Removal of Reactive Orange 16 Dye from Aqueous Solution by Using Modified Kenaf Core Fiber

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1. Introduction

Effluents from the textile industry and many other industries contain various kinds of synthetic dyestuffs, and there has been growing interest in regard to decolonization of these effluents in the last few years [1]. Removing the color from wastewater is often more significant than other colorless organic substances because the presence of small amounts of dyes (below 1 ppm) is distinctly visible and influences the water environment considerably [2].

Most dyes are nonbiodegradable in nature, which is stable to light and oxidation. Therefore, the degradation of dyes in wastewater either traditional biological process or chemical process has not been very effective [3].

Many conventional methods have been used for removal of dye pollution from industrial wastewaters, including chemical and physical methods. But these methods are often ineffective in the removal of dyes, highly costly, and less adaptable to dye-loaded wastewaters [4]. Adsorption process has been a choice because it allows the removal of different types of dyes and the method is simple, effective, and easy operation [5]. The significant economic cost has increased the concentration of researchers in search of less costly materials and economic as adsorbents for application in wastewater treatment [6–8]. Agricultural products from renewable resource which are less expensive and biodegradable and environmentally friendly [9–12] have been used as an alternative to removing dyes from wastewater [13–20]. But to increase the usability and make agricultural by-products more efficient and reduce the numerous problems when they are directly used, they lower adsorption capacity for anionic pollutants [21, 22]. It is necessary to treat or modify these materials prior to application in adsorption processes [23–26]. Table 1 shows some of the modified agricultural solid wastes.

One of the important agricultural materials is kenaf (Hibiscus cannabinus), which is an ancient crop and has a long history of being planted and used by human beings. It
is one of the best alternative crops that provide a good source of cellulose. Due to its environmental and biodegradability compatibility, the usage of kenaf has increased [27]. Malaysia is in the process of developing kenaf cultivation and processing. Nevertheless, it was only in 2010 that Malaysian government seriously accepted kenaf as the Malaysian seventh commodity, through the setting up of the National Kenaf and Tobacco Board, 2013. The production in Malaysia is estimated at 3,000 tons to 10,000 tons of kenaf fiber annually. Kenaf is annually cultivated from its seeds for the fibers. In this paper, the kenaf was modified using NaOH (as shown in the next paragraphs). In this research, the objective is to evaluate the adsorption potential of modified kenaf for the removal of anionic dyes. The effects of different factors on the adsorption such as pH, contact time, and initial dye concentration are studied in batch method. The kinetic data and equilibrium of the adsorption are processed to comprehend the adsorption.

### 2. Materials and Methods

#### 2.1. Preparation of Modified Kenaf Core Fibers (MKCF)

The kenaf fibers (core chips) were ground using pulverization, then stainless steel sieves with sizes 1 mm and 0.25 mm were used to obtain kenaf core fibers in size range from 0.25 mm to 1 mm.

Kenaf core fibers modification consists of alkali treatment; this kind of treatment is very important to make many pores on the kenaf surface-wide. There are three steps to modified kenaf core fibers which are cleaning, mercerization, and quaternization. For a cleaning process, the kenaf core fibers were washed with distilled water several times and then dried in the oven at a temperature of at 50°C for 24 hours. Then the clean kenaf core fibers were mercerized by soaking them in 20% weight of NaOH solution for 24 hours. It is important to let kenaf fibers swell enough. Mercerization is a treatment of fibers with an alkali. The alkali causes the fibers walls to swell and become active, thus increasing in strength, luster, and absorbency. Then mercerized kenaf fibers were rinsed with distilled water and dried at 50°C. For quaternization process, each gram of kenaf core fibers was reacted with a solution consisting of 1.5 g: 6.67 mL: 2.5 mL of NaOH, 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHMAC), and distilled water, respectively. Hence, the solution added to each gram of kenaf core fibers contained 37 mmol of NaOH and 62.5 mmol of (3-chloro-2-hydroxypropyl)trimethyl ammonium chloride (CHMAC). The mixture was kept in sealed container at room temperature. After 24 hours, 0.2% acetic acid solution was added to the blend to stop the reaction followed by washing with distilled water until pH (7-8) which is a neutral condition. Then modified kenaf core fibers were dried at 50°C and stored in a dry place.

