Vol 8 No. 1 (2023) 166-175 ISSN (Online) : 2502-0943

Jurnal Katalisator

THERMODYNAMIC STUDY OF METHYLENE BLUE DYE ADSORPTION USING KAPOK HUSK

Hamdhan Fathony*[1], Suci Wulandari[1], Putri Ramadhani[1], Rahmiana Zein[1], Deswati[2]

[1]*Laboratory of Environmental Analytical Chemistry, Department of Chemistry, Andalas University, Padang 25163, Indonesia.*

[2]*Laboratory of Applied Analytical Chemistry, Department of Chemistry, Andalas University, Padang 25163, Indonesia.*

*Email : fhamdhan@gmail.com

Detail Artikel

Diterima : 12 Maret 2023
Direvisi : 23 April 2023
Diterbitkan : 30 April 2023

Kata Kunci

Adsorption
kapuk husk
methylene blue
thermodinamic

Penulis Korespondensi

Name : Hamdhan Fathony
Affiliation : Andalas University
E-mail : fhamdhan@gmail.com

A B S T R A C T

Adsorption is one method that is developing in the process of wastewater treatment. This method uses an adsorbent to absorb contaminants such as dyes, metal ions, and other pollutants from industrial wastewater. Currently, efforts are being developed to produce better low-cost adsorbents as alternatives, such as using organic solid waste derived from agricultural by-products such as kapok husk (KH). This study discusses the thermodynamics of adsorption, which aims to look at the energy and distribution of methylene blue (MB) dye particles during the adsorption process using kapok husks (KH) and kapok husks modified with citric acid (CA-KH). The two biosorbents obtained thermodynamic results with a negative value of the Gibbs energy change (ΔG), indicating that the adsorption process took place spontaneously, a negative enthalpy value (ΔH) indicating an exothermic process adsorption process, and a negative entropy value (ΔS) indicating an increase. The regular distribution of methylene blue dye on the surface during the adsorption process is proven by the results of SEM photo analysis at 3000x magnification with the distribution of methylene blue dye on the surface of the two biosorbents.

http://doi.org/10.22216/jk.v5i2.5717
Published by LLDIKTI Wilayah X

Jurnal Katalisator Vol 8 No. 1 (2023) 166-175

INTRODUCTION

Biosorption is the ability of biological materials (biomaterials) to accumulate heavy metals or dyes from wastewater through the absorption of metabolic or chemical-physical media. This biosorption process can occur due to the presence of biological materials called biosorbents and solutions containing heavy metals or dyes so that they are easily bound to biosorbents (Ramadhani *et al*., 2019). Several agricultural and fishery wastes have been used to absorb dyes, including ketapang shells(Hevira et al., 2020), cassava peels(Scheufele *et al*., 2020), wheat (Araújo *et al*., 2020), pensi shells(Zein, Ramadhani, et al., 2019), corn silk (Mbarki *et al*., 2018), psyllium seeds(Malakootian & Heidari, 2018), Lemongrass leaves biowaste (Zein, Purnomo, *et al*., 2022), water hyacinth modified with citric acid (Siswoyo *et al*., 2018).

Kapok (Ceiba pentandra L.) is a plant cultivated in Indonesia. The kapok plant has many benefits for the community, such as its fiber used as stuffing for mattresses and pillows. However, using kapok fiber produces waste such as kapok husks are thrown away by the community; this causes the accumulation of biomass waste, reducing the aesthetic value of the environment. Based on its chemical content, kapok husk has high cellulose and lignin and active groups such as hydroxyl, carbonyl, and carboxylate to absorb cationic pollutants (Farooq et al., 2019). Research on the use of kapok husk as an adsorbent for metal ions Pb(II) and Cd(II) has previously been carried out(Zein, Nofita, *et al*., 2019). However, adsorbents for dyes using kapok husk have not been carried out before, so in this study, Kapok husk is used as an adsorbent for methylene blue dye by looking at the energy value produced through adsorption thermodynamic studies.

Adsorption thermodynamics is studied to predict the spontaneity of an adsorption process and predict the properties of the adsorbent and adsorbate at equilibrium. Adsorption thermodynamics also investigates temperature variations and whether adsorption processes are advantageous or unfavorable used in industrial wastewater treatment processes(Lombardo & Thielemans, 2019). For thermodynamic studies, adsorption experiments were carried out at different temperature conditions, and the calculated parameters included enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG)(Batool et al., 2018).

