MJFAS
Malaysian Journal of Fundamental and Applied Sciences

Amran *et al.* | Malaysian Journal of Fundamental and Applied Sciences, Vol. 17 (2021) 768-775

RESEARCH ARTICLE

Two-Stage Batch Adsorber Design for Methylene Blue Removal by Coconut Shell Activated Carbon

Fadina Amran[a,b], Nur Fatiah Zainuddin[a], Muhammad Abbas Ahmad Zaini[a,b,*]

[a] School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia; [b] Centre of Lipids Engineering & Applied Research, Ibnu-Sina Institute for Scientific & Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

Abstract The present work was aimed at evaluating the performance of two-stage adsorber for methylene blue removal by coconut shell activated carbon in minimizing the adsorbent mass and contact time. The Langmuir constants were used to evaluate the optimum mass, while the pseudo-second-order constants for contact time. Results show that the adsorbent mass can only be minimized by 0.01 % due to the high adsorbent affinity towards methylene blue, while the contact time has been optimized to 12.2 min at the studied conditions. The effect of adsorbent affinity in two-stage adsorber was analyzed to shed some light about its importance in the design of two-stage adsorber. The performance evaluation was also discussed to bring insight into wastewater treatment applications.

Keywords: Activated carbon, adsorption, methylene blue, optimization, two-stage adsorber.

Introduction

Cocos Nurcriferain or coconut palm is abundantly available around the globe. In Malaysia, the annual coconut production is about 5×10^5 tons, with an average of 5.97 tons per hectare [1]. The vast production and consumption have consequently resulted in the generation of solid wastes, which has shown an increase to 7.34×10^6 tons from all industrial and domestic sectors [2]. In order to lessen the burden of the solid waste management, measures are sought to convert the coconut wastes into sustainable materials such as solid fuel and activated carbon.

Activated carbon has been widely adopted as effective adsorbent in wastewater treatment because of its excellent physicochemical properties to remove pollutants at low concentration [3]. Among others, coconut shell is a promising feedstock of activated carbon because of its hard texture that contains more than 40 % carbon [3]. Generally, the so-called carbonaceous material can be chemically converted into activated carbon at temperatures ranging between 500°C and 800°C using potassium hydroxide [4, 5], sodium hydroxide [6, 7], phosphoric acid [8, 9], zinc chloride [10, 11] and calcium carbonate [12, 13].

Several studies have been documented to demonstrate the adsorptive performance of coconut shell activated carbons to remove various water pollutants [14, 15, 16, 17]. Yasin et al. [14] reported a 45.9 mg/g removal of methylene blue by KOH-activated coconut shell carbon with a high surface area of 1389 m^2/g. Recently, Oribayo et al. [17] showed a higher removal of methylene blue at 321 mg/g using $ZnCl_2$-activated carbon. Nonetheless, the former [14] exhibits a tremendous affinity towards the pollutant, that brings insight into real-scale applications.

***For correspondence:**
abbas@cheme.utm.my

Received: 2 Jun 2021
Accepted: 8 Nov 2021

One-stage batch adsorber has been accepted as a standard protocol in adsorption studies. However, the setting is incapable to forecast high removal performance at optimum adsorbent dosage and contact time for process scaling-up. Hence, a two-stage adsorber is designed to simulate the adsorbent mass and contact time in achieving the desired removal percentage at any effluent volume. Palanisami et al. [18] reported a mass reduction of 14 % in a two-stage adsorber of coffee residue activated carbon for phenol removal. The same design also projects the improvement in the mass of date stones by 44 % for malachite green removal [19]. In a related work, the time for methylene blue adsorption is anticipated to decrease from 100 min to 37.5 min in a two-stage adsorber of sawdust activated carbon [20]. The present work was aimed to broaden the horizon in a two-stage adsorber design by employing high affinity activated carbon as base-case study [14]. The Langmuir and pseudo-second-order constants were used to establish the profiles of adsorbent mass, contact time and performance evaluation. The findings were discussed to shed light into sustainable wastewater treatment.

