Response surface methodology approach for optimization of methylene blue adsorption using activated carbon from rice husk

Lam Van Tan¹,²,*, Hong-Tham T. Nguyen¹,²
¹NTT Hi-Tech Institute, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam.
²Center of Excellence for Green Energy and Environmental Nanomaterials, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam

Corresponding author: labasm2013@gmail.com; lvtan@ntt.edu.vn

Abstract. In this study, an activated carbon (AC) material was derived from rice husk and tested for adsorption efficiency against methylene blue (MB). Response surface methodology (RSM) and central composite design (CCD) were adopted as the optimization techniques. The affordable, non-toxic and easily obtainable rice husk was carbonized and thereafter activated by KOH to produce porous AC, which was then characterized by XRD, FTIR, SEM and BET analyses. In the optimization study, the independent and collaborative effects of three experimental parameters, including dye concentration, pH solution and contact time, were taken into account. The adsorption capacities showed up to follow the direction that was well congruent with the confirmation experiments, which disclosed the robustness and viability of the optimization technique.

Keywords: adsorption, response surface methodology, methylene blue, activated carbon, rice husk

1. Introduction
One of the most contemporary issues that are causing paramount concerns in various parts of the world is the alarming rate of environmental pollution. Among many types of contaminants, colorants, notably those categorized as aggressive, prompt, basic, and acidic nature, have been regarded as a persistent threat to the water ecosystem [1]. They express higher water solubility, presenting difficulty in removing them from the water using the conventional methods [2,3]. Therefore, removal of industrial dyes has been an issue that attracts extensive attention from many fields.

Methylene Blue (MB) is a cationic dye whose usage is prevalent among garment and paper industries and has been known for the ability to reduce water transparency, hinder the activity of photosynthesis, and increase the demand for chemical oxygen, which interferes with the bacterial metabolism of waterlogged bacteria [4]. Due to the complicated structure and synthetic origin, the removal of MB dyes could not be easily realized by conventional wastewater treatment techniques, hence calling for further studies dealing with treatment of dye-containing wastewater [5,6].

It is a fact that porous materials play an important role in treating wastewater owing to a number of...
advantages including large contact area and reactivity of the material surface, fine porosity and ability to be tailored to adapt to different pollutants and media [7]. In this sense, the present work aims to investigate the optimal factors to the efficiency adsorption process of methylene blue dye by using response surface methodology.

2. Material and methods

2.1. Materials

The activated carbon was synthesized from rice husk source materials according to the previous report. Firstly, rice husk was hand-distributed upon the floor to be sun dried. This drying process takes from some days to a week depending on the amount available sun irradiation. Then, the rice husk was crushed into powder to prepare for the next activated stage. In this stage, solid KOH was used to activate dry powder according to ratio 1:1 (g/g) for 24 hours. The impregnated sample was dried at 105°C for 24 hours prior to the physical carbonization phase with 99.9 % N₂ gas flow at 500°C. Residual KOH was removed from activated carbon by washing with distilled water and HCl solution. The obtained carbon was then dried in an oven for 24 hours. The final product renders an adsorbent suitable for wastewater treatment, which was abbreviated AC_RH.

2.2. Instrumentation

Powder X-ray diffraction (PXRD) patterns were recorded with a Jasco-4700 diffractometer equipped with an X'Celerator detector and using Cu Kα radiation (λ=1.54060). FT-IR spectra were collected on a Jasco-4700 spectrometer (Japan). The specific area and pore distributions of as-prepared samples were calculated from the N₂ isotherm adsorption branch by BET (TriStar 3000 V6.07 A). Field Emission Scanning electron microscopy (FESEM) studies were carried out by Hitachi FE-SEM S4800 (Japan). 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, the amount of AC_RH and 100 mL of MB solution 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 withdrawn 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 following equation used to calculate the removal efficiency was calculated based on concentration before and after the adsorption process:

\[ q_e = \frac{(C_o - C_e)m.V}{m} \]  

where, \( C_o \) and \( C_e \) are respectively initial and equilibrium dye concentrations (mg/L).

