Minimizing river pollution by batik dye wastewater using palm oil fuel ash (POFA) as an environmentally friendly, low-cost adsorbent alternative

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Abstract

The rise of the batik industry in Jambi Province causes the accumulation of waste in the environment. Disposal of batik dye wastewater directly into the environment is one source of heavy metals entering the river. Palm Oil Fuel Ash (POFA), as a part of waste originating from combustion residues of oil palm, is potential to be used as a low-cost adsorbent in overcoming the batik dye wastewater problem. The POFA is also potential to be used in the removal of heavy metals and chemical and organic compounds in industrial waste treatment. This paper reported the potential use of POFA and the modification of POFA as batik dye adsorbents in overcoming waste problems from the batik industry. Results of this study showed that POFA could adsorb the dye in batik waste with up to 22% removal efficiency and adsorption capacity up to 62 mg/g. The isotherm adsorption in this study was in accordance with the Freundlich model that showed adsorption occurred at multi-layer and heterogeneous surfaces. The adsorption process occurred endothermically and spontaneously.

Keywords:
adsorption
batik dye
dye removal
dye wastewater
palm oil fuel ash (POFA)

Introduction

Batik has been recognized by UNESCO as a typical Indonesian craft as one of the world’s cultural heritage from Indonesia. However, the batik and textile industries produce wastewater from the dyeing process. Not only contains dyes, but batik wastewater also contains synthetic materials that are difficult to be degraded. Wastewater generated from the batik or textile industry is generally an organic compound that cannot be degraded biologically; thus, it could cause environmental pollution, which mainly affects waters (Lellis et al., 2019). Some of the most common substances used in the batik and textile industries are remazole black, red and golden yellow. Only 5% of these compounds would be used in the coloring process, while the remaining 95% will be disposed of as liquid waste. The dye has quite a stable state; thus, its presence in nature is very hard to be degraded and at a high concentration. This compound is highly harmful to the environment because it could increase the levels of COD and BOD in water (Rashidi et al., 2012) and cause the emergence of intolerable traces of harmful heavy metals (Reddy and Osborne, 2020).

Several technologies to treat waste from dyeing waste have been investigated, such as the use of coagulation technology (Núñez et al., 2019), ion exchange and separation technology using membranes, reverse osmosis, microbial agent and aeration (Bian et al., 2020) and also adsorption (Peláez-Cid et al., 2013). Adsorption is considered to be the most effective method among the previously mentioned method to deal with dye waste because it has a large absorption capacity, can be used for various
kinds of dye and be regenerated. However, adsorbent requires a large amount of money (Katheresan et al., 2018). Therefore, it is necessary to study alternative adsorbents that are cheap and effective to adsorb dyeing waste.

Agricultural waste in the form of wood residues, palm shells, bagasse, corn husks and so on has the potential to be adsorbents. Although adsorbents have a large potential, there are few studies that explain dye adsorption by utilizing agricultural waste. One of the agricultural wastes that have the potential to be used as a dye adsorbent is Palm Oil Fuel Ash (POFA). POFA is waste from biomass as fuel in boilers, which raw materials are agricultural waste (Rainiyati et al., 2022). Currently, a lot of industries utilize agricultural waste as fuel because it is cheaper compared to coal. This, of course, causes a surge in the amount of POFA waste generated by industry. Although POFA has no side effects on the environment, the large number of them and no application that can be used directly, of course, makes POFA accumulate in nature which of course requires a large place to store it (Acquah et al., 2016).

This study aimed to apply palm oil fuel ash (POFA) as dye removal. Modification of adsorbent using sodium hydroxide or citric acid increases the adsorption capacity towards dye removal (Stawiński et al., 2017). However, POFA application is not economical because of its high chemical price. Another daily waste which is considered highly abundant is Eggshell (EG). EG’s high composition of CaCO₃ makes EG desirable for EG feasibility as a low-cost activation substitute for POFA’s alkaline treatment (Hasan et al., 2019). The use of orange peel as an adsorbent for dye removal has been investigated (Temesgen et al., 2018). The content of citric acid in orange peel makes orange peel have the potential to be used as a substitute for POFA’s acidic hydrothermal treatment. Besides being used directly, this study also examined the effect of POFA’s acid-base modification, eggshell and orange peel on dye removal.