Methods

Adsorption Data

Activated carbon with specific surface of 1389 m^2/g was derived from coconut shell by potassium hydroxide activation [14]. The adsorption data for equilibrium and kinetics were fitted into Langmuir and pseudo-second-order models, respectively. The models are expressed as Equations (1) and (2), respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{2}$$

Where, q_e (mg/g) is the capacity at equilibrium, q_m (mg/g) is the maximum capacity at surface saturation, q_t (mg/g) is the capacity at any time, t (min), C_e (mg/L) is the equilibrium concentration, K_L (L/mg) is the sorption affinity, and k_2 (g/mg.min) is the rate constant. The constants are summarized in Table 1 and were used to simulate the two-stage batch adsorber aimed at capitalizing the adsorbent mass and minimizing the contact time.

Table 1. Langmuir and pseudo-second-order constants [14]

Langmuir model			Pseudo-second-order		
q_m (mg/g)	K_L (L/mg)	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2
9.97	4.64	0.99	11.24	0.012	0.95

Two-Stage Adsorber Design

In two-stage adsorber, the effluent, V passes through stage-1, in which the mass m_1 brings the process to equilibrium at concentration C_1 before the treated effluent enters stage-2, wherein the mass m_2 brings the process to final equilibrium at concentration C_2. Figure 1 visualizes the schematic of two-stage batch adsorber design. Each stage is supplied with fresh activated carbon for the same volume of dye to achieve the adsorption capacities, q_1 and q_2. The dye concentration declines from C_o to C_1 in the stage-1 and C_1 to C_2 in stage-2.

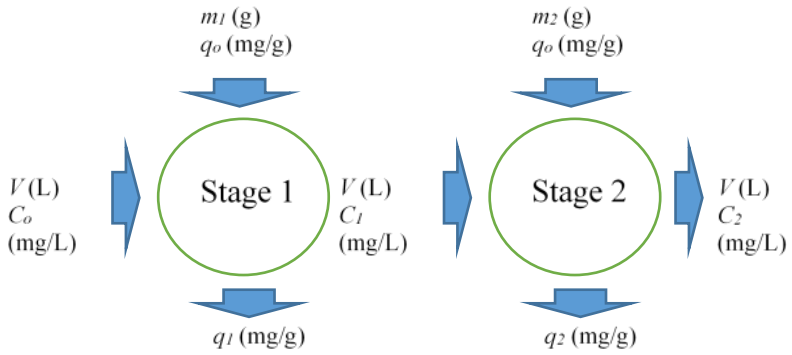

Figure 1. Two-stage adsorber design [21]

The overall process can be represented by mass balance as follows,

$$V(C_o - C_1) = m_1(q_1 - q_o) \tag{3}$$

For mass optimization, the two-stage adsorber was designed using the following experimental conditions: volume, V=0.025 L, initial concentration, C_o=100 mg/L, equilibrium concentration, C_2=84 mg/L, and adsorbent mass (one-stage adsorber), m=0.04 g [14]. A series of sorption system number for C_1 from 100 to 84 mg/L in a 1.0 mg/L step-size was assembled. The mass of activated carbon was calculated for each decrement. For example, in sorption system number 1, the design objective is to reduce the initial dye concentration from 100 to 99 mg/L in stage-1. Similarly in sorption system numbers 2, 3, and so on, the design objectives are to reduce the initial dye concentration from 99 to 98 mg/L, 98 to 97 mg/L, and lastly down to 84 mg/L. While, in stage-2, the design objective for sorption system number 1 is to reduce the concentration from 99 to 84 mg/L. The same approach applies for determination of minimum contact time. Equation (1) was incorporated in Equation (3) to yield,

$$\frac{m_1}{V} = \frac{(C_O - C_1)(1 + K_L C_1)}{K_L q_m C_1} \tag{4}$$

and so, for both stages,

$$\frac{m_1 + m_2}{V} = \frac{1}{K_L q_m}\left(\frac{(C_O - C_1)(1 + K_L C_1)}{C_1} + \frac{(C_1 - C_2)(1 + K_L C_2)}{C_2}\right) \tag{5}$$