The ratio of the effective concentration of the dye to the solid adsorbent to the aqueous solution is a constant called the equilibrium constant, Kc of the adsorption process:

$$Kc = \frac{Q_e}{C_e} \quad (1)$$

The classical Van’t Hoff reaction isotherm equation correlates the free energy change (ΔG), the standard free energy change (ΔG^0), and the equilibrium constant (Kc) at constant temperature (T) as:

Jurnal Katalisator Vol 8 No. 1 (2023) 166-175

$$\Delta G = \Delta G^0 + RT\ln Kc \quad (2)$$

At equilibrium, the change in free energy (G) is zero; then the equation changes to the following:

$$\Delta G^0 = - RT\ln Kc \quad (3)$$

This is the most crucial Equation used in sorption thermodynamics to predict the feasibility of a sorption process. To predict the standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o), Equation (3) is rearranged in terms of the equilibrium constant (Kc) as:

$$\ln Kc = \frac{\Delta G^0}{-RT} \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

Where R = 8.314 J / mol / K and (absolute temperature in K)(Osagie et al., 2021). the van't Hoff equation becomes:

$$\ln Kc = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (6)$$

The positive value of ΔH confirms the endothermic nature of the adsorption process. Positive values of ΔH, ΔG, and TΔS indicate that the adsorption reaction takes place spontaneously at high temperatures and not at low temperatures. Decreasing the value of ΔG^o with increasing temperature confirms that absorption is more efficient at higher temperatures. The positive value of the entropy change means that the randomness of the solid/liquid interface increases(Elwakeel et al., 2017).

METHOD

Time and Place of Research

This research was conducted from October 2021 to June 2022 at the Chemical Laboratory for Environmental Analysis, Faculty of Mathematics and Natural Sciences, Andalas University, and the Laboratory of the Department of Mechanical Engineering, SepuluhNopember Institute of Technology (ITS) Surabaya.

Tools

The equipment used in this study were glassware (Erlenmeyer flasks, volumetric flasks, measuring pipettes and pipettes), analytical balances (Kern & Sohn GmbH), rotary shakers (Edmun Buhler 7400 Tubingen), pH meters (Metrohm), ovens (Memmert), crusher (Fritsch,

Jurnal Katalisator Vol 8 No. 1 (2023) 166-175

Germany), sieve (Fritsch, Germany), SEM-EDS (Hitachi FLEXSEM 1000) and UV-Vis Spectrophotometer (Genesys 20 Thermo Scientific)

Materials

The materials used in this study were kapok skin (Ceiba pentandra L gaertn) obtained from the kapok ombilin plantation in Singkarak, West Sumatra, methylene blue dye (Merck), distilled water, HNO_3p.a (Merck), technical NaOH (Merck), citric acid ($C_6H_8O_7$) (Merck), Sodium Citrate dihydrate ($C_6H_5Na_3O_7.2H_2O$) (Merck), Acetic Acid (CH_3COOH) (Merck), Sodium Acetate (CH_3COONa) (Merck), Monobasic Sodium Phosphate (NaH_2PO_4) (Merck), Dibasic Sodium Phosphate (Na_2HPO_4) (Merck), Sodium Carbonate (Na_2CO_3), Sodium Bicarbonate ($NaHCO_3$), Potassium Chloride (KCl), and filter paper (all chemicals used are analytical grade).

Procedure

As much as 0.1 g of the biosorbent was put into a 50 mL Erlenmeyer which was filled with 10 mL of methylene blue dye solution with various concentrations of 10, 20, 30, 40, and 50 mg/L and adjusted the pH and optimum contact time that has been obtained previously. The temperature was varied respectively 25, 35, and 45 ºC, then stirred at a speed of 150 rpm. The mixture was filtered and analyzed with a UV-Vis spectrophotometer at λmax 664 nm(Miyah et al., 2018; Zein et al., 2020). Furthermore, the biosorbent powder from the absorption of dyes was analyzed using SEM-EDX to see the distribution of dyes on the surface of the biosorbent.

