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Research Paper

# Rice Husks as Green Adsorbents for Removal of Anionic Dye: Kinetic, Isotherm, and Thermodynamic Adsorption Studies

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**Abstract**
Rice husk, a green adsorbent, was used for procion red adsorption. Analysis with BET, XRD, FTIR, and SEM confirmed the formation of rice husk. The results indicate that rice husk is more porous and has a rougher surface. The surface of the rice husk has a non-uniform shape and uneven morphology. The pore of rice husk is critical to the adsorption process of procion red. The procion red will enter the pore of the rice husk to make an interaction. The rice husk has a surface area, pore volume, and pore diameter of 7.08 $m^2/g$, 0.011 cc/g, and 3.14 nm, respectively. The vibrational peak at 3448 1620, 1103, and 794 $cm^{-1}$. the XRD powder patterns of rice husk characterization diffraction peak at $2\theta$ 23°. Rice husk's adsorption system for procion red removal follows PSO kinetic and Freundlich isotherm models with a maximal removal capacity of 158.730 mg/g. This study sheds light on the effectiveness of rice husk as an adsorbent for procion red contaminants.

**Keywords**
Green Adsorbent, Rice Husks, Procion Red, Adsorption

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## 1. INTRODUCTION

The maintenance of water quality in the face of diminishing water resources and a growing population is currently one of the most pressing environmental concerns (Yang et al., 2022). For many years, contamination of groundwater and surface water with organic and inorganic pollutants as a threat to human and animal health has been analyzed (Ghibate et al., 2021). Industrial and agricultural effluents are the primary sources of water contamination due to the presence of hazardous compounds (Siraorarnroj et al., 2022). Synthetic and reactive dyes, which are widely used in textiles, carpets, paper, and cosmetics, are one of the other major classes of organic pollutants (Fraga et al., 2019; Sriramoju et al., 2021).

The degradability of procion red makes it a possible environmental pollutant (Nor et al., 2015). Various techniques have been used to remove dyes from aqueous media, including adsorption, photodegradation, and membrane filtering (Dhaneswara et al., 2022; Liu et al., 2018; Yuliasari et al., 2022). Using an adsorbent to remove colors from a solution is a frequent application of adsorption (Ahmad et al., 2023b). This strategy is simple to employ, highly effective, and inexpensive (Chaari et al., 2021). This approach relies on the quality of the adsorbent for its success. Often used to remove dyes from solution are inorganic adsorbents such as zeolites, clays, activated carbons, and carbon nanotubes (Ahmad et al., 2023a; Nyika and Dinka, 2022). On the other hand, organic adsorbents such as chitosan, lignin, cellulose, and algae are also efficient and renewable adsorbents for removing numerous types of dyes (Heo et al., 2022; Vedula and Yadav, 2022). Among these adsorbents, organic adsorbents have advantages because they are derived from renewable sources such as rice husk (Shamsollahi and Partovinia, 2019).

Consequently, utilizing waste items such as rice husks can be a more efficient and cost-effective option. Due to the significance of bio-based adsorbents for pollution removal, rice husk is also an excellent adsorption component (Phan et al., 2022). Important for environmental applications are these biosorbents, which are renewable and environmentally friendly due to their abundance, free availability, low cost, and high adsorption capacity, as well as their simple processing and regeneration, insensitivity to toxicants, and good performance (Araichimani et al., 2022). Haider et al. (2022) used rice husk-modified silica for the adsorption of methylene blue with a maximum adsorption capacity of 107 mg/g. Previous research from Naik et al. (2023) used rice husk for the removal of heavy metals. Meanwhile, Bai et al. (2021) remove ammonia using rice husk-decorated silica carbon, activated carbon, and silicon dioxide.