#### 2.2. Preparation of Stock Solution

The stock solution was prepared by dissolving (1) gram from the dye in 1 L of distilled water in the volumetric flask. The mixture was kept in storage bottle with screw cap at room temperature for 24 hours to make sure that the stock solution becomes homogeneous and keeps away from light to reduce the external influences. The experimental solution was prepared by diluting the specified volume of the stock solution to get the desired concentration. The general characteristics of reactive orange 16 dye are shown in Table 2. In this study, the decolorization of the aqueous solution was studied in batch mode.

For absorbance measurements, a spectrophotometer UV-1800 (SHIMADZU) was employed. The maximum wavelength for RO16 dye is 493 nm. Concentrations during experimental work were determined from a standard calibration curve. The dye solution was filtered through filter paper to separate the adsorbent prior to running the UV spectrophotometer analysis. The amount of adsorbent adsorbed at equilibrium

### Table 1: Previous studies of uptake of dyes using adsorbents based on agricultural solid wastes.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Dyes</th>
<th>$q_{\text{max}}$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almond shell activated carbon at 750°C</td>
<td>Methylene blue</td>
<td>1.33</td>
<td>[37]</td>
</tr>
<tr>
<td>Peanut hull</td>
<td>Sunset yellow</td>
<td>13.99</td>
<td>[38]</td>
</tr>
<tr>
<td>Waste apricot activated carbon</td>
<td>Methylene blue</td>
<td>102.04</td>
<td>[39]</td>
</tr>
<tr>
<td>Treated coconut male flowers carbons</td>
<td>Crystal violet</td>
<td>60.42</td>
<td>[40]</td>
</tr>
<tr>
<td>Jute fiber</td>
<td>Eosin yellow</td>
<td>31.489</td>
<td>[41]</td>
</tr>
<tr>
<td>Wheat bran</td>
<td>Malachite green</td>
<td>66.57</td>
<td>[33]</td>
</tr>
<tr>
<td>Coconut coir pith</td>
<td>Direct Red 12B</td>
<td>76.3</td>
<td>[42]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Indigo carmine</td>
<td>29.2799</td>
<td>[43]</td>
</tr>
<tr>
<td>Neem sawdust</td>
<td>Malachite green</td>
<td>4.35</td>
<td>[44]</td>
</tr>
<tr>
<td>Thespesia populnea pods activated carbon</td>
<td>Orange G dye</td>
<td>9.129</td>
<td>[45]</td>
</tr>
<tr>
<td>Kenaf fiber char</td>
<td>Methylene blue</td>
<td>18.18</td>
<td>[46]</td>
</tr>
<tr>
<td>Quaternized flax shive</td>
<td>Reactive red 22B</td>
<td>190.0</td>
<td>[47]</td>
</tr>
<tr>
<td>Modified kenaf core fibers</td>
<td>Reactive orange</td>
<td>416.86</td>
<td>This work</td>
</tr>
</tbody>
</table>

### Table 2: General properties of reactive orange 16.

<table>
<thead>
<tr>
<th>Name of the commercial dye</th>
<th>Reactive orange 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>493 nm</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>617.54</td>
</tr>
<tr>
<td>Dye content</td>
<td>$\geq$70%</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C$<em>{20}$H$</em>{17}$N$_3$Na$<em>3$O$</em>{11}$S$_3$</td>
</tr>
</tbody>
</table>
condition, $q_e$ (mg/g), and the percentage of removal efficiency ($R\%$) were calculated using (1) and (2), respectively. One has

$$q_e = (C_o - C_e) \times \frac{V}{W} \quad (1)$$

$$R(\%) = \left( \frac{C_o - C_e}{C_o} \right) \times 100, \quad (2)$$

where $C_o$ and $C_e$ are initial dye concentrations and final dye concentrations (mg/L), respectively, $V$ is the volume of solution (L), and $W$ is the weight of MKCF (g).

