite in degrading used lubricating oil. The research began by synthesizing Bentonite-TiO_2 where the composite results obtained were characterized. Based on the results of the FTIR spectrum analysis of Bentonite-TiO_2, Ti was successfully modified in bentonite because the wave number 1419.84 cm^{-1} shows the presence of Al-O groups and the wave number 1423.92 cm^{-1} shows the presence of Ti-O-Ti vibrations. The results of XRD characterization show that TiO_2 has formed in the bentonite-TiO_2 composite, this makes the bentonite-TiO_2 more stable and can be used as photocatalysis in the processing of used lubricating oil. The results of SEM-EDX analysis of Bentonite-TiO_2 show the chemical composition of C, O, Al, Si, Ca, and Ti. In photodegradation, the mass variation viscosity value with an optimum time of 5 hours is the highest viscosity value, namely with a viscosity value of 5.11 cSt.

Keywords: *Bentonite, Bentonite-TiO_2, Photodegradation, Used lubricating oil, Nanocomposite*

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Abstrak (Indonesian)

Limbah minyak pelumas lama mengandung logam berat yang akan menghalangi cahaya jika masuk ke perairan. Pelumas bekas mengandung bahan beracun dan berbahaya (B3) yang membutuhkan pengolahan tambahan sebelum digunakan kembali atau dibuang. Ini merupakan bahaya bagi lingkungan dan kesehatan manusia. Tujuan penelitian ini adalah untuk mengetahui apakah komposit Bentonit-TiO_2 efektif atau tidak dalam mendegradasi minyak pelumas bekas. Penelitian dimulai dengan mensintesis Bentonit-TiO2, yang memberikan gambaran tentang produk komposit yang dihasilkan. Menurut hasil analisis spektrum FTIR bentonit-TiO_2, ada gugus Al-O pada 1419,84 cm^{-1} dan vibrasi Ti-O-Ti pada 1423,92 cm^{-1}, yang menunjukkan bahwa TiO_2 terbentuk pada komposit bentonit-TiO_2, Dengan demikian, bentonit-TiO_2 menjadi lebih stabil dan dapat digunakan sebagai fotokatalisis dalam pengolahan minyak pelumas bekas. Hasil analisis SEM-EDX bentonit-TiO_2 menunjukkan komposisi kimia C, O, Al, Si, Ca, dan Ti. Pada fotodegradasi, nilai viskositas variasi massa tertinggi mencapai 5,11 cSt dengan waktu terbaik 5 jam.

Kata Kunci: *Bentonit, Bentonit-TiO_2, Fotodegradasi, Minyak pelumas bekas, Nanokomposit*

INTRODUCTION

The growth of Indonesia's manufacturing, food, automotive, chemical, and other industries has led to a steady rise in the use of lubricants. Particularly in the automotive industry, as the number of motor vehicles and motorized machinery rises, so does the volume of lubricating oil [1]. The Province of Riau had 4,216,014 motor vehicles in 2022, with 3,617,512 of those being motorbikes, according to data from the Central Bureau of Statistics of Riau (BPS) [2].

The Government Regulation Number 22 of 2021 [3] and the Minister of Environment Regulation Number 6 of 2021[4] both contain regulations pertaining to the handling of spent lubricating oil waste. Waste from spent lubricating oil can be recycled and used as an alternative to petroleum-based non-renewable energy sources. Because of their harmful and toxic nature and environmental characteristics, old lubricants must be managed [5]. It is anticipated that used lubricating oil waste won't leak and contaminate soil and water [6],

Many heavy metal components, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) are found in used oil waste. If these substances get into the water, they will obstruct the entry of sunlight and oxygen, which will negatively impact the aquatic ecosystem. Furthermore, unlawfully dumping used oil waste onto the ground without first treating it might cut off the oxygen supply to the soil layers, which can lead to oil waste poisoning and the death of soil microorganisms. In addition to changing the structure and function of the soil, the presence of hydrocarbon chemicals in used lubricating oil can cause nutrient loss and a decline in soil productivity [7]. Numerous caustic, acidic, and carcinogenic heavy metal combustion remnants are found in used lubricants. Due to their detrimental effects on both human health and the environment, old lubricants must undergo additional processing before being reused or disposed of, since they are categorized as hazardous and toxic waste (B3) [8].

