Influence of Chicken EggShell Powder Ratio with Coarse Rice Husk on Methyl Orange Removal from Aqueous Solution

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Abstract
Chicken eggshell and rice husk waste have been successfully used as a potential adsorbent of methyl orange (MO). In this study, after the washing and drying process, chicken eggshells were mashed while the rice husk was left intact. Chicken eggshell powder and coarse rice husk were combined and varied its composition ratio by 3:1, 2:1, 1:1, 1:2, and 1:3. The adsorption process of 50 mL MO 20 ppm in aqueous solution with 11 grams of adsorbent was measured using the UV-Vis Spectrophotometer Genesys 20 at 465 nm. Based on the results of the study, the adsorbent with a variation of 1:1 in ratio was able to adsorb MO from the solution up to 27.70% within 60 minutes.

Keywords: Adsorption, chicken eggshell, low-cost adsorbent, methyl orange, rice husk.

INTRODUCTION
Methyl Orange (MO) with the formula C₁₄H₁₄N₃NaO₃S is a type of textile dyes that is often used in Indonesia. Methyl Orange is also used as an indicator for acid-base titration. Azoids and their derivatives are carcinogenic and are not easily degraded (Widjajanti, 2009). Thus, environmental pollution by textile dye waste disposed into the water without proper processing is very dangerous. Therefore, it is necessary to process waste through chemical, physical and biological processes. Among several methods, the dyes processing explored by many scientists is adsorption. This method is simple, low cost, and more efficient in its application (Karaçetin et al., 2014; Yagub et al., 2014; Lafi & Hafiane, 2016).

Indonesia is an agricultural country that generated biomass as source of adsorbent material that has been developed...
to address environmental pollution problems. It’s reported that bagasse and sawdust have been used as an adsorbent for staining waste jeans (Sutiyani & Sukarnen, 2015). Bagasse can be used as an adsorbent for cibacron red dyes (Diapati, 2009) and in wastewater, it can be used as an adsorbent for metal ions (Apriliani, 2010). Corn cob as an adsorbent for blue reactive dyes (Purnama & Kurnianto, 2016) and as an adsorbent for an iron element in ground water (Rahayu & Adhitiyawarman, 2014). Rice husks are the most abundant biomass generated by the rice milling industry as the main agriculture product in Indonesia. Rice husk has also been studied its potential as an adsorbent of heavy metal ions in water (Wardalia, 2016), Methyl red (Hassan & Abdulhussein, 2015), methylene blue (Sharma et al., 2010), malachite green (Chowdhury et al., 2011) and as methyl orange adsorben (Mittal et al., 2007; Bamroongwongdee et al., 2018; Purbaningtias et al., 2015). Rice husk consists of cellulose, hemicellulose, lignin, silica, soluble, and moisture (Leiva et al., 2007; Ludueña et al., 2011).

Another material that is equally potent as adsorbent is chicken eggshell. Some applications of chicken eggshell as an adsorbent are to reduce the metal content of electroplating industrial wastewater (Susanto et al., 2017), improve the quality of used cooking oil (Fitriyana & Safitri, 2015), the process of chromium separation (Daraei et al., 2013), and pergasol red adsorption by the batch process (Sanredina et al., 2017). Chicken eggshell’s ability to adsorb textile dye from aqueous solutions has been studied by researchers (Salman et al., 2012). There are three types of adsorbent samples studied, they are chicken eggshells, chicken eggshells and membranes, and chicken eggshell’s membranes, while textile dye shell’s membranes, while textile dye samples used are methylene blue (cation), methyl orange (anion), and bromophenol blue (anion). Based on the results of the study, three forms of adsorbent have potential to reduce intensity of cationic and anionic dyes from water and liquid waste.

The methyl orange dye itself has been studied by several researchers. Methyl orange adsorption by utilizing chitosan (Mahatmani & Sumarni, 2003; Saha, 2010; Zhao et al., 2017), powdered pumpkin seed (Subbaiah & Kim, 2016), zeolite (Widjajanti et al., 2011), kaolinite (Sejie & Nadiye-Tabbiruka, 2016), bark powder (Egwuonwu, 2013), activated carbon (Chen et al., 2010), and eggshells (Nurlaili et al., 2017; Belay & Hayelom, 2014) have been investigated for its activity under various conditions. However, the studied of MO removal using the combination of chicken eggshell and rice husk, in our knowledge, were not much reported in literature.

Literature studies have proven the potential of chicken eggshell and rice husk as adsorbents. The factors that support this potential are because of its ease of being found, its abundant existence, and its economy. The main factors that play a role in the adsorption process is the presence of functional groups of carbonate, amine, -OH, and \(-\mathrm{C} = \mathrm{O}\). Based on the results of the FTIR analysis, chicken eggshell samples showed carbonate mineral peaks and calcium carbonate vibrations omit in wave number regions 1417-1425.40; 875.68; and 711.73 cm\(^{-1}\) (Tsai et al., 2006; Carvalho et al., 2011; Zulfiqar et al., 2013). As for the rice husk samples, -OH
vibration peak appeared at 3448.72 cm⁻¹ (Badriyah & Putri, 2017), and –C = O which could conjugate around 1649.19 cm⁻¹ (Tarley & Arruda, 2004). This result is not different from the previous research about both materials (Haqiqi, 2018a,b). In the previous research, two powders materials were combined and varied the ratio to see their activity as an adsorbent (Haqiqi, 2018c). Hence, in this research used coarse rice husk for comparison. Data collected by measuring the absorbance of methyl orange in aqueous solution both before and after the reaction with UV-Vis Spectrophotometer Genesys 20.