In this research, rice husk is employed as a procion red adsorbent. SEM, FTIR, XRD, and BET were utilized to evaluate the characteristic of the adsorbent. The factors that impact the success of adsorption, such as kinetic, isotherm, and thermodynamic, were investigated.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

This investigation utilized rice husk, distilled water (H2O), and procion red as its materials. X-Ray Diffraction analysis (Rigaku 600), Fourier Transfer Infra-Red spectrophotometer (Shimadzu Prestige-21), Surface Area Analyzer (ASAP 2020), Scanning Electron Microscope, and UV-Visible spectrophotometer (Biobase BK-UV1800) were utilized for material characterization.

### 2.2 Adsorbent Preparation

Rice husks samples were cut into small pieces, and rinsed with clean water, after that oven at 100°C. The rice husks were then crushed with a mortar and sieved at 200 mesh.

### 2.3 Kinetic Study

Rice husk weighing up to 0.04 g was added to a beaker glass that had been filled with 40 mL of a 100 mg/L procion red solution. The solution was agitating for varying durations between 5 and 180 minutes, followed by separation. The separation was accomplished and the resulting filtrate was measured with UV-Vis spectrophotometer.

### 2.4 Isotherm Study

A total of 0.04 g of rice husk was added to a 100 mL beaker glass containing 40 mL of varied concentrations of procion red solutions ranging from 50 to 100 mg/L. The optimum duration for adsorption was determined by a previous study, and the process was carried out by stirring at temperatures ranging from 30 to 60°C. The rise husk and procion red solution were separated by centrifugation, and the absorbance of procion red determined using UV-Vis spectrophotometer.

## 3. RESULTS AND DISCUSSION

Figure 1 depicts the surface morphology of rice husks as observed by scanning electron microscopy (SEM). The results indicate that rice husk is more porous and has a rougher surface. The surface of the rice husk has a non-uniform shape and uneven morphology. The pore of rice husk is critical to the adsorption process of procion red. The procion red will enter the pore of the rice husk to make interaction.

Figure 2 displays the FTIR spectrum of rice husk. The vibrational peak at 3448 cm$^{-1}$ is associated with the -OH group. The spectrum at 1620 cm$^{-1}$ corresponds to the carboxylate group containing C-O bonds. The spectrum at 794 cm$^{-1}$ indicates the presence of a Si-O bond (Palapa et al., 2022). The peak 1103 cm$^{-1}$ corresponds to the C-H stretching of lignin in the rice husk.

Figure 3 depicts the XRD powder patterns of rice husk characterization diffraction peak at $2\theta$ 23°. According to a previous investigation, $2\theta$ diffraction exhibited no diffraction peaks other than one of approximately 23° with reflection (002) (Hasanah et al., 2022). These diffractions demonstrate the presence of amorphous silica in the rice husk.


**Figure 1.** SEM Image of Rice Husks

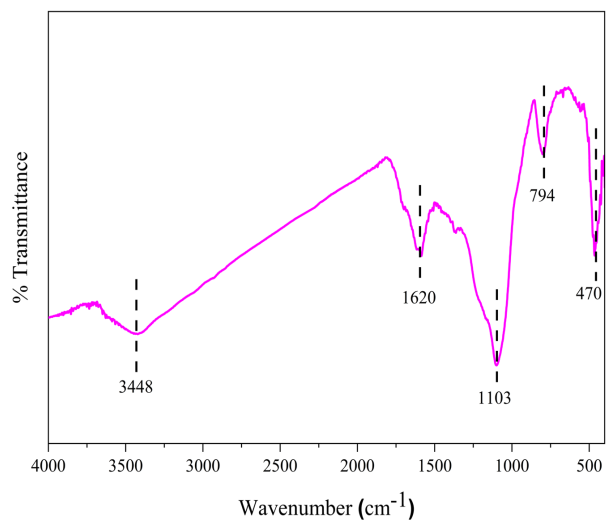


**Figure 2.** FTIR Spectra of Rice Husks

Rice husk is characterized by BET to ascertain its surface area, pore volume, and pore size distribution. Figure 4 depicts the $N_2$ Isotherm adsorption and pore size distribution of rice husk. The $N_2$ adsorption/desorption isotherm on rice husks follows the type IV isotherm (Chouaybi et al., 2022), as shown in Figure 4. This information suggests that the number of adsorbents increases with increasing relative pressure. According to Table 1, the surface area of rice husk is 7.08 m$^2$/g, the total pore volume is 0.011 cc/g, and the average pore diameter is 3.14 nm.

