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Modification of Areca Nut (*Areca catechu L.*) Peel Hydrochar for Photodegradation of Methylene Blue

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Abstract. Synthetic dyes such as methylene blue (MB) are persistent pollutants that pose serious environmental risks due to their toxicity and resistance to biodegradation. This study investigates the development of sustainable photocatalysts derived from *Areca catechu L.* peel through hydrothermal carbonization, followed by activation, zeolite impregnation, and magnetic modification using Fe^{2+}/Fe^{3+} ions. XRD and FTIR analyses confirmed the successful formation of Fe_3O_4, increased porosity, and the presence of functional groups that facilitate adsorption and photocatalytic activity. The results indicate that photodegradation is significantly more effective than adsorption, with magnetic hydrochar and hydrochar–zeolite composites achieving degradation efficiencies above 90%. Optimal performance was observed at a catalyst mass of 0.20 g and an irradiation time of 150 minutes. The high removal efficiency is attributed to synergistic interactions including π–π stacking, hydrogen bonding, and electrostatic attraction between MB molecules and the modified hydrochar surface. Overall, this study demonstrates that *Areca catechu L.* peel waste can be valorized into an efficient, low-cost, and magnetically recoverable photocatalyst for dye-contaminated wastewater treatment.

Keywords: *Hydrochar, Areca catechu L. peel, Photodegradation, Methylene blue*

Abstrak. Zat warna sintetis seperti metilen biru (MB) merupakan polutan persisten yang menimbulkan risiko lingkungan serius karena sifatnya yang toksik dan resisten terhadap biodegradasi. Penelitian ini mengkaji pengembangan fotokatalis berkelanjutan yang berasal dari kulit buah pinang melalui proses karbonisasi hidrotermal, diikuti aktivasi, impregnasi zeolit, serta modifikasi magnetik menggunakan ion Fe^{2+}/Fe^{3+}. Analisis XRD dan FTIR mengonfirmasi keberhasilan pembentukan Fe_3O_4, peningkatan porositas, serta keberadaan gugus fungsi yang mendukung aktivitas adsorpsi dan fotokatalisis. Hasil penelitian menunjukkan bahwa fotodegradasi jauh lebih efektif dibandingkan adsorpsi, dengan hidrochar magnetik dan hidrochar–zeolit mencapai efisiensi degradasi lebih dari 90%. Kinerja optimal diperoleh pada massa katalis 0,20 g dan waktu iradiasi 150 menit. Efisiensi tinggi ini disebabkan oleh interaksi sinergis seperti π–π stacking, ikatan hidrogen, dan gaya elektrostatik antara molekul MB dan permukaan hidrochar termodifikasi. Secara keseluruhan, penelitian ini menunjukkan bahwa limbah kulit buah pinang dapat divalorisasi menjadi fotokatalis efisien, berbiaya rendah, dan mudah dipisahkan secara magnetik untuk pengolahan limbah zat warna.

Kata kunci: *Hidrokar, kulit Areca catechu L, fotodegradasi, metilen biru*

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INTRODUCTION

Water pollution caused by industrial effluents containing synthetic dyes is a serious environmental issue. Dyes such as methylene blue (MB) are widely used in the textile, paper, and printing industries, but their excessive use and untreated disposal lead to water pollution (Palapa et al., 2023). Dyes can be toxic at high concentrations, are not readily biodegradable, and can harm aquatic life and human health if accumulated over the long term. Exposure to these dyes can cause health problems such as

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internal organ damage, skin irritation, respiratory problems, and potential carcinogenic and teratogenic effects (He et al., 2022).