Equation (5) was differentiated with respect to C_1 and set $\frac{d[m_1+m_2)/V]}{dC_1}$=0, solving C_1 as,

$$C_1 = (C_O C_2)^{1/2} \tag{6}$$

Equation (2) was substituted into Equation (3) to yield expression to compute optimum time required to accomplish the desired methylene blue removal in a two-stage adsorber as,

$$t = \frac{\left(\frac{1}{q_e k_2}\right)V(C_o - C_t)}{mq_e - V(C_o - C_t)} \tag{7}$$

The removal percentage, R was calculated by the following equation,

$$R = \frac{C_o - C_2}{C_o} \times 100 \tag{8}$$

Results and Discussion

Mass Optimization

Figure 2 shows the profile of adsorbent mass to achieve 16 % removal of methylene blue in a two-stage adsorber. Figure 2(a) illustrates a decreasing pattern of adsorbent mass as the sorption system number increases from 1 to 9 due to small intermediate concentration to compensate the equilibrium concentration at stage-2. The optimum mass of 40.0980 g was obtained at sorption system number 9. Figure 2(b) depicts the profiles of combined mass in stage-1 and stage-2. Stage-1 displays an increasing pattern, while the opposite is true for stage-2. In a two-stage adsorber design, stage-1 often bears a larger surface load at high concentration driving force to overcome the mass transfer resistance, and consequently, less adsorbent mass would be needed to reach the equilibrium in stage-2 [22]. From the combined mass, the optimum saving of adsorbent mass is only 0.051 % at any effluent volume when compared to one-stage adsorber (sorption system number 1), which is due to the high affinity of activated carbon towards methylene blue (K_L=4.64 L/mg).

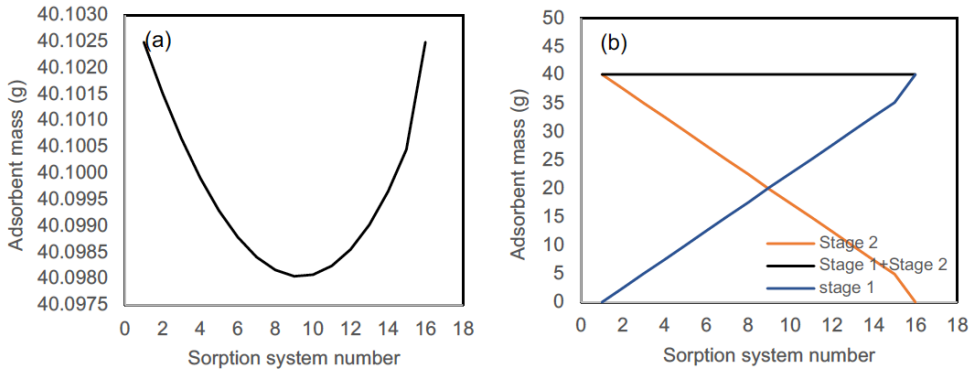

Figure 2. (a) Mass optimization, and (b) profiles of adsorbent mass in stage-1 and stage-2

Time Optimization

Figure 3 shows the profiles of contact time against sorption system number at optimum mass. The contact time increased with sorption system number in stage-1, while it decreased in stage-2. This is associated with the available active sites on the activated carbon surface for dye molecules to bind, and also the driving force as a result of concentration gradient. When the effluent enters stage-2 at lower C_1, less contact time is required to reach the final equilibrium concentration, C_2. The optimum contact time is 12.2 min at sorption system number 9. The magnitude is rapid when compared to 252 min (adsorbent mass=250 mg) as reported using one-stage adsorber [14].