Materials and Methods

Materials used in this research were Palm Oil Fuel Ash (POFA), orange peel, and eggshells. This research was designed based on these data by using eggshells as a substitute for alkaline activation and orange peel as an acid activation material. Because the two materials came in their original form in nature, the process of changing the shape was carried out first through combustion. Both materials were oven to 250 °C for 6 hours and then crushed.

The crushing step is necessary to adjust the size of the adsorbent and to expand the adsorption surface so that there are more active sides of the adsorbent. After the two activators were ready, as much as 50% of each ingredient was mixed, then added with 10 mL of water as a binder and re-oven. Upon completion, the washing step was repeated. The purpose of using orange peel and eggshells in this research was to substitute them for POFA acid and alkaline modification. Other than using POFA and modified POFA, orange peel and eggshells as waste adsorbent was also studied. The purpose was to compare the effectivity of each material to its ability to reduce color in batik waste. POFA modification is conducted through alkaline-acid hydrothermal pretreatment by modifying a method conducted by Chandrasekhar et al. (2021).

Modifications done were changing the ratio to 1:1; changing the operating temperature to 120 °C for 3 hours and adding 20% water from the overall solid, and changing acid and alkaline chemical material to orange peel and eggshell. The mixture was then washed until the washing water was clear. Prior to the adsorption step, the activation process was carried out by preheating at a temperature of 120 °C for 1 hour. Batik’s dye wastewater was received from one of the batik craftsmen in Jambi City. The sample was then diluted to 90%.

The dye removal process was carried out by directly mixing 50 mL dye effluent and 5 g adsorbent for 1 hour and stirring evenly. After one hour, the sample was allowed to stand for 1 hour and then filtered with Whatman filter paper No. 42. The supernatant obtained was then analyzed to see the content of the dye. The research matrix shows the number of samples to be treated and the number of samples to be analyzed. The fixed variables that will be used are the amount of waste to be treated and the required stirring temperature. Stirring was carried out on a hotplate at a speed of 100 rpm and a constant temperature of 30 °C. The research matrix of batik waste treatment using POFA can be seen in Table 1.

### Table 1. Research matrix

<table>
<thead>
<tr>
<th>No</th>
<th>Adsorbent</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>POFA</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>Eggshells</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>Orange Peel</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>Alkaline POFA</td>
</tr>
<tr>
<td>5</td>
<td>E</td>
<td>Acidic POFA</td>
</tr>
</tbody>
</table>

The acidic and alkaline process modification of POFA is shown in Figure 1. The overall dye removal treatment is depicted in Figure 2.

The analysis of POFA characteristics was conducted by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analysis to examine POFA’s mineral content, its chemical bond and its utilisation potential. POFA chemical bond was predicted through FTIR graph reading (Yadav, 2005). Brunauer-Emmett-Teller (BET) analysis was conducted on POFA, alkaline POFA and acidic POFA to analyse the surface area, pore size and pore volume of the adsorbent.
The sample was analysed using UV-Vis Spectrophotometer to see the dye content based on SNI 6989.80:2011 (National Standardization Agency, 2011). The adsorption capacity of batik effluent’s dye by POFA, eggshells, orange peels and modified POFA were calculated using equation 1. The removal efficiency of each metal was calculated using equation 2. The adsorption capacity is needed to calculate the maximum adsorption limit that the adsorbent can do. Dye removal efficiency is needed to test the ability of the adsorbent in its effectiveness in removing dyes (Aprianti et al., 2017; Gusain et al., 2020). Langmuir isotherm and Freundlich were used to analyse dissolved substance data between adsorbent and solution (Temesgen et al., 2018; Zeng et al., 2020).

\[
q_e = \left(\frac{e_o - e_f}{m}\right)V
\]