With increasing awareness of environmental sustainability, various methods have been developed to treat dye waste from industrial wastewater, such as adsorption, coagulation, biodegradation, bioremediation, and photodegradation (Aragaw & Bogale, 2021). Among these methods, adsorption and photodegradation stand out as more environmentally friendly approaches because they produce no secondary waste, have low energy consumption, and are highly efficient in treating organic compounds. However, photodegradation requires the assistance of light and semiconductor materials capable of absorbing photon energy and generating free radicals to chemically destroy the pollutant structure (Khan et al., 2024). The resistance of dyes to biodegradation also necessitates more effective treatment technologies than conventional methods such as coagulation and adsorption. Therefore, alternative technologies capable of degrading complex organic compounds into simpler, more environmentally friendly compounds are needed. (Zavahir et al., 2023).

The use of biomass-based catalysts is gaining popularity due to their abundant availability, low cost, and modifiable properties. Areca nut peel is a very abundant agricultural waste in Indonesia but remains underutilized. Through a hydrothermal process, areca nut peel can be converted into a porous, amorphous carbon hydrochar material with good adsorption capacity and potential as an alternative catalyst. However, the hydrochar's performance can be further enhanced by the addition of Fe^{2+}/Fe^{3+} ions, resulting in magnetic hydrochar with strong magnetic properties, a larger surface area, and ease of separation after the reaction. Magnetic hydrochar has been shown to exhibit higher photocatalytic activity than conventional hydrochar because the presence of iron oxide increases electron transfer, surface reactivity, and the number of active sites involved in the dye degradation process. (Huabin Wang et al., 2023).

In this context, this study addresses the optimization of the photodegradation process using magnetic areca nut hydrochar for the decomposition of methylene blue. Optimizing the adsorbent mass is crucial because the amount of adsorbent directly affects degradation efficiency. Too low a mass limits the number of active sites, while too high a mass can lead to light saturation and reduce the effectiveness of photocatalysis. Therefore, this study focuses on determining the optimum mass of magnetic hydrochar capable of producing the best photodegradation efficiency.

MATERIAL AND METHODS

Material Preparation

Areca nut peels were separated from the seeds, cut into small pieces, and oven-dried at 100 °C for 24 h. A total of 2.5 g of the dried peels was mixed with 50 mL of distilled water and then transferred into a 100 mL hydrothermal autoclave. The autoclave was placed in an oven at 250 °C for 4 hours. The black powder, which was the hydrochar, was washed with distilled water and then oven-dried at 105 °C for 24 hours (Adawiyah et al., 2025).

Procedure

Impregnation process

10 grams of dried areca nut shell hydrochar raw material was first activated with KOH and H_2SO_4 for 24 hours before impregnation. The activated hydrochar was then dried at 80°C overnight. The activated hydrochar was then immersed in a zeolite suspension at a ratio of 1:10 (w/v). The soaking was carried out for 2 hours. Afterward, the biomass-zeolite mixture was dried in an oven at 80 ± 5°C.

The zeolite-impregnated hydrochar modified with magnetics

The zeolite-impregnated hydrochar was then magnetically modified using Fe ions. First, 1 g of $FeSO_4 \cdot 7H_2O$ (0.2 M) and 2 g of $FeCl_3 \cdot 6H_2O$ (0.4 M), in a 2:1 molar ratio, were dissolved in 100 mL of distilled water. The solution was then vigorously stirred and heated to 80 °C, after which approximately 40 mL of a 25% NH_4OH solution was slowly added until the pH reached 12. The resulting solids were separated using a magnet and dried at 75 °C for 3 h. Natural zeolite was prepared by grinding and sieving through a 110-mesh sieve, followed by washing and oven-drying at 110 °C for 4 h. SEM-EDS analysis was then performed on the zeolite surface profile before activation. 100 g of the prepared zeolite was activated with 300 ml of 0.5 M HCl for 30 minutes using a water bath shaker at 200 rpm, and then dried for 24 hours. After reaching a neutral pH, it was oven-dried for 5 hours at 160 °C.

