Removal of Methylene Blue Using Agricultural Waste: A Case Study of Rice Husk and Rice Husk Ash from Chaipattana Rice Mill Demonstration Center

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ABSTRACT
Rice husk (RH) and rice husk ash (RHA) from Chipattana rice mill were studied in order to investigate the physical properties and methylene blue (MB) dye adsorption potential of RH compared with RHA residuals after gasification process. The structural observation using SEM expressed the enhancement of RHA porosity after underwent gasification process, in which coincided with the BET analysis. The BET specific surface area exhibited RH and RHA were 2.56 and 149.66 m²/g. The average pore diameter of RH was 3-fold greater than that of RHA which are 7.0 and 2.7 nm. However, the RH performed as a better adsorbent for MB dye removal with the efficiency at equilibrium 98.95%, while RHA was 92.70%. The study of concentration effect presented the adsorbed amount MB increased with the increase of MB initial concentration. The kinetic studies agreed with pseudo-second-order, while, the sorption process of RH corresponded to chemisorption process, but, RHA rather depended on the physico-chemical mechanism. From isotherm study, RH and RHA adsorbents were well-fitted to Langmuir model; however, the sorption process of RH could possibly be influenced by an intraparticle diffusion mechanism. The results revealed a good potential to utilize RH and RHA residuals from Chaipattana Rice Mill Demonstration Center for dye removal without further modification process.

1. INTRODUCTION
The color is a visible contaminant to be recognized in water as the undesirable appearance that can induce a great concern associated with environmental pollution. It is commonly found that industries that used dyes and pigments in their manufactures discharged dye-containing effluent into river streams, which can interfere living condition of aquatic lives, plants, and human on the food web. Accordingly, methylene blue (MB) dye is categorized as acid dye compound that has been studied in order to represent dye compounds in aqueous solution, since, MB can be widely utilized in several applications such as; paper coloring and fabric dying. Moreover, MB as a contaminant in the environment, through surface water can cause adverse effects to the human and living organism (Vadivelan and Kumar, 2005; Adeleji and Olayinka, 2014). Thus, color removal from effluent before discharging to environment is necessarily considered and still addressed as a problem for conventionally chemical wastewater treatment method, regarding to a few proper processes are employed such as biological oxidation and chemical precipitation (Vadivelan and Kumar, 2005), but these processes are cost effective only when the dye concentration is relatively high.

Hence, the study of alternative methods like adsorption has caught a great attention due to sludge free operation and completeness of dye removal from diluted solutions (Malik, 2003). Nowadays, activated carbon is noteworthy as the most widely used adsorbent in adsorption process regards to its promising properties such as; surface area, microporous structure, high adsorption capacity and degree of surface reactivity (Malik, 2003). In fact, producing activated carbon required high energy input to pyrolyzed raw material to carbonaceous
form. This has led to numerous research to modify low cost and less energy consumption adsorbent for dye removal, such as coal fly-ash, wood, silica gel, and agricultural waste (McKay et al., 1986; Khare et al., 1987; Singh and Rawat, 1994; Theng and Wells, 1995; Juang et al., 1997). Since the adsorption capacities of adsorbent are still limited. The development of adsorbent materials is still on the go. Of late, rice husk (RH) has been reported its feasibility as an adsorbent for acid dye removals such as acid yellow (Malik, 2003) and methylene blue (Vadivelan and Kumar, 2005) in which represented dye adsorption potential of raw RH. In addition, the modification of RH with pyrolysis and carbonization to produce RH ash (RHA) exhibited a greater result for dye elimination (Chandrasekhar and Pramada, 2006; Srivastrava et al., 2006), but those well-controlled manufacture appeared to consume much energy and time.

In Chaipattana Rice Mill Demonstration Center, rice husk was delivered from local rice mill houses (2,400 kg) to undergo gasification in order to produce gas to generate electricity. Each day, the rice husk becomes residuals from the process over 350 kg/day. The residue rice husk has been collected in order to distribute occasionally to the residents nearby, however, the consumption is unsustainable compared to the production. Hence, this research aimed to emphasize the potential of using rice husk (RH) before and after gasification process (RHA) from Chaipattana rice mill unit for MB dye adsorbent without further modification, in order to seek its potential. Adsorption influent factors such as adsorbent dose, retention time, dye concentration, adsorption kinetics and isotherm are included in this study.