3. Results and Discussion

3.1. Dosage Effect. The effect of adsorbent dose was studied in a batch method using 250 mL Erlenmeyer flasks. In each flask, the volume of dye was 100 mL. All flasks were sealed properly using aluminum foil to prevent leakage and evaporation. The shaking rate was set at 150 rpm at the temperature of 30°C, with the contact time of 24 hours. The initial dye concentration of RO16 in this solution was 100 mg/L and the dosages of MKCF were 0.02, 0.04, 0.06, 0.08, 0.1, 0.12, 0.14, 0.16, and 0.2 g/100 mL, respectively. Based on Figure 1, it was observed that the percentage of dye removal increased with respect to MKCF dosage until 1 g/L and then further increase in MKCF dosage resulting in the constant percentage of dye removal due saturation point. MKCF could remove 97.25% for RO16 dye with a dosage of 1 g/L. Therefore, the adsorbent dosage was optimized at 1 g/L of MKCF.

3.2. pH Effect. pH has the significant impact on absorption process and affected absorption capacity, dye solubility [28], solution chemistry, and a surface of absorbent pore [29]. The effect of pH on the adsorption capability was investigated between pH 2.0 and 12 at 30°C (Figure 2). The percentage removal of RO16 increased from 95% to 98.12% with an increase of the pH from 2 to 8. Adsorption rate did not vary significantly and the removal percentage was steady around 98%. The authors attributed this behavior to the availability of a considerable number of active locations on the adsorbent surface and related the solute uptake to the active sites and also to the chemistry of the solute in the solution. The neutral pH system showed good adsorption behavior for the RO16 dye solution.

3.3. Effects of Initial Dye Concentration and Contact Time. Equilibrium time is one of the important aspects in the design of water and wastewater treatment systems because it impacts the size of the reactor and thereby economizes the treatment plant [30].

The effect of contact time on the rate of removal of RO16 dye is shown in Figure 3. The percentage removal of dye increased with an increase in contact time and reached to equilibrium after 110 min for initial dye concentrations (5, 25, 50, and 100 mg/L). The shaking rate was set at 150 rpm, pH 6.5, and a temperature of 30°C used in this study.

4. Adsorption Isotherm

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. Several isotherm equations are available and two important isotherms are selected in this study, which are, namely, the Langmuir and Freundlich models.

An assumption has been made on Langmuir isotherm that adsorption on a homogenous surface containing site will occur with equal energy that is equally available for adsorption [31]. As Langmuir isotherm is monolayer isotherm, there is no transmigration of adsorbate on the surface plane [32]. The Langmuir equation can be described by the linearized form given by

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}, \quad (3)$$
Table 3: Langmuir and Freundlich constants for adsorption of RO16 on MKCF.

<table>
<thead>
<tr>
<th>Name of dye</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>$b$ (L/mg)</td>
</tr>
<tr>
<td>RO16</td>
<td>416.686</td>
<td>0.1244</td>
</tr>
</tbody>
</table>

where $C_e$ is the equilibrium concentration (mg/L), $q_e$ is the equilibrium adsorption capacity (mg/g), and $b$ is the Langmuir constant or rate of adsorption (L/mg or L/mole). A straight line was obtained when $C_e/q_e$ was plotted against $C_e$ and $q_{\text{max}}$ and $b$ could be calculated from the slope and intercepts, respectively. The plotted data is shown in Figures 4 and 5. The essential feature of the Langmuir isotherm can be expressed by means of dimensionless constant separation factor which is calculated using

$$R_L = \frac{1}{1 + b \cdot C_o},$$  \hspace{1cm} (4)$$

where $b$ denotes the Langmuir constant and $C_o$ denotes the initial dye concentration [33].