3. Results and discussion

3.1. Material characteristics

Figure 1 depicts the XRD pattern and FT−IR spectra of AC_RH. According to Figure 1.A, the broad range at 20-30 could be indexed to the amorphous carbon structure [8]. In addition, the weak and broad C (101) diffraction peak (20 = 40-50°) is due to the a axis of the graphite structure [2]. Besides, FT−IR spectra was used to overcome the spectral broadenings and band overlaps (Figure 1.B). A broad spectrum is found in areas of surface functional groups such as phenols, carboxylic acids and carboxylic acid derivatives as well as in the presence of the -OH group on the material's surface in the range 3554-2947 cm⁻¹ [3,4]. These bands are formed by the prolonged oscillation of the OH functional group and become wider in the case of coal oxidation. Covalent fluctuations of C−H bonding of groups −CH₂, −CH₃ were observed at peaks 2898 cm⁻¹ and 2810 cm⁻¹ [5,6]. In addition, the typical positions for C−O and C = O oscillations of the ester, ketone, aldehyde, lactone or carboxylic groups appear in the range of 1486-1728 cm⁻¹. The adsorption of the carbonyl ester group C = O of the lactone and phenol groups was observed in
the range 919-1438 cm$^{-1}$ [7,8]. These functional groups contribute greatly to improving the adsorption efficiency.

![Figure 1. XRD pattern (A) and FT-IR spectra (B) of AC_RH](image)

**Figure 1.** XRD pattern (A) and FT–IR spectra (B) of AC_RH

**Figure 2** illustrate the surface morphology of AC_RH. Visually, the surface of the adsorbent exhibited good porosity and irregular shape with even cavities and fine open pores, indicating relatively high surface area.

![Figure 2. SEM image of AC_RH](image)

**Figure 2.** SEM image of AC_RH

To make sure the porous material evenly, N$_2$ isotherm adsorption / desorption was analyzed (**Figure 3**). AC_RH exhibit the type I isotherm according to definitions of International Union of Pure and Applied Chemistry (IUPAC). In detail, the surface area and pore diameter of AC_RH are 493.46 m$^2$/g and 2.45 nm, respectively. With the presence of large pores, it is very likely that methylene blue molecules were trapped and adsorbed into the pores.
To realize the optimization process of the MB adsorption process with AC_RH, Design Expert software was utilized. The software was configured to adopt the central composite design (CCD) with design inputs taken from the preliminary investigations. A total of 20 experiments were devised as given in Table 1. Those experiments would be attempted to produce data for model estimation.

Table 1. Ranges, levels and thresholds of parameters in the experimental design with Central Composite Design

| Factors           | Units | Low (-) | Central (0) | High (+) | -α    | +α    |
|-------------------|-------|---------|-------------|----------|-------|-------|
| Initial MB Concentration | mg/L  | 40      | 50          | 60       | 33.18 | 66.82 |
| pH                | -     | 7       | 8           | 9        | 6.32  | 9.68  |
| Contact time      | min   | 170     | 180         | 190      | 163.18| 196.82|

Table 2 summarized the detailed experiment runs with the corresponding actual and estimated responses. In this model, the difference between the predicted efficiency removal and the experiment efficiency removal is negligible.

Table 2. Generated parameters for RSM experiments and their corresponding responses

| Standard Runs | Concentration (mg/g) | pH | Time (min) | Tested % | Predicted % |
|---------------|----------------------|----|------------|----------|-------------|
| 1             | 40                   | 7  | 170        | 36.05    | 35.90       |
| 2             | 60                   | 7  | 170        | 32.66    | 33.34       |
| 3             | 40                   | 9  | 170        | 36.53    | 37.40       |
| 4             | 60                   | 9  | 170        | 32.52    | 32.63       |
| 5             | 40                   | 7  | 190        | 36.11    | 36.61       |
| 6             | 60                   | 7  | 190        | 35.81    | 35.55       |
| 7             | 40                   | 9  | 190        | 38.11    | 38.05       |
| 8             | 60                   | 9  | 190        | 34.01    | 34.78       |
| 9             | 33.18                | 8  | 180        | 35.10    | 34.71       |
| 10            | 66.82                | 9  | 180        | 30.28    | 29.80       |
| 11            | 50                   | 6.32| 180        | 36.4     | 36.30       |
| 12            | 50                   | 9.68| 180        | 37.64    | 36.93       |