The study of the rate at which an adsorbent absorbs an adsorbate is known as adsorption kinetics. The adsorption rate exposes the characteristics of the adsorbent's adsorption capacity on the adsorbate. Researchers examined kinetic modeling utiliz-

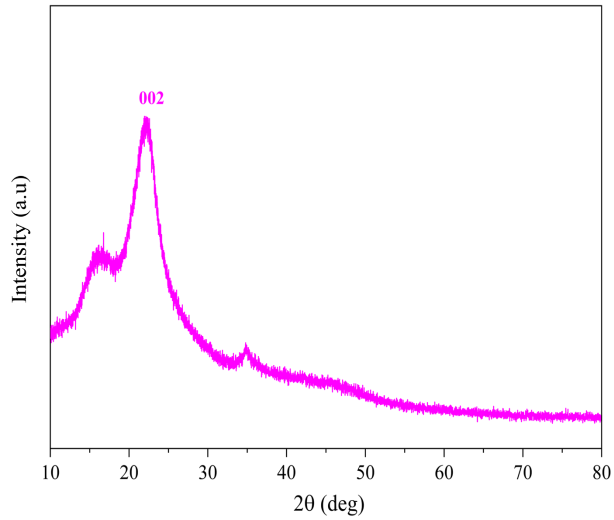


**Figure 3.** XRD Pattern of Rice Husks

**Table 1.** BET Result of Rice Husk

| Parameter | Result |
|---|---|
| Surface area | 7.08 $m^2/g$ |
| Pore size | 3.14 nm |
| Pore volume | 0.011 cc/g |

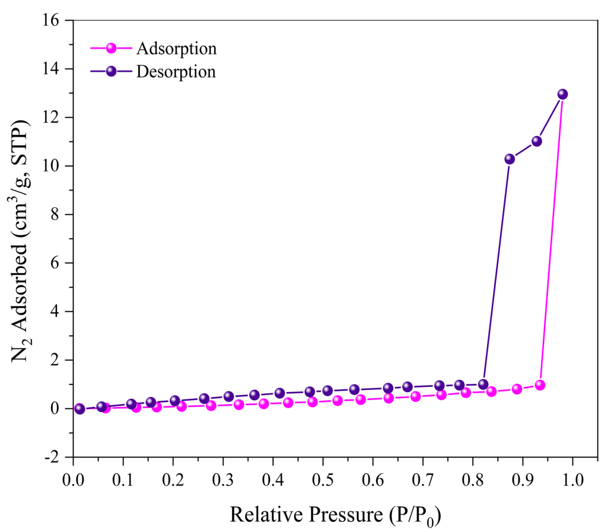


**Figure 4.** Nitrogen Adsorption-Desorption of Rice Husks

ing a first-order pseudo-kinetic model (PFO) and a second-order pseudo-kinetic model (PSO) (Figure 5). Table 2 demonstrates the linear regression of the PFO and PSO kinetic equations. The correlation coefficient value in the PFO model with a lower $R^2$ value, which is supported by $k_2$ data with a smaller value than $k_1$ data. According to the obtained data, the PSO kinetic model is a better fit for the procion red adsorption procedure. This indicated that adsorption of procion red followed chemisorption (Taher et al., 2023).