Dye photodegradation

The photodegradation process of Methylene Blue (MB) was conducted by studying three main parameters: irradiation time and photocatalyst mass. Initial experiments were conducted to assess the optimum conditions to determine the range of each parameter relevant to the dye degradation process. The photodegradation process was carried out in a dedicated reactor equipped with a UV lamp (Philips TUV 15W/G15 T8 – wavelength 280 nm) for 150 minutes with stirring to maintain solution homogeneity. After the irradiation process was completed, the solids were separated using centrifugation at 7000 rpm for 15 minutes. The absorbance of the remaining solution was then measured using UV–Vis. Contact time tests were conducted at the optimum pH with varying irradiation times of 90, 120, 150, 180, and 210 minutes. Meanwhile, the effect of photocatalyst mass was tested at the optimum pH and irradiation time, with variations in mass of 0.05, 0.10, 0.15, 0.20, and 0.25 grams.

RESULT AND DISCUSSION

Material Preparation Results

The hydrochar produced from areca nut peels turned brown after heating and washing. The resulting hydrochar was subsequently modified with zeolite, transforming the fibrous and nonporous raw biomass into porous, heterogeneous hydrocarbon fragments. Zeolite is a porous hydrated mineral with an anionic framework and a crystalline structure composed of silicon (aluminum) and oxygen tetrahedra; its pores are formed by various tetrahedral arrangements (Zheqi Wang et al., 2020). In addition to changes in color and magnetic behavior, the magnetization process indicates the formation of bonds between Fe^{2+}/Fe^{3+} ions and –OH and –COOH functional groups on the hydrochar surface.

X-Ray Diffraction (XRD) and Infrared Spectrum

The XRD diffractogram in Figure 1 shows the structural characteristics of areca nut husk, hydrocarbons (HC). HCZ is magnetic zeolite impregnated areca nut hydrochar; AZ is zeolite; HCPZ is zeolite acera nut hyrochar; HCPM is magnetic areca nut hydrochar nut HCP is area nut hydrochar. HC peaks at 15.88°, 22.92°, and 34.74° indicate increased structural organization after hydrothermal carbonization, with a prominent peak at 22.92° indicating partially ordered carbon, although the structure remains largely amorphous (Sabzoi et al., 2015).