2. METHODOLOGY
2.1 Adsorbent preparation
The rice husk that used in this study was collected from the Chaipattana rice mill (Integrated Renewable Energy Development and Demonstration Center), located in Lat Bua Luang District, Phra Nakhon Si Ayutthaya province, Thailand. The raw rice husk (RH) was obtained from the excessed rice husk that unfed to the biomass gasification system. On the other hand, the rice husk ash (RHA) was taken after processed biomass gasification system (Figure 1). The gas from gasification system was directly sent to operate electricity generator at 200 kW/h. The biomass gasification process includes: 1) dehumidification of rice husk under 100-105 °C to obtain bio-oil and fuel gases; 2) refining breakdown is carried out at 800 °C which energy and CO₂ are produced; and 3) reduction process has undergone at 600-700 °C, in which CO, H, CH₄ and rice husk ash are presented.

The collected RH and RHA were brought to the laboratory and stored in a dried area. The RH and RHA powder were prepared by grinding the materials with herb grinder (Model: RA-04A) and sieved to receive constant particle size of ≤ 40 mesh. The sieved RH and RHA were kept in plastic bottles and placed in the dry area before using.

2.2 Preparation of simulated dye wastewater
The methylene blue (BDH, 85% dye content, C₁₆H₁₈ClN₃S) was used to prepare the synthetic wastewater without further purification. The methylene blue powder 1.127 g were dissolved in DI water and adjusted to 1,000 mL, where the concentration of the solution was 100 mg/L, labeling as a stock solution.

2.3 Sorption experiments
2.3.1 Effect of absorbent concentration
The effect of the absorbent amount on the removal of methylene blue was studied in the batch experiment. The methylene blue stock solution was measured its initial pH which is in the rage of 5.7-6.2. The RH and RHA absorbent were weighed to different amounts (0.06, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 1.0, and 1.5 g) and placed into 125 mL-Erlenmeyer flasks. Then, the synthetic wastewater (50 mL) was filled into the flasks and shake at room temperature (29 °C) using chamber shaker, orbital mixer incubator (Ratek, OM15), at a constant rotation speed (220 rpm) for 24 h to reach the equilibrium. The samples were centrifuged at 3000 rpm for 10 min and the supernatant solution was filtered with nylon syringe filter (diameter of 0.45 μm). The filtered solution was analyzed using a UV-vis spectrophotometer (Shimadzu, UV 1201) at a wavelength of maximum absorbance of 664 nm.
2.3.2 Effect of contact time

The adsorption equilibrium was carried out through batch experiment. The stock solution 100 mg/L was added to 0.3 g adsorbent that stored in 125 mL-Erlenmeyer flasks. The samples then were shake at the constant rate (220 rpm) at room temperature for 30, 60, 90, 120, 150, 240, 300, 360, 720, and 1440 min, respectively. After sampling, each sample was centrifuged at 3000 rpm for 10 min, before filtering through 0.45 μm nylon syringe filter. In order to determine removal efficiency of adsorbent, UV-vis spectrometer was used at 664 nm of the wavelength.

2.3.3 Effect of dye concentration and contact time

Effect of dye concentration and contact time on adsorption efficiency by RH and RHA were carried out using batch experiment. The stock solution was prepared to various concentrations (40, 60, 80, 100 and 120 mg/L). Each concentration was mixed with 0.3 g adsorbent then shake at 220 rpm and sampled after 30, 60, 90, 120, 150, 240, 300, 360, and 720 min, respectively. The samples were centrifuged and filtered before analyzing UV-vis absorbance at 664 nm of the wavelength.

3. RESULTS AND DISCUSSION

3.1 Materials characterization

The textural structure observation of RH and RHA particles was undertaken under scanning electron microscopy (SEM). Figure 2(a) presents the SEM image of side-section RH where the skin is rough and compacted at the outer surface of the skin, while, the side-section of RHA shows a peel-off structure at the top-layer of the skin (Figure 2(b)). The cross-section image revealed porous morphology at the top layer of the particle (inset image).

The alteration of the morphological structure was affirmed by the increase of specific surface area. The BET analysis was applied in order to compare the specific surface area, pore types, and volume of RH and RHA (Table 1). The BET result of RHA sample exhibited a great enhancement of the surface area after underwent gasification in which, over 70-fold greater than the specific surface area of RH.

Furthermore, the effect of pH on the adsorbent surface charge has been reported as an important factor to the degree of ionization and speciation of pollutants. Due to the adsorption process, pH can be changed through dissociation of functional groups on the adsorbent surface at the active sites (Srivastava et al., 2006). The change of pH can effect reaction kinetics and characteristics of equilibrium. Hence,
understand the adsorption mechanism, the point of zero charges (pH\text{PZC}) of adsorbent was determined. From the characterization of pH\text{PZC}, the RH and RHA resulted in the net of surface charge 6.6 and 7.5, respectively. The results indicated that RH and RHA own positive charges when pH is lower than 6.6 and 7.5, therefore, the preference adsorption could be anionic dye like MB.