As a result of these problems, numerous studies on the disposal of spent lubricating oil waste have been carried out in an attempt to lessen contamination in the environment. In the study by [9], old lubricants were re-refined into base oil through a series of steps, including the creation of activated carbon and the adsorption of metals by activated carbon. Based on the research findings, the ideal absorption value was determined to be 17.2 ppm of Fe metal with an efficiency value of 8.44% at an adsorbent particle size with a mesh of 140. The acid and clay method of treating spent lubricant waste was also applied in studies by Siskayanti, *et al*. [10]. Low yields, high pollution output, such as sulfuric acid, trouble eliminating asphalt impurities, the use of flammable and dangerous solvents, such as propane, the production of hazardous byproducts that must be properly disposed of, the requirement for skilled workers, and high operating costs are still some of the drawbacks of this research approach.

Photodegradation is a cost-effective procedure because it is relatively inexpensive when using adsorbents derived from natural, cost-effective, and simple sources. One of the adsorbents that can be utilized is activated bentonite for processing used vegetable oil (edible oil). Bentonite functions as an absorbent for impurities in used cooking oil, because bentonite has a specific (hollow) crystal structure, used cooking oil will become clear as free fatty acids will be absorbed by bentonite [11].

This study is innovative in that it uses a Bentonite-TiO_2 composite material to control and purify used lubricating oil waste by photodegradation. Many hazardous ions can be effectively removed from the solution by using bentonite, which is also a good adsorbent [12]. TiO_2 has the ability to degrade waste because it is a readily available photocatalyst with a relatively high activity [13]. Thus, the goal of this research is to make sure that the material is aimed at becoming an excellent adsorbent and photocatalyst in order to degrade and reuse lubricating oil.

MATERIALS AND METHODS

Materials

Activated bentonite, TiO_2 (Titanium Dioxide), Sulfuric Acid, distilled water, and used lubricating oil.

Methods

The tools used in this research include glassware, hotplate and magnetic stirrer, oven, Fourier Transform Infra-Red (FTIR) instrument, X-Ray Diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX), photoreactor, and personal protective equipment (PPE).

Research procedures

Synthesis of Bentonite-TiO_2

Five hours were spent stirring 500 mL of distilled water with 5 g of bentonite until the clay lumps vanished. After being dissolved in 100 mL of distilled water, 2.5 g of TiO_2 was added to the bentonite mixture and agitated. After that, the bentonit-TiO_2 mixture was oven-dried for two hours at 100 °C. FTIR, XRD, and SEM-EDX were then used to describe the final composite [14].

Preparation of used lubricating oil

800 mL of used lubricant were created, put in a beaker, and swirled at 400 rpm before 160 mL of H_2SO_4 (p.a.) were added. After three hours of stirring to create a homogenous solution, the mixture was left to deposit for 24 hours until two layers had developed. The oil layer was removed for the photodegradation procedure [15].

Bentonite-TiO_2 photodegradation test

Determination of optimum irradiation time

Three beakers, each containing 100 mL of used lubricating oil sample mixed with 10 g of Bentonite-TiO_2 composite. Irradiated with a photoreactor with variations of 1, 3, and 5 hours while stirred with a magnetic stirrer (400 rpm) at a temperature of 70 °C. At each stage, a sedimentation time of 24 hours was allowed [16].

Determination of optimum photocatalyst mass

Three beakers, each containing 100 mL of used lubricating oil samples, were mixed with Bentonit-TiO_2 composites with varying Bentonit-TiO_2 masses of 10, 20, and 30 g at an adsorption temperature of 70 ºC. Irradiated with a photoreactor for an optimum time while stirred with a magnetic stirrer (400 rpm). At each stage, a sedimentation time of 24 hours is provided [16].

RESULTS AND DISCUSSION

In this FTIR characterization test, a success rate of 100% has been achieved, and the FTIR spectrum analysis results for adsorbent (adsorbent that has already been used for the photodegradation of lubricating oil), Bentonite and Bentonite-TiO_2 can be seen in **Figure 1**.

