Activated Carbon based Rice Husk for Highly Efficient Adsorption of Methylene Blue: Kinetic and Isotherm

T V Tan¹,*, and H T T Nguyen¹,²,³
¹ NTT Hi-Tech Institute, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam.
² Center of Excellence for Green Energy and Environmental Nanomaterials, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam
³ Center of Excellence for Functional Polymers and NanoEngineering, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam
Corresponding author: lvtn@ntt.edu.vn

Abstract. Agricultural waste is a resource that is renewable and readily available and is used as a precursor to coal synthesis in industry. In this study, agricultural waste from rice husk was used as precursors to prepare activated carbon, which was activated by KOH. The effectivity factors including time contact, concentration, pH solution, and sorbent dosage play an important role in removing MB in water media. Moreover, the MB adsorption efficiency reached over 80 % at a concentration of 50 mg/L, pH 8 within 180 minutes. The kinetic analysis via pseudo-first-order, pseudo-second-order, Bangham, and Temkin model showed that MB adsorption followed pseudo-second-order (R² = 0.99934). The fitness of equilibrium data to popular isotherm equations such as the Langmuir, Freundlich, Elovich, Temkin and Dubinin-Radushkevich were carried out. Among all tested isotherm models, Langmuir model is the best fitted to equilibrium data (R² = 0.99924). The results of this study show that activated carbon made from rice husk has the potential to be used to remove the dye in wastewater treatment.

1. Introduction
The dye is one of the major effluents, which causes a bad effect on human beings and the ecosystem [1,2]. Methylene Blue was considered as a pharmacist as well as a popular dye. It is a heterocyclic aromatic chemical compound with the molecular formula of C16H18N3SCl [3]. The existence of it even at low concentration on surface water presents a major obstacle in ensuring adequacy of sunlight and aeration in the lower water body, thus impairing photosynthetic activity [4]. Thus, it is imperative to treat dyed aquatic wastewater.

Among the treatment methods, adsorption has been evaluated as an inspiring contestant because of its benefits such as simple to design, easy to operate, and cost-effective [6,7]. Recently, activated carbon was chosen as the candidate for its absorptive efficiency because of the porous structure, and high surface area. Hence, great attention is paid to the preparation of activated carbon from alternative sources. Such sources for fabrication of activated carbon with high adsorption capacity might include coconut husk [7] and durian peel [8]. In Vietnam, rice husk is regard as an abundant and inexpensive agricultural waste and arbitrary disposal of this source might present further environmental issues to the atmosphere and water ecosystem. For example, burning of huge quantities of rice husk by farmers caused the black cloud in the sky, which one of the reasons for greenhouse gases (GHG) [9].

In this study, we utilized the rice husk waste to fabricate activated carbon that was then used to remove Methylene Blue (MB) dye from aqueous solution. We then investigated the effect of various
parameters including contact time, initial MB concentration, pH and dosage on adsorption efficiency. We then fit the data into various kinetic and isotherm models to elaborate the adsorption mechanism. The results are expected to aid in further developments on improving existing processes for manufacture of activated carbon from agricultural sources.

2. Materials and method

2.1. Experimental
The source material for synthesis of activated carbon is rice husk. The rice husk source was first sundried for 2 to 3 days and then subjected to grinding to afford the powdered rice husk. Then, KOH used to activate dry powder according to ratio 1:1 (g/g) for 24 hours. After impregnation, the sample was then dried at 105°C for 24 hours, followed by physical carbonization with 99.9 % N2 gas flow at 500°C. The afforded materials were then washed with distilled water and then with HCl solution several times until pH = 7. Lastly, the sample was dried in an oven for 24 hours. The final product was abbreviated AC_RH.

2.2. Instrumentation
The concentration of MB dyes was determined by using UV-Vis spectra at 664 nm wavelength (UV-Vis Ligent Cary 60).

2.3. Batch adsorption studies
The adsorption efficiency of materials is assessed based on the efficient removal of methylene blue (MB). Briefly, 75-150 mg adsorbent (AC_RH) and 100 mL of MB solution (50 mg/L) were mixed into a 250 ml glass beaker. Then, the solution was stirred at 200 rpm by a shaker in 180 minutes, 4 ml solution was got out in the regulated time period, and centrifuged to separate the solid from the dye solution. Finally, the concentration of the balance dye was determined in wavelength 664 nm by spectrophotometry. The MB removal efficiency was calculated following the subsequent formulae:

\[ q_e = \frac{C_o - C_e}{m} \cdot V \]  
\[ \% \text{Removal} = \frac{C_o - C_e}{C_o} \cdot 100\% \]

where, Co and Ce are the respectively initial and equilibrium dye concentrations (mg/L).