RESULTS AND DISCUSSION

In this research, the adsorbent that was used is a combination of chicken eggshell powder with coarse rice husk. In order to find potential new types of adsorbents, these two economical, abundant, and easily found materials are combined. Previously there are researches that examined the character and adsorption capacity of combination adsorbents from chicken eggshell powder and rice husk (Haqiqi, 2018a,b). As a new variable, in this study coarse rice husk was used. In a bottle containing 11 grams of the adsorbent with vary the ratio of material composition 3: 1, 2: 1, 1: 1, 1: 2, and 1: 3, 50 mL of 20 ppm methyl orange solution is added as shown in Figure 1.

Based on the results of observation, chicken eggshell powder without membrane has a brownish white color, grayish brown rice husk powder, and the dye solution has an orange color. Referring to the research procedure after being washed with tap water, the powder of chicken eggshell and coarse rice husk used only received a heating treatment at 105 °C for 15 minutes. As a preliminary study, the material was not washed with certain organic solvents and without any additives. This is intended to see the
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activity at basic stage whether it is able to adsorb the methyl orange from aqueous solution.

Figure 1. Adsorbent samples with variations in the ratio of chicken eggshells powder with coarse rice husks a) before adsorption, b) after adsorption.

Adsorption of methyl orange from aqueous solution lasts for 60 minutes at room temperature. The process was aided by stirring with the shaker at a speed of 200 rpm. The results showed the decreasing of MO absorbance. That means chicken eggshell powder combined with coarse rice husk successfully used as an adsorbent for methyl orange removal.

Based on the curves in Figure 3, the straight line equation is $y = 0.0097x - 0.0029$. By using this equation, the final concentration of MO solution after adsorption could be found, as presented in Table 1. The %removal of MO was calculated using equation 1:

$$\text{% Removal MO} = \frac{C_i - C_f}{C_i} \times 100\% \ldots \text{eq. 1}$$

Where $C_i$ is the initial MO concentration and $C_f$ is the final MO concentration.

Table 1. Adsorption data of adsorbent from chicken egg shell combined with coarse rice husk

<table>
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<tr>
<th>Sample</th>
<th>M before adsorption (ppm)</th>
<th>M after adsorption (ppm)</th>
<th>% Removal</th>
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<tbody>
<tr>
<td>A (3:1)</td>
<td>20</td>
<td>16.64</td>
<td>16.80%</td>
</tr>
<tr>
<td>B (2:1)</td>
<td>20</td>
<td>14.74</td>
<td>25.80%</td>
</tr>
<tr>
<td>C (1:1)</td>
<td>20</td>
<td>14.46</td>
<td>27.70%</td>
</tr>
<tr>
<td>D (1:2)</td>
<td>20</td>
<td>14.96</td>
<td>25.20%</td>
</tr>
<tr>
<td>E (1:3)</td>
<td>20</td>
<td>15.69</td>
<td>21.60%</td>
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Data from the measurement results of the absorbance using a UV-Vis spectrophotometer Genesys 20 in Table 1, shows that the highest decrease in absorbance was produced by the composite with a mass ratio of chicken eggshell powder with coarse rice husk 1: 1 is 27.70%. The measurement data of 4 others samples with the mass ratio of chicken eggshell powder with coarse rice husk 3: 1, 2: 1, 1: 1, 1: 2, and 1: 3 respectively are 16.80%; 25.80%; 25.20%; and 21.60%. This pattern is different from the methyl orange adsorption research using adsorbent combinations of chicken eggshell powder and rice husk powder. It’s reported that the adsorbent combination of chicken eggshell powder and rice husk powder with the highest %removal up to 55.90% was owned by a mass ratio of 1: 3 (Haqiqi, 2018c). Rice husks are seen to have the ability to absorb methyl orange which is
more dominant than chicken eggshells in these conditions. Whereas, when was not using rice husk powder but coarse rice husk instead, the adsorption ability is different. This shows that the size of adsorbent affects the methyl orange adsorption. The decreases of material’s size increases the surface area of adsorbent so removal efficiency increase.

Based on literature studies, which is shown in Figure 3, factors that play a role in the adsorption process include the presence of functional groups of carbonate, amine, -OH, and -C = O. The results of FTIR analysis showed that the combination of chicken eggshell and rice husk had a functional group of carbonate minerals at wave number 1423.51-1425.44 cm⁻¹, the peak of -OH strain at 3367.82-3431.48 cm⁻¹, and at 1627.97-1647.26 cm⁻¹ the peak of -C = O appears (Haqiqi, 2018a). Differences of FTIR spectra before and after adsorption were on wavenumber shifting. Hydroxyl, amine and sulfonate groups on the surface of the adsorbent capable of reacting with dyes (Koumanova et al., 2002). The active side makes the adsorbent become positively charged so that it plays a large role in the electrostatic attraction of negative charged substances (Pramanpol & Nitayapat, 2006).

**CONCLUSIONS**

Measurement data 5 composite samples (3: 1, 2: 1, 1: 1, 1: 2 and 1: 3) with a UV-Vis spectrophotometer Genesys 20, respectively are 16.80%; 25.80%; 27.70%; 25.20%; and 21.60%. Based on the results of these measurements, the chicken eggshell adsorbent combined with coarse rice husk and a variation of the ratio of 1: 1 were able to adsorb methyl orange from solution up to 27.70%. Thus, the ratio of chicken eggshell and rice husk influence the adsorption capacity, especially their significant size difference between chicken eggshell and rice husk. Advice for the next research, when measure the absorbance, the blank used is not only aquades but using the adsorbent filtrate.

**ACKNOWLEDGMENT**

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