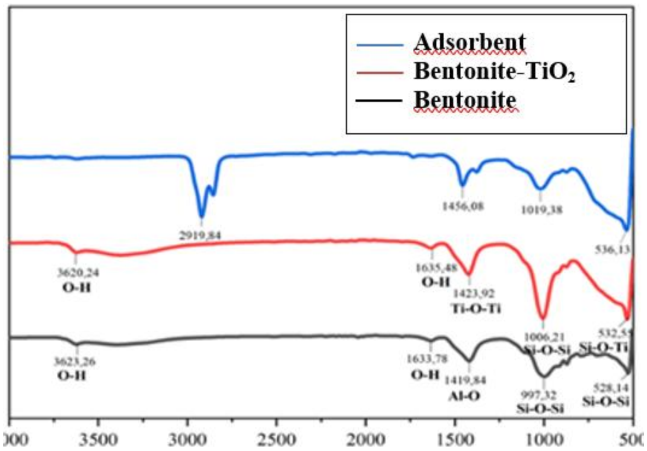


Figure 1. FTIR Spectrum of Bentonite and Bentonite-TiO_2

Figure 1 illustrates the existence of stretching vibrations of the O-H group from adsorbed water molecules, with peaks in the bentonite spectrum at 3623.26 and 1633.78 cm^{-1}. The existence of stretching vibrations of the Al-O group is indicated by an absorption band at 1419.84 cm^{-1}. Additionally, there are strong absorption bands at 997.32 and 528.14 cm^{-1}, which show that Si-O-Si stretching vibrations are present. The molecules found in bentonite are the functional groups O-H, Al-O, and Si-O-Si, according to the results of the FTIR spectrum study.

In the Bentonit-TiO_2 spectrum, there are absorption peaks at wave numbers 3620.24 and 1635.48 cm^{-1}, which correspond to O-H stretching vibrations. At a wavenumber of 1423.92 cm^{-1}, there is a vibration of Ti-O-Ti. At the wavenumber 1006.21 cm^{-1}, it indicates the presence of Si-O-Si stretching vibration. The next identified functional group is at the wavenumber 532.55 cm^{-1}, which indicates the presence of Si-O-Ti stretching vibration. Based on the FTIR spectrum analysis results, the compounds contained in Bentonite-TiO_2 are the functional groups O-H, Ti-O-Ti, Si-O-Si, and Si-O-Ti. Based on the results of the FTIR spectrum analysis in Bentonite and Bentonite-TiO_2. There is an absorption band at 1419.84 cm^{-1} indicating the stretching vibration of the Al-O group and at the wave number 1423.92 cm^{-1} indicating the vibration of Ti-O-Ti. This is evidenced by the position of the Al atom in bentonite being replaced by Ti [17].

The XRD Pattern of Bentonite and Bentonite-TiO_2 show that the interaction process of TiO_2 and bentonite causes structural changes in bentonite, marked by 2θ peaks that indicate characteristic bentonite peaks as shown in **Figure 2**.

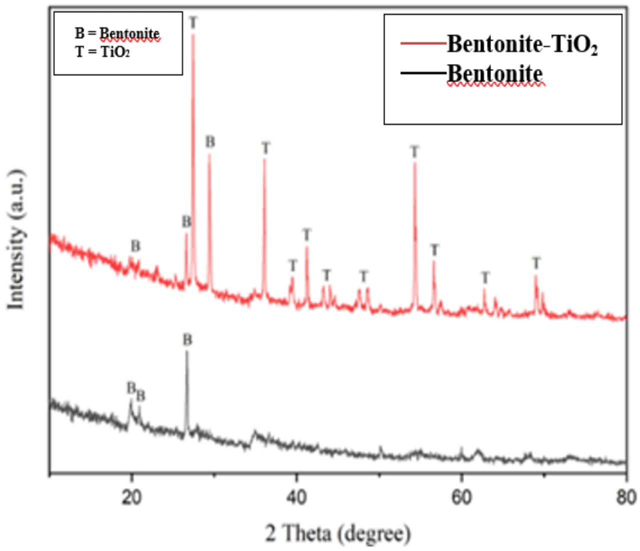
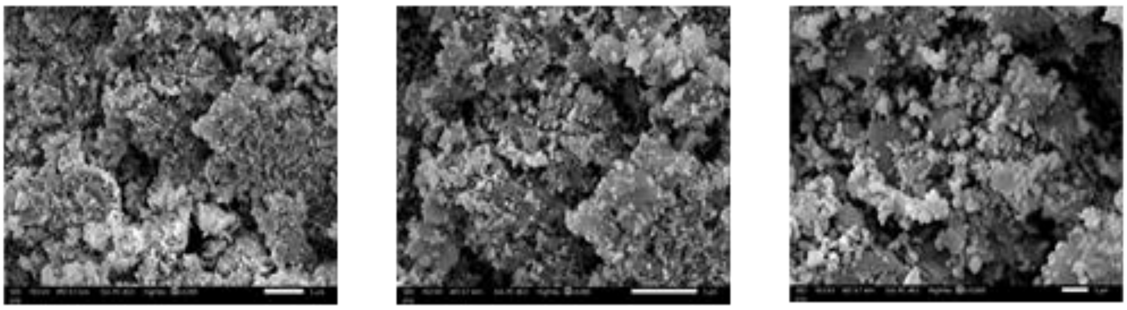