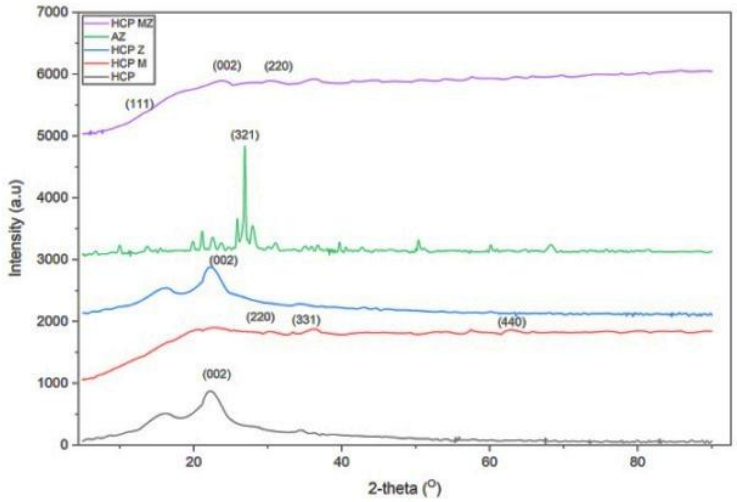

Figure 1. XRD diffractogram

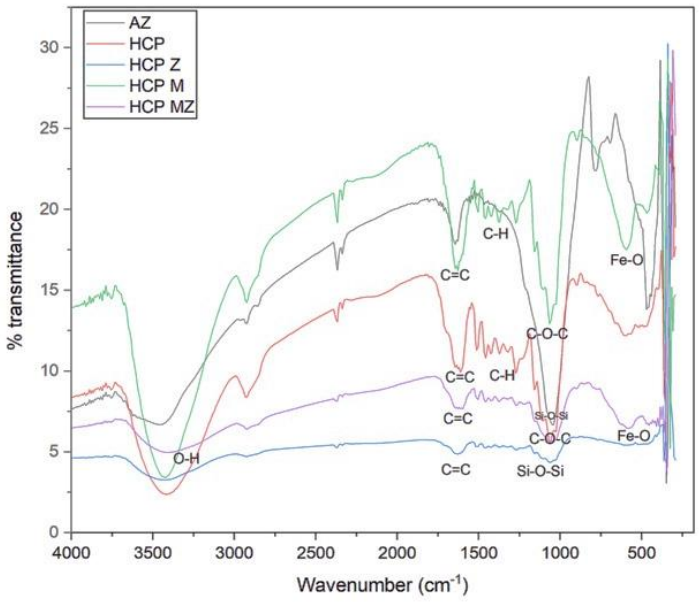

Figure 2. FTIR spectrum

Magnetic hydrochar, on the other hand, exhibits much sharper and more defined peaks. These peaks are located at positions around 2θ ~ 30°, 35°, 43°, 57°, and 62°, which correspond to the (220), (311), (400), (511), and (440) planes of magnetite (Fe_3O_4). The appearance of these peaks indicates that the iron impregnation and hydrothermal heating

processes successfully formed the Fe_3O_4 phase on the hydrochar surface. XRD characterization was performed on HCl-activated zeolite and zeolite-impregnated hydrochar. The zeolite-impregnated hydrochar exhibited 2θ angles at 15.9° and 22.5°. These diffraction peaks were identified as solullose compounds. These diffraction results are consistent with the data provided in ICDD PDF 00-060-1501 (Montoya-escobar et al., 2022).

The FTIR spectra presented in Figure 2 illustrate the functional group compositions of HCPMZ, HCPM, HCPAZ, and HCPZ. In HC, the absorption band at 1650–1600 cm^{-1} corresponds to the C=C stretching vibration of aromatic rings, indicating an increase in aromaticity during hydrothermal carbonization. In addition, the band at 1400 cm^{-1} corresponds to C-H bending vibration, while the peak at 1110 cm^{-1} indicates C-O-C stretching, characteristic of ether bonds in carbohydrate residues. The peak at 600-800 cm^{-1} indicates the presence of out-of-plane aromatic bending, which confirms the retention of aromatic structures in the adsorbent material (Mara Olivares, Silvia Román, 2019). After the magnetization process, which involves the addition of Fe^{2+}/Fe^{3+} ions, the FTIR spectrum shows a new peak at 500 cm^{-1}, which is a characteristic band for Fe-O bonds, indicating the formation of a magnetite phase (Fe_3O_4) on the hydrochar surface (Herbei et al., 2025). This magnetization process does not remove active functional groups such as -OH and -COOH, so the adsorption properties of the hydrochar are maintained.

Material Application in Adsorption and Photodegradation Processes

In this study, hydrochar material was utilized primarily for the adsorption process, as this study compared the effectiveness of the adsorption and photodegradation processes

Determination of maximum wavelength of methylene blue

Measurements were made using a UV-Vis spectrophotometer in the range of 500–700 nm. The scan results showed the highest absorption peak at 664 nm, which is the typical λmax of methylene blue. Research by Odoemelam also reported a λmax value for methylene blue at 660–664 nm, thus these results are consistent with the literature (Odoemelam et al., 2018).