3. Results and discussion

3.1. The effect of time contact and initial concentration
The influence of initial concentration and contact time on adsorption performance of activated carbons based rice husk (AC_RH) was shown in Figure 1(A–B). Figure 1–A illustrates the process of MB removal over 180 minutes of contact. The MB removal efficiency seemed to increase rapidly in the first 60 minutes. The equilibrium was attained at the 180-minute mark, at which point the efficiency ceased to improve and remained stable for the rest of the duration. To assess the removal efficiency of adsorbents, contact time and adsorbent dosage were fixed at 180 min and 1 g/L, respectively. Figure 1–B shows that the AC_RH sample has the highest MB removal efficiency, reaching 39.27 mg/g at 50 mg/L.
The effect of pH solution
The point of zero charge (pHPZC) of the material is the pH value point at which the total charge of the material surface is zero. Determining pHPZC value helps to better understand the properties of the material adsorption by the influence of the pH of the reaction solution. In this study, pHPZC value of the AC_RH material was calculated through experimental experiments according to the previous research process of Tran Van Thuan et al [6]. According to the result of Figure 2–A, pHPZC value of AC_RH was determined at 7.01. From Figure 2–B, we can see that the optimal pH for MB adsorption is 8. The existence of protons in aqueous solutions at low pH can lead to the formation of positive charges on the surface of AC_RH. It leads to an abundance in electrostatic repulsion between the surface of the molecules AC_RH and MB. It indicates that a low pH may be unfavorable for the adsorption of MB. Furthermore, when the pH of the MB solution increases, the adsorption process decreases. The major cause is the electrostatic repulsion between the negatively charged MB molecules and the surface of AC_RH. Therefore, pH 8 is a suitable condition for MB adsorption for AC_RH.

The effect of sorbent dosage
The effect of sorbent dosage on removal efficiency was examined by introducing different amounts of AC_RH (75 – 150 mg) to a mixture containing 100 ml of dye solution of initial concentration 50 mg/L. The mixture was allowed to contact till the equilibrium was attained. From the experimental results, it
seemed that the carbon dosage positively correlated with dye removal. To be specific, minimal efficiency, at 59.98%, was recorded at carbon dosage of 75 mg while the highest removal, at 84.86%, was achieved at dosage of 150 mg (Figure 3). The relationship could be elaborated by increased contact surface area of adsorbent when used at larger quantity, escalating the number of adsorption sites that could be occupied by MB molecules and thus improving removal efficiency [10]. Contrarily, increasing the dose apparently induced reductions in dye adsorption capacity, from 39.27 mg/g to 30.45 mg/g. This could be explained by the division of the flux or concentration gradient between the adsorbent surface and the solution concentration of the dye. This same trend was also observed in previous studies where an increase in the adsorbent dosage was related to higher amount of dye adsorbed per unit weight, resulting in a decrease in the adsorption capacity [11,12].

![Figure 3. Effect of dosage adsorbent](image)

Table 1 shows adsorption capacities of various activated carbons prepared from various source. Our prepared material exhibited superior adsorption capacity in comparison to that prepared from another agricultural waste (Posidonia oceanica (L.) dead leaves). However, activated carbon pales in comparison with other advanced composite materials or materials prepared from more expensive source. Current results suggest rice straw is a renewable, cost-efficiency raw materials for manufacture of activated carbon for environmental applications.

| No | AC adsorbent                              | MB adsorption capacity (mg/g) | Ref. |
|----|-------------------------------------------|------------------------------|------|
| 1  | Zr_3O/AC                                   | 208.33                       | [13] |
| 2  | Posidonia oceanica (L.) dead leaves        | 6.72                         | [14] |
| 3  | Citrullus lanatus                          | 231.48                       | [15] |
| 4  | Rice husk                                  | 39.72                        | This study |

3.4. Adsorption kinetic
The kinetic results are tested by the pseudo-first-order kinetic model, pseudo-second-order kinetic model, Elovich, and Bangham model as shown in Figure 4 and Table 2.

The goodness of fit of the used models was assessed by the coefficient of determination ($R^2$). The $R^2$ values are 0.935, 0.99934, 0.99898, and 0.9965, respectively for Pseudo-first-order, Pseudo-second-
order, Elovich and Bangham model. Moreover, the value of $q_e^{(exp)}$ approximates $q_e^{(cal)}$, suggesting the suitability of the pseudo-second-order model in describing the adsorption process of MB by AC_RH. This result is corroborated by previous studies which advocated the pseudo-first-order model in fitting the whole adsorption process.

![Figure 4. The kinetic models: A) Pseudo-first-order, B) Pseudo-second-order, C) Elovich, D) Bangham](image)

**Table 2. Parameter of kinetic**

| Model                  | Parameter | Value |
|------------------------|-----------|-------|
| Pseudo-first-order     | $k_1 (min^{-1}/(mg/L)^{1/n})$ | $0.8.10^{-3}$ |
|                        | $Q_1 (mg/g)$ | 28.67 |
|                        | $R^2$       | 0.935 |
| Pseudo-second-order    | $k_2 (g/(mg.min))$ | $1.3.10^{-3}$ |
|                        | $Q_2 (mg/g)$ | 42.73 |
|                        | $H = k_2Q_2^2$ | 2.39 |
|                        | $R^2$       | 0.99934 |

| Model                  | Parameter | Value |
|------------------------|-----------|-------|
| Elovich (3.3)          | $\beta (g/mg)$ | 0.164 |
|                        | $\alpha (mg/(g.min))$ | 21.11 |
|                        | $R^2$       | 0.99898 |
| Bangham (3.4)          | $k_B (mL/(g/L))$ | 0.025 |
|                        | $a_B$       | 0.3816 |
|                        | $R^2$       | 0.9965 |
3.5. Adsorption isotherm