![Figure 2. SEM image of skin particles side-section of (a) RH (rice husk), (b) RHA (rice husk ash) and (inset image) cross-section skin of RHA](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micro pore volume (cm³/g)</th>
<th>Meso pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>2.56</td>
<td>0.0045</td>
<td>0.00207</td>
<td>0.00243</td>
<td>7.0</td>
</tr>
<tr>
<td>RHA</td>
<td>149.66</td>
<td>0.1010</td>
<td>0.08868</td>
<td>0.01232</td>
<td>2.7</td>
</tr>
</tbody>
</table>

### 3.2 Effect of adsorbent concentration

The effect of adsorbent concentration or adsorbent dose was investigated in order to determine the amount of adsorbent versus the change of removal efficiency of methylene blue. In Figure 3, the percentage of MB removal efficiency increased with the increasing of adsorbent dosage after 24 h retention. The adsorbent dosages higher than 0.3 g (0.3-2.0 g) showed the removal efficiency up to 99.9%. These corresponded to the availability of sorption sites at the surface of adsorbent was increased (Namasivayam and Kavitha, 2002; Mahmoud et al., 2012). Hence, the results implied that the 0.3 g adsorbent dosage of RH and RHA exhibited as a minimum concentration concern that needed for methylene blue removal at 100 mg/L concentration.

![Figure 3. Effect of adsorbent concentration (C₀=100 mg/L, V=50 mL)](image)

### 3.3 Effect of contact time

Effect of contact time experiment was carried out at room temperature (29 °C). A single adsorbent dosage (0.3 g) was mixed with 100 mg/L MB solution and sampled the mixture at different times (30, 60, 90, 120, 150, 240, 300, 360, 720, and 1,440 min).

As shown in Figure 4(a), the removal efficiency of RH and RHA elevated with increasing
contact time. The RH adsorbent presented removal efficiency of 75.54% during the first 30 min and the percentage of removal efficiency slowly increased up to 98.95% after 300 min, while the RHA adsorbent performance was vice versa. The removal efficiency of RHA at the first 30 min presented only 42.73% and gradually increased to 92.70% after 1440 min. Hence, it can be considered that the equilibrium of RH and RHA attained after 1440 min or 24 h.

![Figure 4. The comparison of effects of contact time of RH and RHA; (a) efficiency versus contact time and (b) adsorbed amount MB versus contact time (C₀=100 mg/L, V=50 mL, W=adsorbent weight (0.3 g))](image)

### 3.4 Effects of dye concentration and contact time

The effects of dye concentration and contact time on adsorbed amount MB onto RH and RHA particles were computed as qₑ (mg/g) using mass balance equation given by:

$$qₑ = \frac{(C₀-Cₑ) \times V}{M}$$  \hspace{1cm} (1)

Where C₀ (mg/L) and Cₑ (mg/L) are the solution concentration at equilibrium time (t), V corresponds to solution volume (L), and M is the adsorbent amount (g). In Figure 5, RH and RHA adsorbents after sorption process resulted in the increase of adsorbed amount MB with the increasing contact time. The RH adsorbent showed the elevation of adsorbed amount MB correlated with the increase of initial dye concentration, while the results of RHA represented an inverse direction. From the results, at the initial concentration of 120 mg/L, RH presented the greatest adsorbed amount MB from the first 30 min, but, RHA revealed an overwhelming adsorption behavior exhibited a slow adsorption progress. However, the different dye initial concentrations presented no effect on adsorption equilibrium of MB adsorption using RH and RHA. As seen in the Figure 5, RH and RHA have reached the adsorption equilibrium after 60 min at any initial concentrations. On the other hand, the adsorbed amount MB tended to increase from 11.2833 to 23.4064 mg/g toward the increasing initial concentration for RH adsorbent. The greatest adsorbed amount MB onto RH was 21.4553 mg/g at the initial concentration of 120 mg/L after 300 min. Likewise, the RHA adsorbed amount MB increased from 7.4732-12.5119 mg/g with the increasing initial concentration, in which the greatest adsorbed amount found MB at 12.8777 mg/g at the initial concentration 80 mg/L after 360 min. According to the result, sorption rate can be computed to compare at the first 30 min of RH and RHA, where the sorption process was rapid. For RH, the initial concentration of 120 mg/L represented the greatest sorption rate of 0.4867 mg/g, while the fastest sorption rate of RHA was 0.0302 mg/g at the initial concentration of 80 mg/L. This has agreed with the tendency of higher initial dye concentration tends to enhance the adsorption process (Pavan et al., 2008; Mahmoud et al., 2012). Regarding the results, the higher sorption rate at the initial period (first 40 min) corresponded to the increase of vacant site numbers at the initial stage, which caused concentration gradients between adsorbate in solution and adsorbate on the adsorbent surface. The increase of concentration gradient tends to increase
the dye adsorption. Thus, after time processed the concentration gradient decreased from the accumulated dye particles in the vacant sites, then the adsorption rate is reduced (Vadivelan and Kumar, 2005).