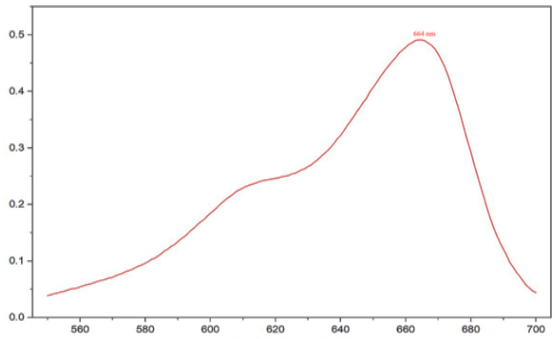

Figure 3. UV-VIS spectra

The adsorption experiments were conducted by adding 0.02 g of areca nut peel and hydrochar (HC) adsorbents to a 100 mL Erlenmeyer flask containing 20 mL of methylene blue solution with a concentration of 50 mg/L, without pH adjustment. The mixture was stirred using a magnetic stirrer for varying periods. After stirring, the adsorbent was separated from the solution by filtration, and the resulting filtrate was analyzed using a UV-Vis spectrophotometer to measure absorbance (Herbei et al., 2025). Data for varying adsorption times are shown in Table 1 and Figure 4, showing the % adsorption versus % degradation of areca nut peel, and HC, analyzed using UV-VIS spectroscopy.

Table 1. Comparison of adsorption and photodegradation methods at 150 minutes.

Ad-sorbent	Initial Concentration (mg/L)	% Adsorption	% Degredation
Area catechu Peel	50.74	32.343	70.204
Hydrochar	50.74	48.874	89.145

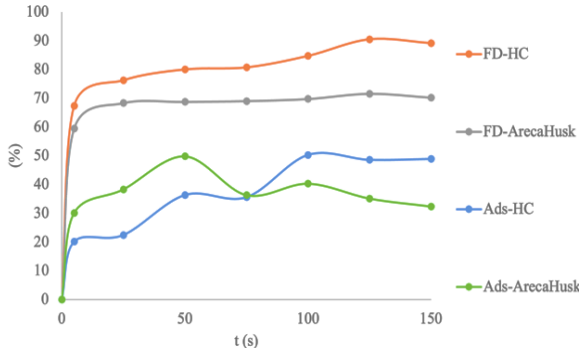

Figure 4. Percentage of degraded and adsorbed

Figure 4 shows a comparison of the percentages of adsorption and degradation calculated from the residual concentrations. These calculations were based on UV–VIS absorbance measurements at the characteristic wavelength of methylene blue and the final concentrations obtained for each treatment. Figure 4 and Table 1 indicate that the raw material being tested is more effective in the photodegradation process than in the adsorption process at the same time and dye concentration. The application of the modified material is then carried out through the photodegradation process.

Effect of material mass variation on the amount of MB degradation

The results of photodegradation tests at different adsorption masses, namely with zeolite activated with HCl and hydrocarbons from areca nut shells impregnated with zeolite (Figure 5). Based on the data in the graph, hydrocarbons from areca nut shells were impregnated with zeolite at a mass of 0.05 g showed a lower decomposition rate than activated zeolite. At a mass of 0.1 g, hydrocarbons from zeolite-impregnated areca nut shells (HCP Z) tended to be slightly more effective or equivalent to activated zeolite (AZ). Even at a mass of 0.2 g, hydrocarbons from zeolite-impregnated areca nut shells showed better adsorption capacity or higher photodegradation effectiveness at higher masses.

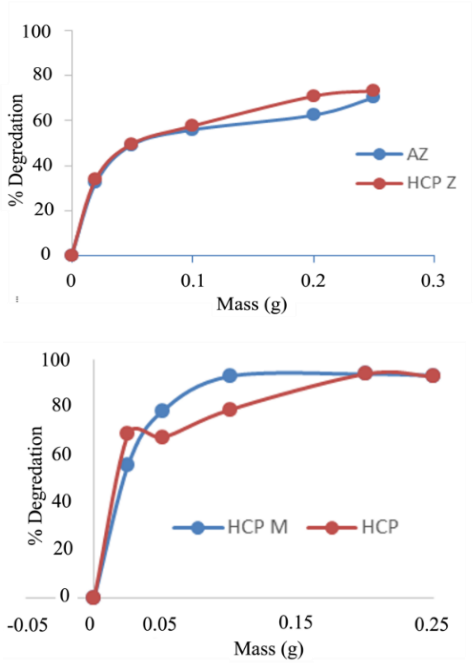

Figure 5. Mass variation graph

Based on the adsorbent mass variation data, it was found that increasing the mass of magnetic hydrochar and hydrochar had a significant effect on the degradation percentage. In magnetic hydrochar material, a mass of 0.025 g showed 55.69% degradation, and at a mass of 0.05 g the degradation percentage was 78.18%. When the mass was increased to 0.10 g, the degradation reached 92.90%, then increased to 93.79% at a mass of 0.20 g and stabilized at 93.17% at 0.25 g.