Figure 2. XRD Patterns of Bentonite and Bentonite-TiO_2 (JCPDS No. 21-1276 and No. 21-1272).

The bentonite diffractogram in this study shows the characteristic peaks of the bentonite mineral at 2θ = 19.91, 20.93 and 26.70° with basal spacing of 4.4538, 4.2403 and 3.3355 Å, respectively. After being modified with TiO_2, the 2θ peaks experienced a shift in interplanar spacing to 19.76, 20.80, 26.62 and 29.4091° with respective basal spacing of 4.4886, 4.2665, 3.3451 and 3.0346 Å.

In this diffractogram, the appearance of TiO_2 peaks at 2θ = 27.43, 41.23, 54.29 and 69.00° indicates the formation of rutile crystals in the bentonite-TiO_2. The main peaks of the rutile structure TiO_2 appear relatively sharp, indicating that TiO_2 is relatively easy to form on the surface of bentonite-TiO_2. In this diffractogram, peaks of anatase TiO_2 appear at 2θ = 39.4451, 43.2671, 48.6491 and 62.7411°. Based on the characterization results, it is known that TiO_2 has formed in the bentonite-TiO_2 composite. This can make the bentonite-TiO_2 more stable and can be used as a photocatalyst in the processing of used lubricating oil.

Based on the SEM results (**Figure 3**), it can be seen that at a 10,000x SEM magnification shown several particles with a layered structure, which is the morphology of bentonite, are produced. In the image, it can also be seen that TiO_2 consists of particles that are still in clumps, indicating that the layered material is not well-formed and remains clumped and uneven. This is due to insufficient stirring time, which will affect the resulting morphology structure of the Bentonite-TiO_2.



(a) **(b)** **(c)**

Figure 3. SEM Characterization of Bentonite-TiO_2, (a). magnification 3000x, (b). 5000x and (c). 1000x

The results of the EDX analysis of Bentonite-TiO_2 are shown in **Table 1**. The composition of the Bentonit-TiO_2 Spectrum shows the chemical composition of C, O, Al, Si, Ca, and Ti. These results confirm the presence of Ti in this Bentonite-TiO_2 composite. Based on these results, it can be determined that the TiO_2-Bentonite composite contains components C at 5.99%, O at 42.22%, Al at 4.64%, Si at 8.15%, Ca at 5.78%, and Ti at 33.22%. [17].

Table 1. EDX Characterization Results of Bentonite-TiO_2

Element	%Mass	%Atom
C	5.99	11.24
O	42.22	59.47
Al	4.64	3.87
Si	8.15	6.54
Ca	5.78	3.25
Ti	33.22	15.63
Total	100	100

Viscosity test over time variations

The Viscosity over time variation is shown in **Figure 4**.