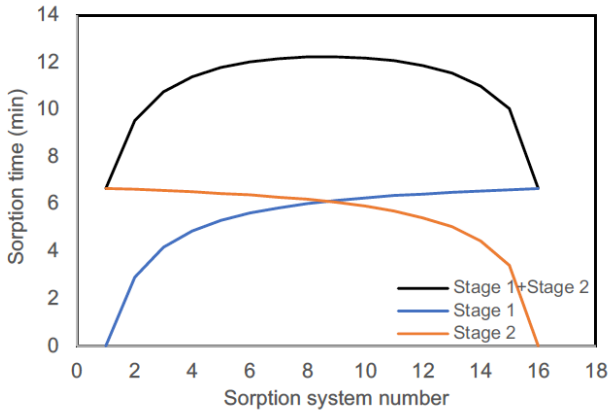

Figure 3. Time optimization at optimum mass

Performance Evaluation

Figure 4 shows the effect of initial concentration on intermediate concentration, C_1 at different target removal percentages and equilibrium concentrations. From Figure 4(a), for C_o=500 mg/L, stage-1 has to reduce the concentration down to C_1=224 mg/L to achieve 80 % dye removal, while for 99.8 % removal, stage-1 needs to utilize more adsorbent mass to bring C_1 to 22.4 mg/L. Similarly, C_1 increased with C_o, but C_1 decreased as the target concentration at stage-2, C_2 decreases to yield higher adsorption performance as shown in Figure 4(b). A smaller C_1 as the target removal increases permits the removal of remaining dye concentration in stage-2 at low equilibrium. The profiles bring insight into the effectiveness of two-stage adsorber to accomplish a bigger removal percentage of concentrated effluent from the viewpoint of minimum adsorbent mass.

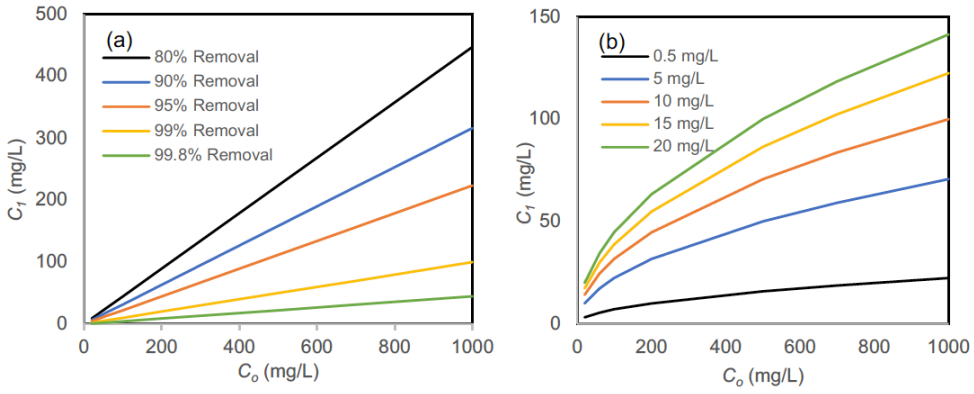

Figure 4. Effect of initial concentration, C_o on intermediate concentration, C_1 at different (a) removal percentages, and (b) equilibrium concentrations, C_2

Figure 5 shows the effects of C_o on the total adsorbent mass for different removal percentages and equilibrium concentrations in two-stage adsorber. The adsorbent mass required to accomplish the methylene blue removal using two-stage adsorber is linearly increased against C_o for any target removal percentage, while for any C_o, the magnitude increased with increasing removal percentage. The higher the removal percentage, the more the mass of coconut shell activated carbon would be consumed for the whole process to provide enough sites for adsorbent-adsorbate interactions leading to adsorption [23]. At any target C_o, more adsorbent will be consumed to meet the high performance between 80 % and 99.8 %. For example, 2007 g of adsorbent would be needed to bring the performance to 80 %, while the amount increased to 2526 g for 98.8 % removal. A relatively small increase in mass of 26 % could be related to the affinity of coconut shell activated carbon towards methylene blue dye. Figure 5(b) also shows a rising of mass against C_o, but the lines are visibly overlapping with one another for different target C_2 between 0.5 mg/L and 20 mg/L, due to strong adsorption affinity as previously discussed.