Meanwhile, in hydrochar, the degradation percentage was 68.57% at a mass of 0.025 g. At a mass of 0.05 g, the degradation decreased slightly to 67.16%, but increased again at 0.10 g to 78.83%. The highest degradation value was achieved at a mass of 0.20 g, namely 93.85%, and slightly decreased to 92.81% at 0.25 g. Overall, both materials showed an increasing trend of degradation with increasing adsorbent mass, with the optimum value at 0.20 g, where the percentage degradation reached its highest value before stabilizing at subsequent masses.

Effect of variation in material contact time on the amount of MB dye degraded

The percentage degradation increased with time, up to 150 minutes (Figure 6), indicating a percentage degradation of 91.8% for HCP; 90.0% for HCP-M; 82.8% for HCP Z; and 93% for AZ, respectively.

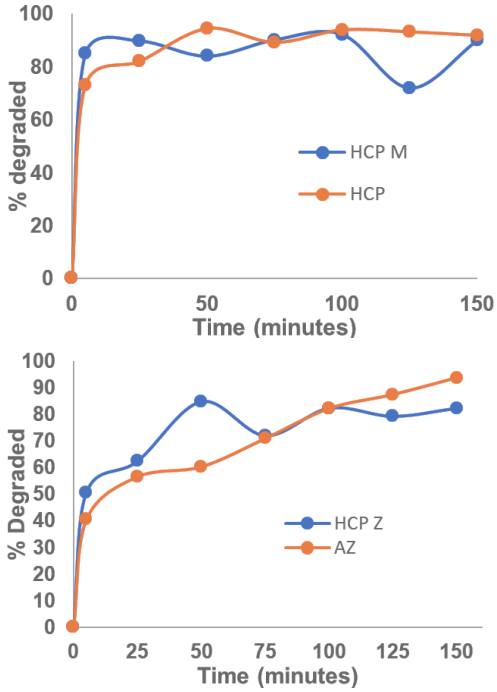

Figure 6. Time Variation Curve

CONCLUSION

Based on the results of preparation, characterization, and adsorption and photodegradation performance tests, it can be concluded that areca nut peel–based materials were successfully modified into hydrochar, magnetic hydrochar, and hydrochar–zeolite. These materials exhibited structural and physicochemical properties that are more suitable for applications as adsorbents and photocatalysts. Activation and modification with zeolite further enhanced the photodegradation efficiency. Application tests demonstrated that photodegradation was more effective than adsorption under identical conditions. Hydrochar-based materials, particularly magnetic hydrochar and hydrochar–zeolite, showed the highest degradation performance at an optimum mass of 0.20 g, achieving degradation efficiencies exceeding 90%. In addition, contact time had a positive effect, with maximum degradation observed at 150 min.

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REFERENCES

Adawiyah, R., Hanifah, Y., & Palapa, N. R. (2025). Analysis Congo red dye adsorption on hydrochar and nano- hydrochar from Areca catechu : Synthesis, characterization, and comparative study. *Journal of Ecological Engineering.* 26(5), 239–254. https://doi.org/10.12911/22998993/201235

Aragaw, T. A., & Bogale, F. M. (2021). Biomass-Based Adsorbents for Removal of Dyes From Wastewater : A Review. *Frontiers in Environmental Science.* 9(7). Bhttps://doi.org/10.3389/fenvs.2021.764958