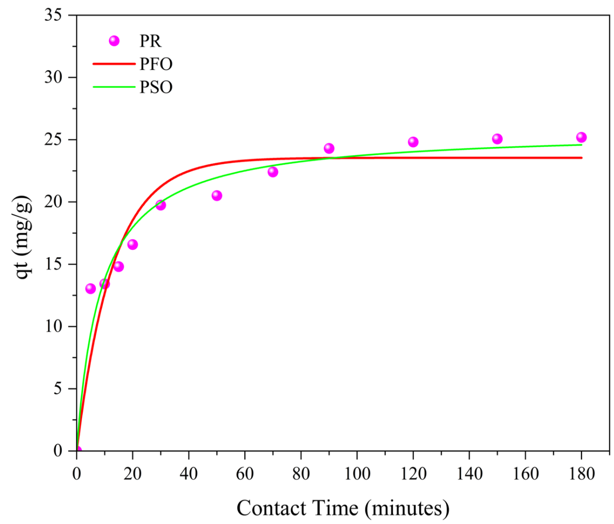


**Figure 5.** Contact Time Between Adsorbents and Adsorbate

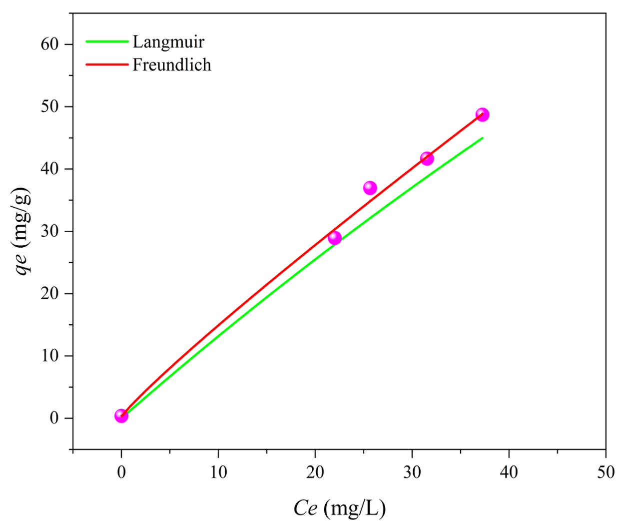


**Figure 6.** Isotherm Adsorption

Adsorption isotherms describe the properties and varieties of adsorption as well as the interaction between the adsorbate and adsorbent. Using two isotherm models, the equilibrium of procion red adsorption on rice husk was investigated: the Langmuir isotherm model and the Freundlich isotherm model (Figure 6). The Langmuir isotherm model assumes that procion red adsorption occurs chemically and is monolayer at a limited number of specific sites. Meanwhile, the Freundlich isotherm model is utilized for multilayer chemical adsorption, which is characterized by a nonuniform distribution of adsorption heat and heterogeneous surface affinities (Palapa et al., 2021). Based on the data presented in Table 3, it is demonstrated that the Freundlich adsorption isotherm model is more appropriate for

 

**Table 2.** Kinetic Data of Rice Husk

| Adsorbent | $Qe_{exp}$ (mg/g) | Pseudo-first-order | | | Pseudo-second-order | | |
|---|---|---|---|---|---|---|---|
| | | $Qe_{calc}$ (mg/g) | $k_1$ ($min^{-1}$) | $R^2$ | $Qe_{calc}$ (mg/g) | $k_2$ (g/mg.min) | $R^2$ |
| Rice Husk | 59.215 | 43.262 | 0.025 | 0.936 | 61.958 | 0.001 | 0.997 |

**Table 3.** Isotherm Data of Rice Husk

| T (°C) | Freundlich | | | Langmuir | | | ΔH (kJ/mol) | ΔS (J/K.mol) | ΔG (kJ/mol) |
|---|---|---|---|---|---|---|---|---|---|
| | n | kF | $R^2$ | Qmax | kL | $R^2$ | | | |
| 30 | 1.303 | 2.473 | 0.999 | 158.730 | 0.009 | 0.983 | 7.039 | 0.024 | -0.072 |
| 40 | 1.459 | 3.966 | 0.982 | 153.846 | 0.010 | 0.889 | | | |
| 50 | 1.349 | 3.037 | 0.981 | 129.870 | 0.014 | 0.929 | | | |
| 60 | 1,469 | 4.035 | 0.873 | 111.111 | 0.020 | 0.941 | | | |

describing the adsorption of procion red by rice husk biosorbent. This is indicated by the linear regression coefficient in the Freundlich adsorption isotherm equation, which approaches the value 1. When the dye adsorption using rice husk biosorbent satisfies the Freundlich isotherm equation, the multilayer adsorption process takes place. The maximum adsorption capacity of procion red on rice husk is 158.730 mg/g at 30°C.