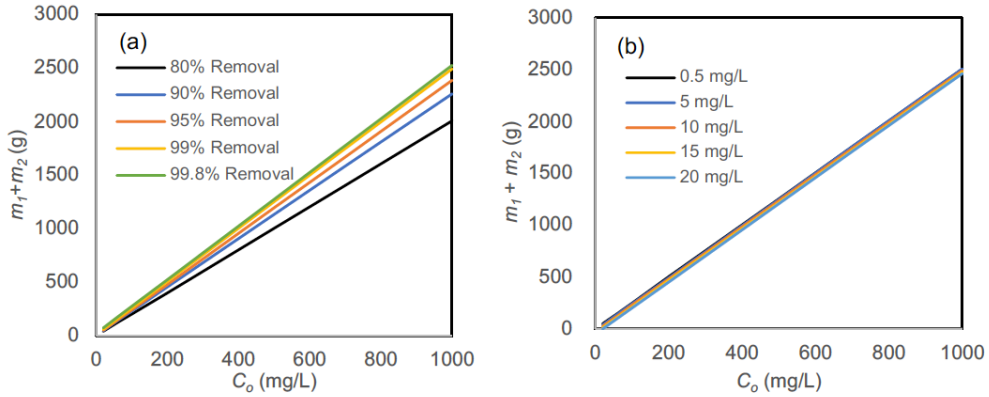

Figure 5. Effect of initial concentration, C_o on total mass at different (a) removal percentages, (b) equilibrium concentrations, C_2 (K_L= 4.64 L/mg)

Figure 6 visualizes the effect of K_L=0.001 L/mg on adsorbent mass for different target concentration at stage-2. Obviously, the lower affinity of adsorbent significantly broadens the gap among the target performance with the lower C_2 actually utilizes greater adsorbent mass for higher performance. At lower affinity, the adsorbent mass has shown a substantially increase of nearly 28 folds from 2426 g (K_L=4.64 L/mg) to 68403 (K_L=0.001 L/mg) for the target C_2=0.5 mg/L at C_o=1000 mg/L. It implies the importance of having high affinity adsorbent to fully exploit the benefits of two-stage adsorber while capitalizing the adsorbent mass. The inset in Figure 6 further explains the small increase in adsorbent mass saving for smaller K_L values.

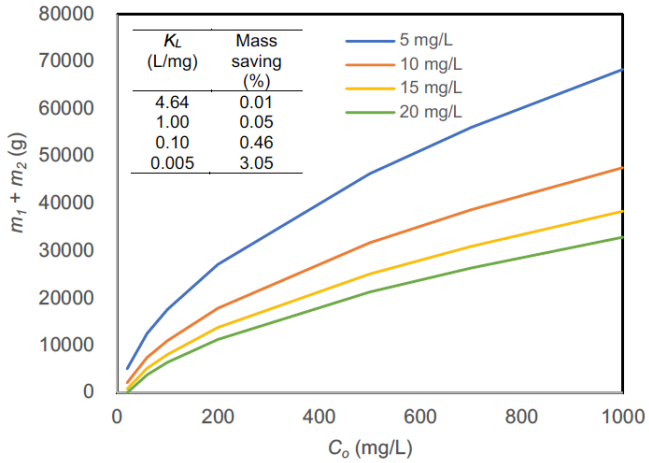

Figure 6. Effect of C_o on total mass in two-stage adsorber at different C_2 for K_L= 0.001 L/mg (inset: adsorbent mass reduction at different K_L)

Figure 7(a) shows the profiles of adsorption capacity at each stage for different removal percentages. The efficiency for methylene blue removal in stage-2 is always lower than that in stage-1 as the removal percentage increases because of the lower concentration of dye leaving stage-1. For example, the breakdowns of 99.8 % methylene blue removal are 8 mg/L/mg in stage-1 and 0.36 mg/L/mg in stage-2. In other words, stage-2 usually operates at low equilibrium in order to meet the overall desired target performance. Figure 7(b) shows the efficiency in stage-2 for different target C_2. The efficiency in stage-2 increases as C_2 increases. However, the performance of stage-2 is marginal when compared to that of stage-1. Nonetheless, introducing the stage-2 at higher initial concentration is essential as greater removal percentage can be achieved.