He, L., Michailidou, F., Gahlon, H. L., & Zeng, W. (2022). Hair Dye Ingredients and Potential Health Risks from Exposure to Hair Dyeing This manuscript is part of a special collection : Chemical Exposures and Impact on Human Health. *Toxicology*. 35(4), 656-672. https://doi.org/10.1021/acs.chemrestox.1c00427

Herbei, E. E., Buruiana, D. L., Muresan, A. C., Ghisman, V., Bogatu, N. L., Basliu, V., Vasile, C., & Barbu-tudoran, L. (2025). Tailored Magnetic Fe 3 O 4 -Based Core – Shell Nanoparticles Coated with TiO 2 and SiO 2 via Co-Precipitation : Structure – Property Correlation for Medical Imaging Applications. *Diagnostics.* 15(15). 1–19. https://doi.org/10.3390/diagnostics15151912

Huabin Wang, Yi Wu, Yi Wen, Dingxiang Chen, Jiang Pu, Yu Ding, Sailian Kong, Shuaibing Wang Xu, and R. (2023). Simultaneously Cationic and Anionic Dyes Elimination via Magnetic Hydrochar Prepared from Copper Slag and Pinewood Sawdust. *Toxics.* 11(6). 45-67. https://doi.org/10.1021/acsomega.4c00887

Khan, S., Noor, T., Iqbal, N., & Yaqoob, L. (2024). Photocatalytic Dye Degradation from Textile Wastewater : A Review. *ACS Omega.* 9(15), 45-67. https://doi.org/10.1021/acsomega.4c00887

Mara Olivares, Silvia Román, B. L. and A. Á. (2019). Magnetic Behavior of Carbon Materials Made from. *Molecules,* 24(8) 1–13. https://doi.org/10.3390/molecules240814213

Montoya-escobar, N., Ospina-acero, D., Andr, J., Catalina, G., Felisinda, P., Rojo, G., Maria, L., Escobar, J. P., Correa-hincapi, N., Triana-ch, O., Gallego, R. Z., & Stefani, P. M. (2022). Use of Fourier Series in X-ray Diffraction (XRD) Analysis and Fourier-Transform Infrared Spectroscopy (FTIR) for Estimation of Crystallinity in Cellulose from Different Sources. *Cellulose Chemistry and Technology,* 56(7-8). 635-649

Odoemelam, S. A., Emeh, U. N., & Eddy, N. O. (2018). Experimental and computational chemistry studies on the removal of methylene blue and malachite green dyes from aqueous solution by neem (Azadirachta indica) leaves. 3655. *Journal of Taibah University for Science*, 12(3), 255-265. https://doi.org/10.1080/16583655.2018.1465725

Palapa, N. R., Ahmad, N., Utami, H. P., Zahara, Z. A., Mohadi, R., & Lesbani, A. (2023). Adsorption of Phenol Using Hydrochar Modified Layered Double Hydroxide – Kinetic , Isotherm , and Regeneration Studies. *Ecological Engineering & Environmental Technology*, 24(5), 275–281. https://doi.org/10.12912/27197050/166010

Sabzoi Nizamuddin, Natesan Subramanian Jaya Kumar, Jaya Narayan Sahu, P. an, & Ganesan, Nabisab Mujawar Mubarak, S. A. M. (2015). Synthesis and Characterization of Hydrochars Produced by Hydrothermal. *The Canadian Journal of Chemical Engineering,* 93(11), 1916-1921. https://doi.org/10.1002/cjce.22293

Zavahir, S., Elmakki, T., Ismail, N., Gulied, M., Park, H., & Han, D. S. (2023). Degradation of Organic Methyl Orange (MO) Dye Using a Photocatalyzed Non-Ferrous Fenton Reaction. *Nanomaterials.* 12(3), 639. https://doi.org/10.3390/nano13040639

Zheqi Wang, Guohua Zhang, and Y. L. (2020). Preparation of Chitosan / Polyacrylamide / Graphene Oxide Composite Membranes and Study of Their Methylene Blue Adsorption Properties. *Materials*, 13(20), 4598. https://doi.org/10.3390/ma13204598