Table 3 displays the thermodynamic parameters for the adsorption of procion red on rice husk, including ΔH (enthalpy), ΔG (Gibbs free energy), and ΔS (entropy) (Georgin et al., 2018). Positive values (0.024 J/K.mol) of ΔS indicate that the degree of irregularity between the adsorbate and adsorbent is increasing. The positive value (7.039 kJ/mol) of ΔH indicates the endothermic adsorption of procion red onto rice husk. The negative value (-0.072 kJ/mol) of ΔG suggests that the adsorption of procion red is spontaneous. The adsorption of procion red by some adsorbents is displayed in Table 4.

**Table 4.** Adsorption of Procion Red by Some Adsorbents

| Adsorbent | Qmax (mg/g) | Reference |
|---|---|---|
| Rice husk | 158.730 | This study |
| *Spirulina sp* | 11.23 | (Mohadi et al., 2017) |
| Tamarint-seed | 61.10 | (Chaiyapongputti et al., 2014) |
| AC-bagasse | 6.90 | (Fahira et al., 2021) |
| Parkia Speciosa peel | 8.20 | (Anuar et al., 2020) |

## 4. CONCLUSIONS

Rice husk, a green adsorbent, was used for the adsorption of procion red. Analysis with BET, XRD, FTIR, and SEM confirmed the formation of rice husk. Rice husk's adsorption system for procion red removal follows PSO kinetic and Freundlich isotherm models with a maximal removal capacity of 158.730 mg/g. This study sheds light on the effectiveness of rice husk as an adsorbent for procion red contaminants.

## 5. ACKNOWLEDGEMENT

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## REFERENCES

Ahmad, N., F. S. Arsyad, I. Royani, and A. Lesbani (2023a). Charcoal Activated as Template Mg/Al Layered Double Hydroxide for Selective Adsorption of Direct Yellow on Anionic Dyes. *Results in Chemistry*, **5**; 100766

Ahmad, N., F. S. Arsyad, I. Royani, P. M. S. B. N. Siregar, T. Taher, and A. Lesbani (2023b). High Regeneration of ZnAl/NiAl-Magnetite Humic Acid for Adsorption of Congo Red from Aqueous Solution. *Inorganic Chemistry Communications*, **150**; 110517

Anuar, F., T. Hadibarata, M. Syafrudin, and Z. Fona (2020). Removal of Procion Red MX-5B from Aqueous Solution by Adsorption on *Parkia speciosa* (Stink Bean) Peel Powder. *Biointerface Research in Applied Chemistry*, **10**; 4774–4779

Araichimani, P., K. Prabu, G. S. Kumar, G. Karunakaran, S. Surendhiran, M. Shkir, and H. E. Ali (2022). Synthesis of $Fe_3O_4$-Decorated $SiO_2$ Nanostructure using Rice Husk as a Source by Microwave Combustion for the Development of a Magnetically Recoverable Adsorbent. *Ceramics International*, **48**(7); 10339–10345

Bai, W., M. Qian, Q. Li, S. Atkinson, B. Tang, Y. Zhu, and J. Wang (2021). Rice Husk-Based Adsorbents for Removing Ammonia: Kinetics, Thermodynamics and Adsorption Mechanism. *Journal of Environmental Chemical Engineering*, **9**(4); 105793

Chaari, I., A. Touil, and M. Medhioub (2021). Adsorption-Desorption of Phenolic Compounds from Olive Mills Wastewater using Tunisian Natural Clay. *Chinese Journal of Chemical Engineering*, **40**; 287–292