RESULTS AND DISCUSSION

Adsorption thermodynamics is important to study to determine an adsorption process's spontaneity and the adsorbate's mass transfer mechanism to the adsorbent under equilibrium conditions. Adsorption thermodynamics also investigates whether the adsorption process is favorable or unfavorable at varying temperatures(Cheruiyot et al., 2019). The Gibbs free energy (ΔG) describes whether an adsorption process is spontaneous or non-spontaneous, where a negative value indicates a spontaneous adsorption process. Entropy (ΔS) predicts the magnitude of the structural change in reversibility, which is affected by the negative values obtained. Enthalpy (ΔH) provides information on whether the adsorption process is exothermic or endothermic and describes the adsorption process occurring physically or chemically(Ullah et al., 2020).The thermodynamic adsorption parameters were obtained from the batch adsorption process at various adsorption temperatures of 298 K, 308 K, and 318 K, with concentration variations for each temperature of 10, 20, 30, 40, and 50 mg/L. The values of ΔH, ΔG, and ΔS obtained from the slope and intercept of the Van’t Hoff plot are presented in Table 1.

Jurnal Katalisator Vol 8 No. 1 (2023) 166-175

Table 1. Thermodynamic parameters of methylene blue adsorption by KH (Kapok Husk) and CA-KH (Citric Acid-Kapok Husk)

Biosorbent	Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
	298	-2.4550		
KH	308	-1.8413	-5.2469	-0.0099
	318	-2.2561		
	298	-14.3826		
CA-KH	308	-11.1053	-19.2150	-0.0197
	318	-13.9894		

The negative value of the change in Gibbs free energy (ΔG) at all investigated temperatures is because the adsorption process is spontaneous and confirms the feasibility of the process(Caroline et al., 2020). A negative value of ΔG also indicates physisorption for the absorption of methylene blue biosorbent. The significant negative value of ΔH indicates that the biosorption of methylene blue by the two biosorbents is an exothermic process, a low ΔH value indicates that the system does not require energy from the environment and weak energy is involved in the absorption of methylene blue by kapok husk(Bencheikh et al., 2020). A negative Entropy (ΔS) value indicates that methylene blue molecules exhibit increased orderliness at the solid/solution interface during adsorption on the biosorbent surface and indicate that the adsorption process promotes rearrangement on the adsorbent surface. The negative value of the change in entropy ΔS means that during adsorption, it will increase homogeneity on the surface of the biosorbent, and there is no significant change in the internal structure of the biosorbent(Zein, Purnomo, et al., 2022).The distribution of methylene blue dye on the surface of the biosorbent can be seen in Figure 1.

http://doi.org/10.22216/jk.v5i2.5717
Published by LLDIKTI Wilayah X

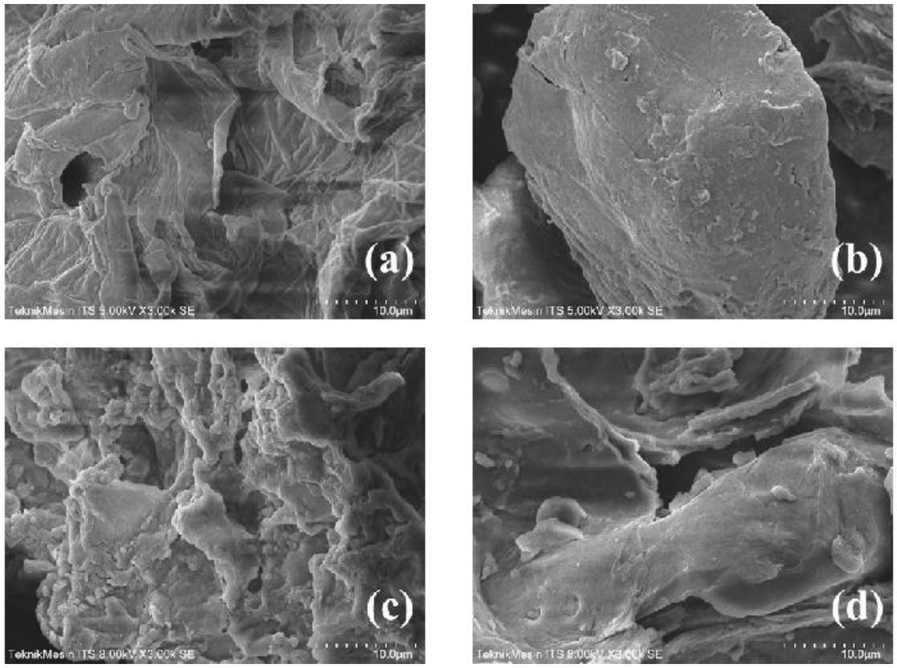

Figure 1. SEM photo of kapok husk before and after absorbing methylene blue at 3000x magnification (a) kapok husk before adsorption, (b) kapok husk after adsorption, (c) kapok husk modified with citric acid before adsorption, (d) Kapok huskn modified citric acid after adsorption