(1)

Dye Removal Efficiency = \left(\frac{e_o - e_f}{e_o}\right) \times 100

(2)

where :

\(q_e\) (mg/g) = adsorption capacity,

\(C_o\) (mg/L) = the initial dye content in the solution

\(C_e\) (mg/L) = the final dye content in the solution

\(V\) (L) = Batik effluent’s volume

\(m\) (g) = adsorbent mass

Results and Discussion

According to XRD analysis presented in Figure 3, it is known that raw POFA contains 47.4% SiO\(_2\), 43.1% CaCO\(_3\), and 9.5 Ca(OH)\(_2\). Other than POFA, according to the research of Hasan et al. (2019), eggshells mostly contain CaCO\(_3\). Calcium content has an important role that is considered able to increase absorption capability (Dai et al., 2018).

Both combinations enrich the calcium content of the adsorbent; this is the reason why activation by utilizing eggshells could increase adsorption capacity and batik’s dye removal efficiency. POFA chemical bond is shown in Figure 4. The interpretation result is as follows: the band 3642.81 cm\(^{-1}\) indicated the Free O–H group, the band 3439.07 cm\(^{-1}\) indicated intermolecularly H-bonded O–H, the band 2515.97 cm\(^{-1}\) indicated Intramolecularly H-bonded O–H of the chelate type and as found in carboxylic acids, the band 1111.68 cm\(^{-1}\) indicate C–O stretching, \(\rightarrow\)C–OH, and the band 877.56 cm\(^{-1}\), 791.62 cm\(^{-1}\), 713.29 cm\(^{-1}\) indicate C–H out-of-plane deformation with conjugation shifts the band towards 990 cm\(^{-1}\). The BET analysis result is shown in Table 2. POFA surface area becomes smaller when modified with acid. Modification by utilising acid reduces 25% of the surface area, and modification by utilising alkali reduces surface area up to 56%. Pore volume was also reduced by acid or alkali addition. Acid treatment reduces pore volume by up to 41%, and alkali treatment reduces pore volume by up to 61%. Likewise, to pore size, either acid or alkali modification causes pore size reduction. Acid treatment reduces pore size by up to 21%, while alkali
treatment only reduces pore size by up to 12%. BET profile described in Figure 5 shows the amount of adsorption compared to relatively pressure. According to Figure 5, it can be known that the wider the surface, the higher the adsorption. However, in this research, this occurrence does not apply because the research result shows that the best dye adsorption is in alkaline POFA adsorbent, which has a smaller surface area. This confirms that batik dye adsorption occurrence works chemically rather than physically.

![Figure 3. XRD analysis of POFA.](image)

![Figure 4. FTIR analysis of POFA.](image)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POFA</td>
<td>131.534</td>
<td>0.16738</td>
<td>2.54511</td>
</tr>
<tr>
<td>Acidic POFA</td>
<td>98.4695</td>
<td>0.098498</td>
<td>2.00059</td>
</tr>
<tr>
<td>Alkaline POFA</td>
<td>57.7528</td>
<td>0.064579</td>
<td>2.23638</td>
</tr>
</tbody>
</table>
Dyes treatment certainly has a special treatment because the intensity of the dye concentration is strongly influenced by the adsorbent, so the important step of the raw material preparation stage is the washing stage (Nguyen and Juang, 2019). Figure 6 shows the density order of adsorbent washing results are orange peel, POFA and eggshells. The concentration of the washing results would result in the inclusion of the concentration in the dye being tested; thus, the results of the study would not be effective. The washing was carried out until the washing water was clear, as shown in Figure 7. In general, chemical substances are required for activation; for example, sodium hydroxide is required to activate alkaline and hydrochloric acid to activate acid. A recent research work stated that the use of compounds in nature could replace the role of chemicals (Hasan et al., 2019); hence researchers tried to apply them in their study. Pictures of each type of adsorbent produced are shown in Figure 8.