Figure 5. The effects of contact time of methylene blue on removal efficiency of (a) RH and (b) RHA at adsorbent dose 0.3 g towards different dye concentrations: (■) 40 mg/L, (●) 60 mg/L, (▲) 80 mg/L, (□) 100 mg/L, and (●) 120 mg/L.

3.5 Adsorption kinetic study

The study of sorption kinetics was studied in order to confirm the kinetic of methylene blue adsorption onto rice husk was determined by pseudo-second-order. Ho’s pseudo-second-order kinetics was used, which is represented by eq. (2) (Ho, 2003).

\[
\frac{dq}{dt} = K_2 (q_e - q)^2
\]  

(2)

Where, \(K_2\) is the pseudo-second-order rate constant (g/mg min), \(q_e\) and \(q\) represent the amount of dye adsorbed (mg/g) at equilibrium and at any time, \(t\). The equation can be separated in eq. (3).

\[
\frac{dq}{(q_e - q)^2} = K_2 \ dt
\]  

(3)

To integrate eq. (3) to the conditions at \(t=0\) to \(t=t\), when \(q=0\) and \(q=q_e\) the equation was written as;

\[
\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t
\]  

(4)

A plot of \(t/q\) versus \(t\) represents the value of \(K_2\) (g/mg h) and \(q_e\) (mg/g) constants, which can be computed. Furthermore, the \(K_2\) constant is also used to calculate the initial sorption rate \(h\), at \(t\rightarrow0\) (eq. (5))

\[
h = K_2 q_e^2
\]  

(5)

The sorption data of RH and RHA were plotted between \(t/q\) versus time (\(t\)) as presented in Figure 6. From the plot, we computed initial sorption rate (\(h\)), pseudo-second-order-rate constant (\(K_2\)), adsorbed amount MB at equilibrium (\(q_e\)), and the corresponding linear regression correlation coefficient (\(r^2\)) are given in Table 2. From the Table 2, the \(r^2\) values of both RH and RHA in every initial concentration were perfectly linear. The \(r^2\) values of RH aligned in the range of 0.9384 to 1.000, while RHA \(r^2\) values were in the range of 0.9696 to 0.9997. The RH and RHA sorption profile determined pseudo-second-order behavior, especially the values of \(r^2\) of RH that nearly to 1, which confirmed the ideal pseudo-second-order mechanism of sorption process (Ho, 2003). The result of pseudo-second-order mechanism was used to describe chemisorption process (Ho and McKay, 1999) in which valency forces are involved through the sharing or exchange of electrons of adsorbent and adsorbate (Ho, 2006). It can be implied that the RH and RHA in this study treated MB through chemisorption process, where the functional groups on the surface played an important role rather than porous structural influence. This explanation can be well supported the results of BET. As mentioned, the BET surface area of RHA was proved to have a greater specific surface area than RH, but, the adsorption efficiency of RHA was lower. This indicated that the adsorption process...
using RH is more likely to depend on chemisorption mechanism, while RHA is advantageous from physicochemical adsorption mechanism.

**Figure 6.** Linear fitting of adsorption data with pseudo second order of the effects of contact time on adsorbed amount MB of (a) RH and (b) RHA towards different dye concentrations; (■) 40 mg/L, (○) 60 mg/L, (▲) 80 mg/L, (□) 100 mg/L, and (●) 120 mg/L

**Table 2.** Pseudo-second-order rate constant for the sorption of methylene blue onto RH and RHA

| C₀ (mg/L) | RH | | | | | | RHA | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | K₂ (g/mg min) | h (mg/g min) | qₑ (mg) | r² | | | K₂ (g/mg min) | h (mg/g min) | qₑ (mg) | r² |
| 40 | 0.00309 | 0.3751 | 11.2541 | 1.0000 | | | 0.01121 | 0.2128 | 6.3836 | 0.9761 |
| 60 | 0.00628 | 0.2617 | 7.8508 | 0.9993 | | | 0.01673 | 0.1372 | 4.1165 | 0.9997 |
| 80 | 0.00600 | 0.4180 | 12.5409 | 0.9384 | | | 0.00576 | 0.3017 | 9.0523 | 0.9774 |
| 100 | 0.00392 | 0.3848 | 11.5426 | 0.9999 | | | 0.00918 | 0.2174 | 6.5211 | 0.9939 |
| 120 | 0.00353 | 0.4868 | 14.6037 | 0.9990 | | | 0.00838 | 0.2021 | 6.0642 | 0.9696 |