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems. The Freundlich isotherm is given in logarithmic form as shown in (5) [34]. Consider

$$\log q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e,$$  \hspace{1cm} (5)$$

where $K_F$ is the Freundlich constant and $n$ is the adsorption intensity. $1/n$ is the empirical parameter that is related to the adsorption intensity and this indicated whether the adsorption is favorable or not [35]. The values of $K_F$ and $n$ can be calculated directly, from the slope and intercept that were obtained from the straight line when $\log q_e$ was plotted against $\log C_e$ (Figure 5).

Langmuir and Freundlich constants and correlation coefficients were listed in Table 3. From the table, it can be shown that the values of $q_{\text{max}}$ are 416.686 mg/g for RO16. The correlation coefficients ($R^2$) were found to be 0.9088 and 0.9924 for Langmuir and Freundlich isotherm, respectively. This confirmed that the Freundlich isotherm represented the adsorption of RO16 on MKCF. It can be concluded that the adsorption process for RO16 is heterogeneous.

5. Kinetics Study

Adsorption kinetics can measure the efficiency of adsorption process by several applications of kinetic modeling. To evaluate the rate of adsorption of modifying kenaf core fiber, the data in Figure 4 were used with pseudo-first-order and pseudo-second-order kinetic models. The formula of pseudo-first-order equation is shown in (6) [36]. Consider

$$\log (q_e - q_t) = \log q_e - \left( \frac{K_1}{2.303} \right) \cdot t,$$  \hspace{1cm} (6)$$

where $q_e$ indicates the amount of MKCF adsorbed (mg/g) at equilibrium, while $q_t$ means the amount of MKCF adsorbed at a time (min) and $K_1$ is the rate constant of adsorption process of the pseudo-first-order (min$^{-1}$). The values of $K_1$ and $q_{\text{cal}}$ were calculated from the slopes and intercepts, respectively, of the plots of $\log (q_e - q_t)$ versus $t$ (Figure 6) and are presented in Table 4. The calculated $q_e$ values obtained from this kinetic model did not satisfy the...

Figure 4: Langmuir adsorption isotherm for RO16 onto MKCF at 30°C.

Figure 5: Freundlich adsorption isotherm for RO16 onto MKCF at 30°C.

Figure 6: Kinetic study of adsorption of RO16 on MKCF by using pseudo-first-order kinetic model ($C_o = 100$ mg/L).
### Table 4: Parameters and correlation coefficient ($R^2$) of pseudo-first- and pseudo-second-order kinetic model for adsorption of RO16 by MKCF.

<table>
<thead>
<tr>
<th>Name of dye</th>
<th>$q_{exp}$ (mg/g)</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{cal}$</td>
<td>$K_1$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>RO16</td>
<td>94.73</td>
<td>26.7</td>
<td>0.0309</td>
</tr>
</tbody>
</table>

![Figure 7: Kinetic study for adsorption of RO16 on MKCF by using pseudo-second-order kinetic model ($C_0 = 100$ mg/L).](image)

The correlation coefficient value for pseudo-second-order ($R^2$) was 0.9924, which indicates that kinetic adsorption fitted well with pseudo-second-order model. Closer values between calculated adsorption capacities ($q_{cal}$) and the experimental adsorption capacities ($q_{exp}$) were also observed.

### 6. Conclusion

Until this moment, research is still standing at the low material cost and high ability removal; through qualitative study, we conclude that MKCF has a good ability to remove dye from aqueous solutions compared with other materials, and environmentally friendly. Moreover, MKCF can be used as alternatives to activated carbons reported in earlier studies and there are no secondary harmful effects from MKCF after removal dyes. In this research, RO16 dye was used and the maximum percentage removal was 97.24%; it is a high percentage removal compared with other materials studied in other researches. The maximum adsorption capacity was 416.86 mg/g; it is a good adsorption capacity for economic cost. The equilibrium data were analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients were determined from graphs of their linear equations. Both Langmuir and Freundlich isotherms were demonstrated to provide a meaningful correlation for the adsorption of reactive dye, respectively.

### Competing Interests

The authors declare that they have no competing interests.

### References