![Figure 5. BET Profile of POFA (a), Acidic POFA (b), Alkaline POFA (c).](image)

### Table 3. Experimental result tabulation.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Dye Content (Pt.Co)</th>
<th>Dye Removal Efficiency (%)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Quality Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>28472.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>32906.40</td>
<td>-15.571</td>
<td>-44.335</td>
<td>200</td>
</tr>
<tr>
<td>B</td>
<td>29950.74</td>
<td>-5.190</td>
<td>-14.778</td>
<td>200</td>
</tr>
<tr>
<td>C</td>
<td>24039.41</td>
<td>15.571</td>
<td>44.335</td>
<td>200</td>
</tr>
<tr>
<td>D</td>
<td>22192.12</td>
<td>22.059</td>
<td>62.808</td>
<td>200</td>
</tr>
<tr>
<td>E</td>
<td>25517.24</td>
<td>10.31</td>
<td>29.557</td>
<td>200</td>
</tr>
</tbody>
</table>
The test results of batik’s dye after treatment, adsorption capacity and calculation of dye removal efficiency are shown in Table 3. Based on Table 3, it is known that there is a decrease in color levels in Pt.C. scale.

According to research data, POFA utilisation and non-modification of eggshells is not effective in reducing batik’s dye level, indicated by an increase in color level after the adsorption process. Directly utilising orange peel able to reduce color level, even so with acid as well as alkali modified POFA utilisation. The optimum adsorption capacity and dye removal efficiency were shown in sample D using alkaline POFA. Sample D result is in line with Stawinski's research, which states that alkaline activation is better than acidic activation of the dye removal (Stawiński et al., 2017).

Obtaining parameters from Langmuir and Freundlich Isotherm model provides important information about the adsorption mechanism and the nature of the adsorbent surface. Langmuir adsorption parameter was determined by changing the Langmuir equation (3) to linear form, as shown in equation (4).

$$q_e = \frac{C_0 q_m}{1 + C_0 K_L} \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{q_L} + \frac{1}{q_m K_L C_0} \tag{4}$$

$q_L$ and $K_L$ values have been calculated from intercept, and each $1/q_e$ Vs $1/C_e$ Langmuir plot slant. The coefficient correlation value ($R^2$) was calculated from both models. Langmuir Isotherm has been declared in not dimensions constant called separation factor ($R_L$) and called in the equation (5).

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

Where $K_L$ is Langmuir, a constant that corresponds to adsorption energy (L/mg), and $C_0$ is a starting color substance (mg/L). $R_L$ value obtained from this research is 0.000035, between 0 and 1 and shows favourability of adsorption. Langmuir model equation (3) is suitable for single-layer adsorption that happens on a homogenous surface (Zeng et al., 2020).

Where $R_L$ value is tabulated in Table 4 to identify favorability adsorption (Temesgen et al., 2018). $q_L$ and $K_L$ values have been calculated from the intercept and plot slant of each $1/q_e$ particle $1/C_e$ Langmuir. Langmuir Isotherm to batik waste color remover in this research is shown in Figure 9. Freundlich adsorption isotherm applications have been analyzed with the same collection of experimental data and served in Figure 10. The Freundlich model is commonly used to describe multi-layer adsorption and is suitable for adsorbents with the heterogenic surface.
Figure 9. Langmuir and Freundlich Isotherm.

Figure 10. Thermodynamic Prediction’s data.

Table 4. Langmuir and Freundlich isotherm model for Batik’s dye adsorption over POFA and modified POFA.

<table>
<thead>
<tr>
<th>Isotherm Models</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$K_L$</td>
<td>1.1114</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.000035</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.56</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>1.972</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.928</td>
</tr>
</tbody>
</table>

Freundlich adsorption parameters have been determined by changing Langmuir equation (6) to linear form as in equation (7).

\[
q_e = K_F C_e^{1/n} \quad (6)
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)
\]

where $K_F$ and $1/n$ are a constant related to adsorption capacity and adsorption intensity.