Chaiyapongputti, P., P. Tooptompong, J. Setthayanond, and P. Munsuwan (2014). Development of Adsorbent Material from Tamarind-Seed Testa for Reactive Dye Adsorption. In *Applied Mechanics and Materials*, **535**; 650–653

Chouaybi, I., H. Ouassif, M. Bettach, and E. M. Moujahid (2022). Fast and High Removal of Acid Red 97 Dye from Aqueous Solution by Adsorption Onto a Synthetic Hydrocalumite: Structural Characterization and Retention Mechanisms. *Inorganic Chemistry Communications*, **146**; 110169

Dhaneswara, D., H. S. Marito, J. F. Fatriansyah, N. Sofyan, D. R. Adhika, and I. Suhariadi (2022). Spherical SBA-16 Particles Synthesized from Rice Husk Ash and Corn Cob Ash for Efficient Organic Dye Adsorbent. *Journal of Cleaner Production*, **357**; 131974

Fahira, C. A., D. R. Damayanti, A. Febrianti, and R. A. Lestari (2021). Adsorb Red Procion in Batik Waste used Baggase Adsorbent. In *AIP Conference Proceedings*, **2349**; 020069

Fraga, T. J. M., L. E. M. de Lima, Z. S. B. de Souza, M. N. Carvalho, E. M. P. d. L. Freire, M. G. Ghislandi, and M. A. da Motta (2019). Amino-$Fe_3O_4$-Functionalized Graphene Oxide as a Novel Adsorbent of Methylene Blue: Kinetics, Equilibrium, and Recyclability Aspects. *Environmental Science and Pollution Research*, **26**; 28593–28602

Georgin, J., B. da Silva Marques, J. da Silveira Salla, E. L. Foletto, D. Allasia, and G. L. Dotto (2018). Removal of Procion Red Dye from Colored Effluents using $H_2SO_4$-/$HNO_3$-Treated Avocado Shells (*Persea americana*) as Adsorbent. *Environmental Science and Pollution Research*, **25**; 6429–6442

Ghibate, R., O. Senhaji, and R. Taouil (2021). Kinetic and Thermodynamic Approaches on Rhodamine B Adsorption Onto Pomegranate Peel. *Case Studies in Chemical and Environmental Engineering*, **3**; 100078

Haider, J. B., M. I. Haque, M. Hoque, M. M. Hossen, M. Mottakin, M. A. Khaleque, M. Johir, J. L. Zhou, M. B. Ahmed, and M. Zargar (2022). Efficient Extraction of Silica from Openly Burned Rice Husk Ash as Adsorbent for Dye Removal. *Journal of Cleaner Production*, **380**; 135121

Hasanah, M., N. Juleanti, A. Priambodo, F. S. Arsyad, A. Lesbani, and R. Mohadi (2022). Utilization of Rambutan Peel as a Potential Adsorbent for the Adsorption of Malachite Green, Procion Red, and Congo Red Dyes. *Ecological Engineering & Environmental Technology*, **23**(3); 148–157

Heo, J. W., L. An, J. Chen, J. H. Bae, and Y. S. Kim (2022). Preparation of Amine-Functionalized Lignins for the Selective Adsorption of Methylene Blue and Congo Red. *Chemosphere*, **295**; 133815

Liu, Y., Q. Liu, J. Li, H. H. Ngo, W. Guo, J. Hu, M.-t. Gao, Q. Wang, and Y. Hou (2018). Effect of Magnetic Powder on Membrane Fouling Mitigation and Microbial Community/Composition in Membrane Bioreactors (MBRs) for Municipal Wastewater Treatment. *Bioresource Technology*, **249**; 377–385

Mohadi, R., Z. Hanafiah, H. Hermansyah, and H. Zulkifli (2017). Adsorption of Procion Red and Congo Red Dyes using Microalgae *Spirulina sp. Science and Technology Indonesia*, **2**(4); 102–104