Herein, four isotherm model (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were applied to fit the data experiment for adsorption isotherms (Figure 5). The values of the correlation coefficient \( R^2 \) and the isotherm parameters were displayed in Table 3. We can see that the value of \( R^2 \) of Langmuir model (0.99924) is relatively high, which can describe the experimental data accurately. In addition, AC_RH has a homogeneous surface, and the adsorption of Methylene Blue is in a monolayer. Thus, Langmuir model can use in this case to describe the adsorption isotherm.

![Figure 5. The isotherm models:](image)

A) Langmuir, B) Freundlich, C) Temkin and D) Dubinin-Radushkevich

### Table 3. Parameter of isotherm

| Model                        | Parameter          | Value       |
|------------------------------|--------------------|-------------|
| Langmuir (3.5):              | \( k_L \) (L/mg)   | 14.5        |
| \( \frac{1}{Q} = \left( \frac{1}{Q_m K_L} \right) \frac{1}{C} + \frac{1}{Q_m} \) | \( Q_m \) (mg/g) | 555.5       |
|                              | \( R_L = \frac{1}{1+K_L C_o} \) | 0.001       |
|                              | \( R^2 \)         | 0.99924     |
| Freundlich (3.7):            | \( k_F \) (mg/g)/(mg/L)^{1/n} | 4.43        |
| \( \ln Q_s = \ln K_F + \frac{1}{n} \ln C_s \) | \( 1/n \) | 0.097       |
|                              | \( R^2 \)         | 0.844       |
| Temkin (3.8):                | \( k_T \) (L/mg)   | 22636.64    |
| \( Q_s = B_T \ln K_T + B_T \ln C_s \) | \( B_T \) | 3.11        |
|                              | \( R^2 \)         | 0.85        |
| Dubinin-Radushkevich (3.10): | \( B \) (kJ/mol^2) | 1.422       |
| \( \ln Q_s = \ln Q_m - R E z^2 \) | \( Q_m \) (mg/g) | 37.87       |
|                              | \( E \) (J/mol)    | 592.97      |
|                              | \( R^2 \)         | 0.951       |
4. Conclusion
Thank the surface consists of many functional groups, Ac-RC acts as a value candidate, contributing to enhanced adsorption capacity. Thus, the results of adsorption experiments showing activated carbon from rice husk with the highest MB removal efficiency reaching 84.86% over 180 min. Besides, pH solution, time contact, and adsorbent dosage play an important role in removal capacity. Current results suggest the potential of activated carbon prepared from rice straw in manufacture of adsorbent that is effective for removal of MB from aqueous media.

Acknowledgements. This study was supported by Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam.

5. References
[1] Mohammed A A and Kareem S L 2019 Alexandria Eng. J. 58 917–28
[2] Litefti K, Freire M S, Stitou M and González-Álvarez J 2019 Sci. Rep. 9 1–11
[3] Guedidi H, Reinert L, Lévêque J M, Soneda Y, Bellakhal N and Duclaux L 2013 Carbon N. Y. 54 432–43
[4] Fil B A, Ozmetin C and Korkmaz M 2012 Korean Chem. Soc. 33 3184–90
[5] Yu Z, Peldszus S and Huck P M 2009 Environ. Sci. Technol. 43 1474–9
[6] Van Tran T, Bui Q T P, Nguyen T D, Le N T H and Bach L G 2017 Adsorpt. Sci. Technol. 35 72–85
[7] Sartape A, Mandhare A, Salvi P, Pawar D, Raut P, Anuse M and Kolekar S 2012 Chinese J. Chem. Eng. 20 768–75
[8] Adunphatcharaphon S, Petchkongkaew A, Greco D, D’Ascanio V, Visessanguan W and Avantaggiato G 2020 Toxins (Basel). 12 108
[9] Abd-Elhamid A I, Emran M, El-Sadek M H, El-Shanshory A A, Soliman H M A, Akl M A and Rashad M 2020 Appl. Water Sci. 10 1–11
[10] Bach L G, Van Tran T, Nguyen T D, Van Pham T and Do S T 2018 Res. Chem. Intermed. 44 1661–87
[11] Pham V T, Nguyen H-T T, Tran T Van, Nguyen D T C, Le H T N, Nguyen T T, Vo D-V N, Le T H N and Nguyen D C 2019 J. Chem. 2019 1–16
[12] Thuan T Van 2018 Vietnam J. Sci. Technol. 54 277
[13] Ait Ahsaine H, Anfar Z, Zbair M, Ezahri M and El Alem N 2018 J. Chem. 2018 1–14
[14] Dural M U, Cavas L, Papageorgiou S K and Katsaros F K 2011 Chem. Eng. J. 168 77–85
[15] Üner O, Geçgel Ü and Bayrak Y 2016 Water, Air, Soil Pollut. 227 247