### 3.6 Adsorption isotherm study

The equilibrium isotherm value is fundamental information to design and optimize the adsorption system of an aqueous phase, in particular (Saeed et al., 2010). Several isotherm models have been used to observe the validity of the adsorption experiment. In this study, two most common models, Langmuir and Freundlich isotherms, were used to explain the adsorption equilibrium. In Figure 7, Freundlich (Figure 7(a)) and Langmuir (Figure 7(b)) isotherms were plotted to investigate the best fit isotherms for MB dye onto RH and RHA. The sorption characteristics of MB onto RH and RHA are close to Langmuir isotherms, evidenced by their correlation coefficients (r²), 0.9845 and 0.9886 for RH and RHA, respectively. The Langmuir isotherm suggests monolayer adsorption behavior on the homogeneous structural adsorbent, where the adsorption takes place at specific homogeneous sites that only a single molecule of dye molecule can occupy. Thus, it is used to predict the existence of monolayer coverage of adsorbate at the outer surface of the adsorbent (Saeed et al., 2010).

Furthermore, the Langmuir isotherm can be used to express in terms of dimensionless constant separation factor or equilibrium parameter (R_L), which has been identified as eq. (6):

\[
R_L = \frac{1}{(1+K_LC_0)}
\]  

(6)

The value of R_L can be used to predict affinity between adsorbate and the adsorbent whether the sorption system is “favorable” or “unfavorable”. In Table 3, the R_L values of MB onto RH and RHA adsorbents were 0.012 and 0.035, respectively, indicated that the sorption is favorable for both RH
and RHA (when 0 < RL < 1 is favorable). The RHA presented a higher RL values, indicated that at lower concentration was more favorable for adsorption process.

**Table 3.** Langmuir constants for the adsorption of methylene blue on RH and RHA

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Sm (mg/g)</th>
<th>K_L (L/mg)</th>
<th>R_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>21.9</td>
<td>0.739</td>
<td>0.012</td>
</tr>
<tr>
<td>RHA</td>
<td>12.8</td>
<td>0.270</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Regarding the isotherm, RH and RHA presented as suitable adsorbents for MB adsorption at high concentration. The RH adsorbent can strongly attach MB molecules on its active sites as a monolayer on the surface, as explained by Langmuir isotherm. However, the sorption results of MB onto RHA could depend on mesoporous volume in which expressed by BET analysis (Srivastava et al., 2006). However, the RH adsorbent had revealed an unclear explanation using BET. It was able to assume that the sorption mechanism of MB on RH has been influenced by intraparticle diffusion when dye ions loaded on adsorbent particles through film diffusion. This sorption process took place in the system with good mixing, large particle size adsorbent and high concentration adsorbate (Vadivelan and Kumar, 2005).

**Figure 7.** Linear fitting adsorption data with (a) Freundlich and (b) Langmuir isotherms regarded to the effects of contact time on adsorbed amount MB of (■) RH and (●) RHA

### 4. CONCLUSIONS

In this study, RH and RHA from Chaipattana Rice Mill Demonstration Center were investigated their potential for methylene blue adsorbents from solution. Physical properties of adsorbents were characterized using SEM and BET. The BET profile of RHA affirmed the higher surface area (149.66 m²/g) and microporosity (0.08868 cm³/g) existence. The pH factor was well controlled in the range of 5-7, where the sorption efficiency of RH represented as a better adsorbent in which correlated with greater RH dosage and MB concentration. The kinetic study of RH and RHA affirmed linear relation of pseudo-second order with correlation coefficient (r²) 0.9384 to 1.00 indicating the valency forces involve through the sharing or exchange electrons of adsorbent and adsorbate. The isotherm study fitted with Langmuir model with R² value of RH and RHA adsorbents are 0.9845 and 0.9886, respectively. The RL (0.012 and 0.035) results can be concluded that the sorption process of both RH and RHA are favored for anion dye adsorption such as methylene blue. The RH sorption system has been influenced by intraparticle diffusion, according to good mixing, large particle size adsorbent and high concentration adsorbate. The RHA after gasification process has retarded adsorption efficiency of RH.

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