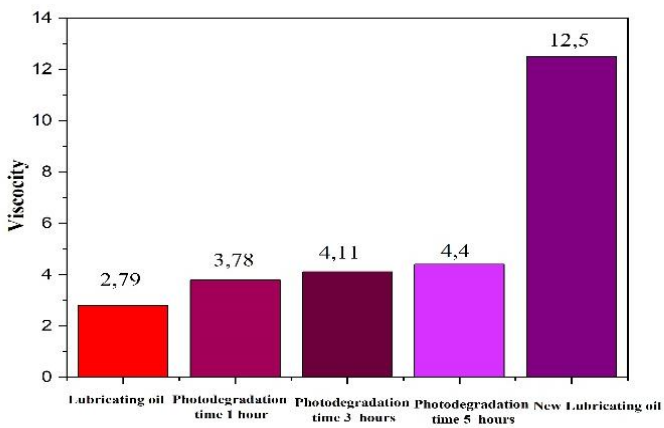


Figure 4. Viscosity Results Over Time Variations

The viscosity value of the new lubricant oil is 12.5 cSt and the used lubricant oil is 2.79 cSt. In the viscosity value of used lubricating oil that has undergone photodegradation with 10 g of Bentonite-TiO_2 composite mass, there is an increase of 3.78 at 1 hour (m10 t1), 4.11 at 3 hours and 4.4 at 5 hours (mass 10 g and time 5 hour). It can be seen that the optimum time for this photodegradation is in the test sample m10 t5 (10 g of Bentonite-TiO_2 composite mass and a photodegradation time of 5 hours).

Viscosity test with mass variation

The Viscosity with mass variation is shown in **Figure 5**.

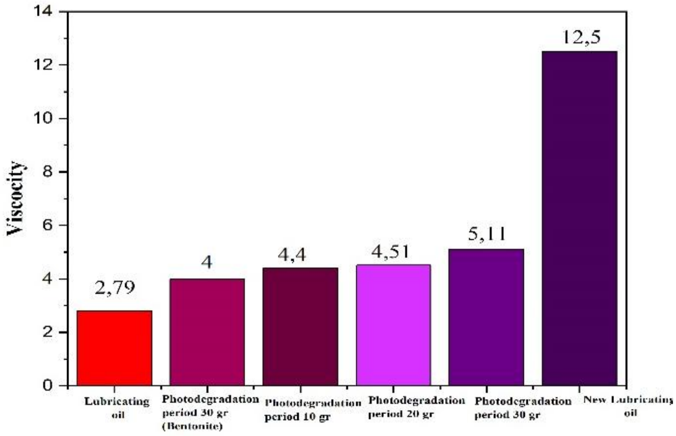


Figure 5. Viscosity Test with Mass Variation

The viscosity test of mass variation on degraded used lubricant oil samples has reached 90% and can be seen in **Figure 5**. The increase in viscosity after photodegradation is caused by the formation of oil degradation intermediate products which have a higher molecular weight and the interaction between Bentonite-TiO_2 and used lubricating oil. The timing and mass of the catalyst play an important role in balancing the process of breaking down hydrocarbon chains and forming new compounds, which directly affects the final viscosity of the oil. At optimum conditions (mass 10 g, time 5 hours), photodegradation takes place effectively in reducing viscosity without producing too many intermediate products which can increase viscosity again [18].

CONCLUSION

The result of the synthesis of the Bentonite-TiO_2 composite obtained a yield of 92.2981%. The Bentonit-TiO_2 composite successfully degraded used lubricating oil, although the increase in viscosity was not significantly higher than before. At the viscosity value of mass variation with the optimum time (5 hours), it is observed that the sample (m30 t50) has the highest viscosity value, which is 5.11 cSt.

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REFERENCES

[1] U.H. Hasyim, D.A. Ningrum, dan E. Apriliani, “Kajian Model Kesetimbangan Adsorpsi Logam Pada Limbah Pelumas Bekas Menggunakan Bentonit,” in *Prosiding SEMNASTEK 2017*, pp. 1-9, 2019.

[2] Badan Pusat Statistik (BPS) Riau. (Feb, 2022). *Jumlah kendaraan bermotor menurut provinsi dan jenis kendaraan (Unit)*. [online]. URL:https://www.riau.bps.go.id/indikator/indikator. [Diakses tanggal 26 Februari 2023].

[3] Kementerian Lingkungan Hidup dan Kehutanan, "Peraturan Menteri Lingkungan Hidup dan Kehutanan Nomor 6 Tahun 2021 tentang Tata Cara dan Persyaratan Pengelolaan Limbah Bahan Berbahaya dan Beracun," 2021.

[4] Pemerintah Republik Indonesia, "Peraturan Pemerintah Nomor 22 Tahun 2021 tentang Penyelenggaraan Perlindungan dan Pengelolaan Lingkungan Hidup," 2021.