Figure 3. N₂ isotherm adsorption/desorption of AC_RH
Table 3. Data ANOVA for MB removal efficiency on the composite adsorbent.

| Source    | Sum of Squares | Degree of Freedom | Mean Square | Value F | Prob. > F | Comment          |
|-----------|----------------|------------------|------------|---------|-----------|------------------|
| Model     | 118.85         | 9                | 13.21      | 32.93   | < 0.0001  | $R^2 = 0.9674$  |
| A-Concentration | 29.01      | 1                | 29.01      | 72.35   | < 0.0001  | $R_{adj}^2 = 0.9380$ |
| B-pH      | 0.4647         | 1                | 0.4647     | 1.16    | 0.3070    |                  |
| C-Time    | 6.93           | 1                | 6.93       | 17.29   | 0.0020    |                  |
| AB        | 2.44           | 1                | 2.44       | 6.07    | 0.0334    |                  |
| AC        | 1.13           | 1                | 1.13       | 2.81    | 0.1244    |                  |
| BC        | 0.0022         | 1                | 0.0022     | 0.0055  | 0.9425    |                  |
| A$^2$     | 74.86          | 1                | 74.86      | 186.66  | < 0.0001  |                  |
| B$^2$     | 7.85           | 1                | 7.85       | 19.57   | 0.0013    |                  |
| C$^2$     | 0.3429         | 1                | 0.3429     | 0.8550  | 0.3769    |                  |

The ANOVA results of methylene blue removal using AC_RH are given in Table 3. It is evident from the data in Table 3 that the predicted $R^2$ value (0.9674) and the adjusted $R^2$ value (0.9380) are closely related to each other and thus ideally aligned with the quadratic model. Given the results of ANOVA (Table 3), the model F-value of 32.93 and the p-value of <0.0001 % implies that the system is clinically meaningful. The above demonstrates that the current mathematical formula fits well into the experimental results demonstrate the feasibility of an inconsequential lack of fit (Table 3).

The plot between both the experimental (actual) and the predicted MB removal values is shown in Fig. 4. Evidently, the difference between predicted and experimental responses was small across observations, at around less than 0.1. This suggests high explanatory power of the estimated model and the well-fitness of the data to the quadratic function. Those results suggest that it is reasonable to assume that the validated numerical vibration.
Figure 4. Normal plot of residuals (A), Residuals versus run plot (B), Predicted versus actual plot (C)

Figure 5. Response surface plots a, b concentration (mg/L) and pH solution; c, d concentration (mg/L) and contact time (min); e, f, contact time (min) and pH solution

Figure 5 show the the 2D-contour and 3D-response surface plots, which were characterized for the adsorption capacity (mg·g⁻¹). The pertinence of dichotomous relationships between three selected variables (pH, contact time, and initial concentration of MB) can be clearly deduced from these graphs. In detail, both two variables including pH solution and contact time affected remarkably the removal capacity of Methylene Blue from aqueous solution. Further addition of initial concentration dye led to decline in adsorption efficiency. From the figure, it is also evident that improvements in adsorption efficiency are due to decreased dye concentration in the media and that decreased contact time could also cause better interaction between dye and adsorbent, which is likely responsible for enhanced adsorption. At low pH
values (2–6.0), the removal of dye seemed to be inefficient and irresponsible to contact time. However, at higher pH range (8.0–9.0) and long contact time, pH value was found to associate with noticeable changes in the response. Current results revealed the dependence of optimal pH on the pH range, which in turn remarkably affect dye removal capacity.

4. Conclusion
In the present study, activated carbon was produced from rice husk source, which was evaluated as a porous material with high surface area (493.46 mg/g). By using response surface method (RSM), three variables (initial MB concentration, pH solution, and contact time) were adopted to explore the individual and combined effects thereof on methylene blue adsorption. The results revealed that each factor individually and significantly affected the adsorption process. The reliability of the developed has been guaranteed by the high magnitude of the coefficient of determination between the predicted experimental and model values. Among all the process variables, the initial dye concentration was found as the most significant factor. Current results support the use of optimization techniques in wastewater treatment processes to find out most suitable conditions and materials for specific contaminants.

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