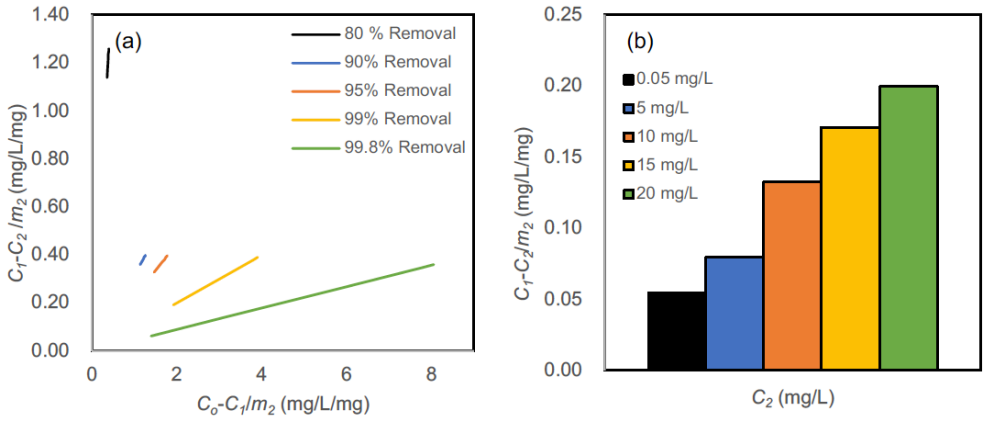

Figure 7. Methylene blue removal at (a) both stages for different removal percentages, and (b) stage-2 for different equilibrium concentrations, C_2

Conclusions

Coconut shell-based activated carbon was used in the design of two-stage adsorber to simulate the performance evaluation of methylene blue removal in view of optimum adsorbent mass and contact time. Only 0.01 % mass saving can be obtained at any effluent volume because of the high affinity (K_L=4.64 L/mg) of activated carbon, while the contact time can be optimized to 12.2 min at the studied conditions. The role of affinity in two-stage adsorber has been visualized by the massive increase in adsorbent mass of about 28 folds if the magnitude of affinity is reduced to 0.001 L/mg for initial and target concentrations of 1000 mg/L and 0.5 mg/L, respectively. The performance evaluation at target removal rates enables the prediction of intermediate concentration and profiles of total mass for real implementation in wastewater treatment.

Acknowledgments

This work was supported by UTM-ICONIC Grant No. 09G54.

References

[1] T. K. Hoe, "The current scenario and development of the coconut industry," The Planter, vol. 94, no. 1108, pp. 413-426, 2018.

[2] M. I. M. Masirin, M. B. Ridzuan, S. Mustapha,"An overview of landfill management and technologies: A Malaysian case study at Ampar Tenang," Proceedings 1st National Seminar on Environment, Development & Sustainability: Ecological, Economical and Social Aspects, Sg. Lang, Selangor, pp. 157-165, 28 – 29 July 2008.

[3] J. Saleem, U. Shahid, M. Hijab, H. Mackey et al., "Production and applications of activated carbons as adsorbents from olive stones," Biomass Conversion and Biorefinery, vol. 9, pp. 775–802, 2019.

[4] S. W. Seo, Y. J. Choi, J. H. Kim et al., "Micropore-structured activated carbon prepared by waste PET/ petroleum-based pitch," Carbon Letters, vol. 29, no. 4, pp. 385-392, 2019.

[5] Z. Asadi-sangachini, M. M. Galangash, H. Younesi et al., "The feasibility of cost-effective manufacturing activated carbon derived from walnut shells for large-scale CO_2 capture," Environmental Science and Pollution Research, vol. 26, no. 26, pp. 26542-26552, 2019.

[6] O. Boujibar, A. Souikny, F. Ghamouss et al., "CO_2 capture using N-containing nanoporous activated carbon obtained from argan fruit shells," Journal of Environmental Chemical Engineering, vol. 6, no. 2, pp. 1995-2002, 2018.

[7] Y. Lei, R. Huang, L. Guo et al., "Effect of activating agents on the structure and capacitance performance of tofu derived porous carbon, "Journal of Materials Science: Materials in Electronics, vol. 30, pp. 10274-10283, 2019.