[5] V. Azteria, dan R.A. Gani “Pengelolaan limbah minyak pelumas sebagai upaya pengendalian pencemaran lingkungan”. *Biolink Jurnal Biologi Lingkungan Industri Kesehatan*, vol. 6, no. 2, pp. 178–185, 2020.

[6] S. Syahrir, R. Tosepu dan H. Harun. “Pengelolaan limbah bahan berbahaya dan beracun (B3) khusus oli bekas pada bengkel motor dan mobil di jalan H.E.A Mokodompit kota Kendari tahun 2019,” *Jurnal Kesehatan Lingkungan*, vol. 1. no. 1. pp. 36-42, 2020.

[7] X. Sui, X. Wang, Y. Li, H. Ji, “Remediation of petroleum-contaminated soils with microbial and microbial combined methods: advances, mechanisms, and challenges,” *Sustainability*. vol. 13, no. 16, p. 9267, 2021.

[8] N. Lina, “Toxic and hazardous waste (b3) management at PT. PAL Indonesia (PERSERO),” *The Indonesian Journal of Public Health*, vol. 16, no. 3, pp. 449–460, 2021.

[9] Siskayanti, R. Kosim dan Riawan, D. “Efektifitas arang aktif dari tempurung kelapa dalam mengadsorpsi logam Fe pada pelumas motor bekas pakai,” *Jurnal Teknik Kimia UMJ, vol.* 5, No. 2, pp. 108-115. 2020.

[10] Boadu, K.O, Joel, O.F., Essumang dan D.K. Evbuomwan, B.O. “A Review of methods for removal of contaminants in used lubricating oil,” *Chemical Science International Journal*, vol. 26, no. 4, pp. 1–11. 2019.

[11] M. Erlinaningrum, A. Rohman, A.A.M.B. Hastuti, “The effects of activated carbon and bentonite on physicochemical characterization of

red fruit oil (*Pandanus conoideus* Lam),” *Journal Food and Pharmaceutical Sciences*, vol. 12, no. 2, pp. 90-96.

[12] R.F. Mutar dan M.A. Saleh “Optimization of arsenic ions adsorption and removal from hospitals wastewater by nano-bentonite using central composite design.” *Materials Today Proceedings*, vol. 60, pp. 1248–1256. 2022.

[13] T. Mao, J. Zha, Y. Hu, Q. Chen, J. Zhang, X. Luo, “Research progress of TiO_2 modification and photodegradation of organic pollutants,” *Inorganics*, vol. 12, no. 7, p. 178, 2024.

[14] E.A.P. Wibowo, N.R. Aji, R. Ujiningtyas, T. Mayasari, N. Widiarti, “Fotokatalis TiO_2/kitosan dan TiO_2/bentonit sebagai penjernih air embung di lingkungan Unnes,” *Jurnal Sains dan Teknolog.* vol. 5, no. 2, pp. 761-766, 2016.

[15] T. Lathifah, N. Yuliani, G.A.P.K. Wardhani, “Bentonit teraktivasi asam sulfat sebagai adsorben dalam pemurnian pelumas bekas,” *Jurnal Sains Natural*, vol. 9, no. 1, pp. 1-10, 2019.

[16] L.E. Suprihatin, N.D. Murdani, I.W. Suarsa, “Bentonit-Fe_3O_4 sebagai fotokatalis dalam proses fotodegradasi naphthol blue black dengan iradiasi UV,” *Jurnal Kimia*, vol 15, no. 1, pp. 59–66, 2021.

[17] H.S. Sri, P. Prasetya, N. Noramizawati, M. Marlian, R.R. Aulia, “Titanium dioxide (TiO_2) modified bentonite for photodegradation of methylene blue,” *Jurnal Kimia Sains dan Aplikasi*, vol. 4, no. 26, pp. 143-150, 2023.

[18] S. Khursheed, R. Tehreem, M. Awais, D. Hussain, M.I. Malik, Y.S. Mok, G.U. Siddiqui, “Visible-light driven photodegradation of industrial pollutants using nitrogen-tungsten co-doped nanocrystalline TiO_2: spectroscopic analysis of degradation reaction path,” *Nanomaterials*, vol. 12, no. 13, p. 2246, 2022.