Figures 1 (a) and (c) show that the surface of the biosorbent before absorbing methylene blue is porous and has many irregular cavities, which are useful as sites for methylene blue absorption. The irregular and porous surface are also caused by the activation process using 0.1 M HNO_3 so that the impurity particles can dissolve in the HNO_3 and the pores on the surface of the biosorbent are wide open. The surface of the biosorbent after absorbing methylene blue was found to be very different compared to before absorption. This is evidenced in Figures 1 (b) and (d) that the surface of the biosorbent after absorption is smoother than before absorption, and there are no well-defined cavities in this SEM photo. Therefore, it can be assumed that there has been the absorption of methylene blue dye on the surface of the biosorbent. This also proves that the distribution of methylene blue on the surface of the biosorbent is very regular; this corresponds to a negative entropy (ΔS) value. Morphological changes are also found in various biomasses, such as leaves dregs of lemongrass(Zein, Suciandica, et al., 2022).

Generally, Energy Dispersive X-Ray Spectrometry (EDX) is combined with SEM tools (SEM-EDX) with online systems. This combination of equipment is useful for correlating the morphological characteristics of the adsorbent with its chemical composition, in addition to obtaining profiles of elements involved during adsorption in the form of maps or spectra so that elements can be analyzed quantitatively(Zein, Purnomo, et al., 2022). The EDX spectrum of the biosorbent before and after absorption of methylene blue can be seen in Figure 2.

http://doi.org/10.22216/jk.v5i2.5717
Published by LLDIKTI Wilayah X

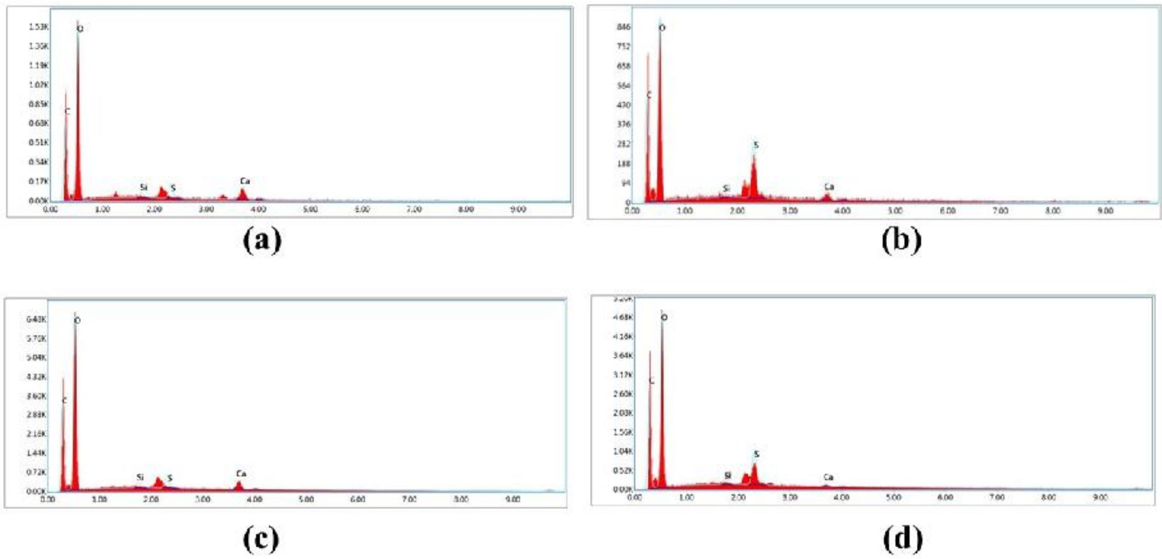

Figure 2. The EDX spectrum of kapok husk and kapok husk modified with citric acid before absorption (a and c) and after absorption of methylene blue (b and d)

The results of the EDX analysis (Figure 2) show a relative abundance of elements such as C, O, Si, and Ca prior to the absorption of methylene blue. After adsorption, the percentage of these elements decreased due to their involvement during the adsorption process, except for carbon (C). The percentage of O, Si, and Ca elements decreased after adsorption due to their involvement during adsorption, such as forming various interactions with methylene blue(Zein et al., 2023). The increase in the percentage of element C and the appearance of elemental S on the two biosorbents after absorption proved that the methylene blue dye had been adsorbed on the surface of the biosorbent. According to Ramadhani et al. (2020), the increase in the percentage of dye-forming elements after absorption proves the strong affinity of the adsorbent in absorbing dyes (Ramadhani et al., 2020).