Naik, R. L., M. R. Kumar, and T. B. Narsaiah (2023). Removal of Heavy Metals (Cu & Ni) from Wastewater using Rice Husk and Orange Peel as Adsorbents. *Materials Today: Proceedings*, **72**; 92–98

Nor, N. M., T. Hadibarata, Z. Yusop, and Z. M. Lazim (2015). Removal of Brilliant Green and Procionred Dyes from Aqueous Solutionby Adsorption using Selected Agricultural Wastes. *Jurnal Teknologi*, **74**(11); 117–122

Nyika, J. and M. Dinka (2022). Activated Bamboo Charcoal in Water Treatment: A Mini-Review. *Materials Today: Proceedings*, **56**; 1904–1907

Palapa, N. R., T. Taher, N. Juleanti, N. Normah, and A. Lesbani (2021). Biochar from Rice Husk as Efficient Biosorbent for Procion Red Removal from Aqueous Systems. *Applied Environmental Research*, **43**(3); 79–91

Palapa, N. R., T. Taher, N. Normah, and A. Lesbani (2022). NiAl Layered Double Hydroxide/Rice Husk Composite for the Efficient Removal of Malachite Green. *Indonesian Journal of Chemistry*, **22**(1); 142–156

Phan, K. A., D. Phihusut, and N. Tuntiwiwattanapun (2022). Preparation of Rice Husk Hydrochar as an Atrazine Adsorbent: Optimization, Characterization, and Adsorption Mechanisms. *Journal of Environmental Chemical Engineering*, **10**(3); 107575

Shamsollahi, Z. and A. Partovinia (2019). Recent Advances on Pollutants Removal by Rice Husk as a Bio-Based Adsorbent: A Critical Review. *Journal of Environmental Management*, **246**; 314–323

Siraorarnroj, S., N. Kaewtrakulchai, M. Fuji, and A. Eiad-ua (2022). High Performance Nanoporous Carbon from Mulberry Leaves (**?** L.) Residues Via Microwave Treatment Assisted Hydrothermal-Carbonization for Methyl Orange Adsorption: Kinetic, Equilibrium and Thermodynamic Studies. *Materialia*, **21**; 101288

Sriramoju, S. K., P. S. Dash, and S. Majumdar (2021). Meso-Porous Activated Carbon from Lignite Waste and its Application in Methylene Blue Adsorption and Coke Plant Effluent Treatment. *Journal of Environmental Chemical Engineering*, **9**(1); 104784

Taher, T., A. Munandar, N. Mawaddah, M. S. Wisnubroto, P. M. S. B. N. Siregar, N. R. Palapa, A. Lesbani, and Y. G. Wibowo (2023). Synthesis and Characterization of Montmorillonite–Mixed Metal Oxide Composite and its Adsorption Performance for Anionic and Cationic Dyes Removal. *Inorganic Chemistry Communications*, **147**; 110231

Vedula, S. S. and G. D. Yadav (2022). Wastewater Treatment Containing Methylene Blue Dye as Pollutant using Adsorption by Chitosan Lignin Membrane: Development of Membrane, Characterization and Kinetics of Adsorption. *Journal of the Indian Chemical Society*, **99**(1); 100263

Yang, Y., T. M. P. Nguyen, H. T. Van, Q. T. Nguyen, T. H. Nguyen, T. B. L. Nguyen, D. Van Thanh, T. V. Nguyen, P. Q. Thang, and M. Yılmaz (2022). ZnO Nanoparticles Loaded Rice Husk Biochar as an Effective Adsorbent for Removing Reactive Red 24 from Aqueous Solution. *Materials Science in Semiconductor Processing*, **150**; 106960

Yuliasari, N., A. Wijaya, R. Mohadi, E. Elfita, and A. Lesbani (2022). Photocatalytic Degradation of Malachite Green by

 

Layered Double Hydroxide Based Composites. *Bulletin of Chemical Reaction Engineering & Catalysis*, **17**(2); 240–249

 