Freundlich isotherm model between log (qe) versus log (Ce), and each parameter value is mentioned in Table 4. Less than 1 $1/n$ value means that a reaction could easily occur and more than 2 of $1/n$ value means that reaction is not hard to occur, showing that reaction is hard to be conducted (Zeng et al., 2020). $1/n$ value obtained in this research is 21.12 shows that adsorption
is hard to be conducted. The likeliness model is characterized in the form of a magnitude exponent (n). If the sorption intensity value (n) is in the range of 2 to 10 represents good, 1 to 2 is quite hard, and less than 1 shows bad adsorption characteristics (Temesgen et al., 2018). Other literature stated that the n=1 value shows that adsorption occurs linearly. If value n<1, then the adsorption process is chemical adsorption and if n>1, then the adsorption process is physical adsorption (Siregar et al., 2022). n value obtained from this research is 0.047 shows not good enough adsorption capability because the adsorption process occurs chemically.

The research result presented in Table 4 shows a higher Freundlich R² coefficient value compared to the regression coefficient value (R²) from the Langmuir model. This shows that batik waste adsorption by utilizing POFA and modified POFA is more suitable for the Freundlich model, seen from R² value is closer to 1. It is clear that experiment data for batik’s dye is more suitable for with Freundlich model, indicating that multi-layer POFA adsorbs with the heterogenic surface.

Thermodynamics parameter calculation is conducted with Vant Hoff equations (8) and (9). Enthalpy value and entropy value could be calculated as slant value and intercept value 1/T to in Qe/Ce as shown in equation (8) (Rahmadan et al. 2021).

$$\ln \frac{Q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$  \hspace{1cm} (8)

The value of Gibb’s free energy changes (∆G) is calculated from enthalpy changes (∆H) and entropy changes (∆S) shown in equation (9).

$$\Delta G = \Delta H - T \Delta S$$  \hspace{1cm} (9)

Table 5. Thermodynamic parameters for the adsorption of batik’s dye.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>∆H (J/mol)</th>
<th>∆S (J/mol.K)</th>
<th>∆G (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>0.121963</td>
<td>0.000387</td>
<td>-0.00469</td>
</tr>
<tr>
<td>323.15</td>
<td>-0.01077</td>
<td>-0.01851</td>
<td></td>
</tr>
<tr>
<td>343.15</td>
<td>-0.00304</td>
<td>-0.01077</td>
<td></td>
</tr>
<tr>
<td>363.15</td>
<td>-0.01851</td>
<td>-0.01077</td>
<td></td>
</tr>
</tbody>
</table>

Thermodynamic prediction data from batik’s dye adsorption is shown in Figure 10, and the thermodynamics parameter is tabulated in Table 5. Enthalpy change values (∆H) and entropy change values (∆G) that show positive values mean that the adsorption process proceeds endothermically (Li et al., 2020), where the adsorption process occurs followed by heat taking from the environment to the system. According to (Rakić et al., 2015), the endothermic process means that adsorbent species replace more than one water molecule for adsorption. Gibb’s free energy changes (∆G) negative value for almost all temperatures shows that the adsorption process in this work is spontaneous and feasible to be conducted (Rajoriya et al., 2021).

Conclusion

Palm Oil Fuel Ash (POFA) is a potential adsorbent for reducing batik’s dye content with up to 22% removal efficiency. The adsorption capacity of batik’s dye by using POFA reaches up to 62 mg/g. According to the isotherm model, batik’s dye adsorption by utilizing POFA and its modification match with the Freundlich isotherm that shows multi-layer adsorption on a heterogeneous surface. In general, it can be concluded that POFA could not directly be used to adsorb batik’s dye but should be modified through acid and alkaline treatment to be able to adsorb or reduce dyes from batik wastewater. Eggshell as base activation of POFA is the best way to improve the adsorption capacity and removal efficiency. Further research is needed on each variable to improve removal efficiency and adsorption capacity. According to the Freundlich model, isotherm adsorption occurs at multi-layer and heterogeneous surfaces. Based on a thermodynamics study, the adsorption process occurs endothermically and spontaneously.

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