[8] H. Wu, R. Chen, H. Du et al., "Synthesis of activated carbon from peanut shell as dye adsorbents for wastewater treatment," Adsorption Science and Technology, vol. 37, no. 1-2, pp. 34-48, 2018.

[9] J. Baek, H. M. Lee, K. H. An et al., "Preparation and characterization of highly mesoporous activated short carbon fibers from kenaf precursors," Carbon Letters, vol. 29, no. 4, pp. 393–399, 2019.

[10] R. Ma, X. Qin, Z. Liu et al., "Adsorption property, kinetic and equilibrium studies of activated carbon fiber prepared from liquefied wood by $ZnCl_2$ activation," Materials, vol. 12, Article ID 12091377, 2019.

[11] A. O. A, E. Naga, M. E Saied, S. A. Shaban et al., "Fast removal of diclofenac sodium from aqueous solution using sugar cane bagasse-derived activated carbon," Journal of Molecular Liquids, vol. 285, pp. 9-19, 2019.

[12] L. L. Zhi and M. A. A. Zaini, "Potassium carbonate-treated palm kernel shell adsorbent for congo red removal from water," Jurnal Teknologi, vol. 75, no. 1, pp. 233-239, 2015.

[13] N. Alias, M. A. A. Zaini, M. J. Kamaruddin, "Roles of Impregnation ratio of K_2CO_3 and NaOH in chemical activation of palm kernel shell," Journal of Applied Science & Process Engineering, vol. 4, no. 2, pp. 195-204, 2017.

[14] Y. Yasin, M. Z. Hussein, F. Ahmad, "Adsorption of methylene blue onto treated activated carbon," The Malaysian Journal of Analytical Sciences, vol.11, no. 11, pp. 400 – 406, 2007.

[15] S. Shrestha, G. Son, S. H. Lee et al., "Isotherm and thermodynamic studies of Zn (II) adsorption on lignite and coconut shell-based activated carbon fiber," Chemosphere, vol. 92, no, 8, pp. 1053-1061, 2013.

[16] R. R. Karri, J. N. Sahu, N. S. Jayakumar, "Optimal isotherm parameters for phenol adsorption from aqueous solutions onto coconut shell based activated carbon: Error analysis of linear and non-linear methods," Journal of the Taiwan Institute of Chemical Engineers, vol. 80, pp. 472-487, 2017.

[17] O. Oribayo, O. O. Olaleye, A. S. Akinyanju et al., Coconut shell-based activated carbon as adsorbent for the removal of dye from aqueous solution: equilibrium, kinetics, and thermodynamic studies," Nigerian Journal of Technology, vol. 39, no. 4, pp. 1076 – 1084, 2020.

[18] H. Palanisami, M. R. M. Azmi, M. A. A. Zaini et al., "Coffee residue-based activated carbons for phenol removal," Water Practice & Technology.

[19] M. Hijab, P. Parthasarathy, H. R. Mackey et al., "Minimizing adsorbent requirements using multi-stage batch adsorption for malachite green removal using microwave date-stone activated carbons," Chemical Engineering and Processing - Process Intensification, Article ID 108318, 2021.

[20] Markandeya, A. Singh, S.P. Shukla et al., "Adsorptive capacity of sawdust for the adsorption of MB dye and designing of two-stage batch adsorber," Cogent Environmental Science, vol. 1, no. 1, Article ID 1075856, 2015.
[21] M. A. K. Anuar, N. S. Mahat, N. M. Rusli et al., "Insight into the optimization of mass and contact time in two-stage adsorber design for malachite green removal by coconut shell activated carbon.
[22] F. M. Mohammed, E. P. L. Roberts, A. K. Campen et al., "Wastewater treatment by multi-stage batch adsorption and electrochemical regeneration," J. Electrochem. Sci. Eng, vol. 2, no. 4, pp. 223-236, 2012.
[23] S. M. S. Bamatraf and M. A. A. Zaini, "Optimization in a two-stage sorption of malachite green by date palm residue carbon."