CONCLUSION

Adsorption of methylene blue dye using kapok husk gives a thermodynamic adsorption value in the form of a negative Gibss free energy (ΔG) which indicates the adsorption process occurs spontaneously, and a negative enthalpy value (ΔH) indicates an exothermic adsorption process. Negative entropy values (ΔS) indicate an increase in order during the adsorption process. adsorption thermodynamics was studied in batches at various temperatures of 298K, 308K, and 318K, with concentrations of 10, 20, 30, 40, and 50 mg/L. SEM analysis gives the results of the distribution of methylene blue dye on the surface of the biosorbent.

http://doi.org/10.22216/jk.v5i2.5717
Published by LLDIKTI Wilayah X

REFERENCES

Araújo, T. P. De, Tavares, F. D. O., Tait, D., & Barros, M. A. S. D. (2020). Biosorption mechanisms of cationic and anionic dyes in a low-cost residue from brewer ' s spent grain. *Environmental Technology*, *0*(0), 1–32. https://doi.org/10.1080/09593330.2020.1718217

Batool, F., Akbar, J., Iqbal, S., Noreen, S., & Bukhari, S. N. A. (2018). Study of Isothermal, Kinetic, and Thermodynamic Parameters for Adsorption of Cadmium: An Overview of Linear and Nonlinear Approach and Error Analysis. *Bioinorganic Chemistry and Applications*, *2018*. https://doi.org/10.1155/2018/3463724

Bencheikh, I., Azoulay, K., Mabrouki, J., El Hajjaji, S., Dahchour, A., Moufti, A., & Dhiba, D. (2020). The adsorptive removal of MB using chemically treated artichoke leaves: Parametric, kinetic, isotherm and thermodynamic study. *Scientific African*, *9*. https://doi.org/10.1016/j.sciaf.2020.e00509

Caroline, T., Siqueira, A., Zanette, I., & Rubio, A. J. (2020). Sugarcane Bagasse as an E ffi cient Biosorbent for Methylene Blue Removal : Kinetics , Isotherms and Thermodynamics. *International Journal of Environmental Research and Public Health*.

Cheruiyot, G. K., Wanyonyi, W. C., Kiplimo, J. J., & Maina, E. N. (2019). Adsorption of toxic crystal violet dye using coffee husks: Equilibrium, kinetics and thermodynamics study. *Scientific African*, *5*, 1–11. https://doi.org/10.1016/j.sciaf.2019.e00116

Elwakeel, K. Z., Elgarahy, A. M., & Mohammad, S. H. (2017). Use of beach bivalve shells located at Port Said coast (Egypt) as a green approach for methylene blue removal. *Journal of Environmental Chemical Engineering*, *5*(1), 578–587. https://doi.org/10.1016/j.jece.2016.12.032

Farooq, U., Jalees, M. I., Iqbal, A., & Zahara, N. (2019). Desalination and Water Treatment Characterization and adsorption study of biosorbents for the removal of basic cationic dye : kinetic and isotherm analysis Characterization and adsorption study of biosorbents for the removal of basic cationic dye : kineti. *Desalination and Water Treatment*, *160*(July), 333–342. https://doi.org/10.5004/dwt.2019.24173

Hevira, L., Zilfa, Rahmayeni, Ighalo, J. O., & Zein, R. (2020). Biosorption of indigo carmine from aqueous solution by Terminalia Catappa shell. *Journal of Environmental Chemical Engineering*, *8*(5), 104290. https://doi.org/10.1016/j.jece.2020.104290

Lombardo, S., & Thielemans, W. (2019). Thermodynamics of adsorption on nanocellulose surfaces. In *Cellulose* (Vol. 26, Issue 1). Springer Netherlands. https://doi.org/10.1007/s10570-018-02239-2

Malakootian, M., & Heidari, M. R. (2018). Reactive orange 16 dye adsorption from aqueous solutions by psyllium seed powder as a low-cost biosorbent: kinetic and equilibrium studies. *Applied Water Science*, *8*(7), 1–9. https://doi.org/10.1007/s13201-018-0851-2

Mbarki, F., Kesraoui, A., Seffen, M., & Ayrault, P. (2018). Kinetic, Thermodynamic, and Adsorption Behavior of Cationic and Anionic Dyes onto Corn Stigmata: Nonlinear and

Stochastic Analyses. *Water, Air, and Soil Pollution*, *229*(3). https://doi.org/10.1007/s11270-018-3749-6

Miyah, Y., Lahrichi, A., Idrissi, M., Khalil, A., & Zerrouq, F. (2018). Adsorption of methylene blue dye from aqueous solutions onto walnut shells powder: Equilibrium and kinetic studies. *Surfaces and Interfaces*, *11*(May 2017), 74–81. https://doi.org/10.1016/j.surfin.2018.03.006

Osagie, C., Othmani, A., Ghosh, S., Malloum, A., Kashitarash Esfahani, Z., & Ahmadi, S. (2021). Dyes adsorption from aqueous media through the nanotechnology: A review. *Journal of Materials Research and Technology*, *14*, 2195–2218. https://doi.org/10.1016/j.jmrt.2021.07.085

Ramadhani, P., Chaidir, Z., Zilfa, Tomi, Z. B., Rahmiarti, D., & Zein, R. (2020). Shrimp shell (Metapenaeus monoceros) waste as a low-cost adsorbent for metanil yellow dye removal in aqueous solution. *Desalination and Water Treatment*, *197*, 413–423. https://doi.org/10.5004/dwt.2020.25963

Ramadhani, P., Zein, R., Chaidir, Z., Zilfa, & Hevira, L. (2019). Pemanfaatan Limbah Padat Pertanian Dan Perikanan Sebagai Biosorben Untuk Penyerap Berbagai Zat Warna: Suatu Tinjauan. *Jurnal Zarah*, *7*(2), 46–56. https://doi.org/10.31629/zarah.v7i2.1396

Scheufele, F. B., Staudt, J., Ueda, M. H., Ribeiro, C., Steffen, V., Borba, C. E., Módenes, A. N., & Kroumov, A. D. (2020). Biosorption of direct black dye by cassava root husks: Kinetics, equilibrium, thermodynamics and mechanism assessment. *Journal of Environmental Chemical Engineering*, *8*(2). https://doi.org/10.1016/j.jece.2019.103533

Siswoyo, E., Adrian, A. R., & Tanaka, S. (2018). Bioadsorbent based on water hyacinth modified with citric acid for adsorption of methylene blue in water. *MATEC Web of Conferences*, *154*, 2–5. https://doi.org/10.1051/matecconf/201815401012

Ullah, R., Ahmad, W., Ahmad, I., & Khan, M. (2020). Adsorption and recovery of hexavalent chromium from tannery wastewater over magnetic max phase composite. *Separation Science and Technology*, *00*(00), 1–14. https://doi.org/10.1080/01496395.2020.1717531

Zein, R., Nofita, D., Refilda, R., & Aziz, H. (2019). Penyerapan Timbal(II) dan Cadmium(II) di dalam Larutan Menggunakan Limbah Kulit Buah Kapuk. *Chimica et Natura Acta*, *7*(1), 37. https://doi.org/10.24198/cna.v7.n1.20813

Zein, R., Purnomo, J. S., Ramadhani, P., Alif, M. F., & Safni, S. (2022). Lemongrass (Cymbopogon nardus) leaves biowaste as an effective and low-cost adsorbent for methylene blue dyes removal: isotherms, kinetics, and thermodynamics studies . *Separation Science and Technology*, *00*(00), 1–17. https://doi.org/10.1080/01496395.2022.2058549

Zein, R., Ramadhani, P., Aziz, H., & Suhaili, R. (2019). Pensi shell (Corbicula moltkiana)as a biosorbent for metanil yellow dyes removal: pH and equilibrium model evaluation. *Jurnal Litbang Industri*, 15–22.

Zein, R., Satrio Purnomo, J., Ramadhani, P., Safni, Alif, M. F., & Putri, C. N. (2023).

Enhancing sorption capacity of methylene blue dye using solid waste of lemongrass biosorbent by modification method. *Arabian Journal of Chemistry*, *16*(2), 104480. https://doi.org/10.1016/j.arabjc.2022.104480

Zein, R., Suciandica, M., & Fauzia, S. (2022). Modification Leaf Dregs of Lemongrass With Citric Acid For Cd(II) Removal. *Jurnal Katalisator*, *7*(1), 63–81. https://doi.org/http://doi.org/10.22216/jk.v5i2.5717

Zein, R., Tomi, Z. B., Fauzia, S., & Zilfa, Z. (2020). Modification of rice husk silica with bovine serum albumin (BSA) for improvement in adsorption of metanil yellow dye. *Journal of the Iranian Chemical Society*, *17*(10), 2599–2612. https://doi.org/10.1007/s13738-020-01955-6