Palm Shell-based Activated Carbon for Removing Reactive Black 5 Dye: Equilibrium and Kinetics Studies

Wei Tze Mook, a Mohamed Kheireddine Aroua, a,* and Małgorzata Szlachta b

Activated carbon derived from biomass waste, namely palm shell, was evaluated as a potential adsorbent for the removal of Reactive Black 5 dye (RB5) from an aqueous solution. This work focused on the equilibrium isotherms and the kinetics of the adsorption process. Batch adsorption tests were conducted to determine the effects of various parameters, such as contact time, RB5 concentration, adsorbent dose, temperature, and initial solution pH, on the treatment performance. The adsorption capacity of the adsorbent used in the study was higher in an acidic medium. The Langmuir model provided the best fit for the obtained equilibrium isotherm data, while the adsorption kinetics was best represented by the pseudo-first-order model. RB5 adsorption was endothermic in nature, with an activation energy of 12.6 kJ/mol. The maximum adsorption capacity of the adsorbent was 25.1 mg/g at pH 2. Palm shell-based activated carbon is shown to have great potential in the adsorption of RB5 from aqueous solution.

Keywords: Adsorption; Palm shell; Reactive Black 5; Isotherms; Kinetics

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INTRODUCTION

Dyes are widely used in a variety of industries, such as textiles, paint, printing ink, and food technology. The use of reactive dyes in the textile industry is increasing, as their vivid colors and the reactive groups easily attach to textile fibers (Hassan et al. 2009). Hence, reactive dyes represent 20% to 30% of the total dye market (Dojčinović et al. 2012). However, a significant amount of residual dye has been found in wastewater produced from the rinsing process in the dyeing of material. Excessive amounts of reactive dyes discharged into receiving bodies are dangerous and threaten aquatic environments and human health (Sathian et al. 2014). Reactive Black 5 dye (RB5) has been utilized as a model dye because of its recalcitrant nature and the fact that it contributes to 50% of the total world demand for reactive dyes (Schumacher 2012).

A variety of methods have been used to treat RB5 solutions, such as coagulation (Furlan et al. 2010), adsorption (Kim et al. 2015), photodegradation (Laohaprapanon et al. 2015), and biological treatment (Vyrides et al. 2014). Among these available methods, adsorption is one of the most recognized to remove dyes because of its low cost, easy operation, high effectiveness, and the absence of unwanted by-products except for the dye-laden adsorbent material itself.

The conversion of agricultural wastes into adsorbent for wastewater treatment has been intensively investigated because it is environmentally friendly and has the potential to reduce the cost of waste disposal (Fernandez et al. 2014). Activated carbon produced
from walnut (Heibati et al. 2014), carob (Güzel et al. 2015) and bamboo (Ahmad and Hameed 2010; Ip et al. 2010) have been successfully applied in RB5 adsorption.

Palm trees are planted on a large scale in Indonesia and Malaysia, contributing approximately 85% of the world’s palm oil. Other countries where palm oil is produced include Thailand, Columbia, Nigeria, Papua New Guinea, and Ecuador. In Malaysia, approximately 77% of agricultural land is used for palm oil plantations (Palm Oil 2014). The waste, such as palm shell from palm fruit processing, is a pressing environmental issue, as it is burned in the open air or is used as boiler fuel to produce steam in the mill (Issabayeva et al. 2006). Palm shell converted to activated carbon could reduce this abundant waste and be beneficial for treatment costs. To our best knowledge, the adsorptive removal of RB5 from aqueous solution using palm shell-based activated carbon as adsorbent was reported only by Nourouzi et al. (2009). Although those authors reported successful removal of RB5, the effects of contact time, temperature, solution pH, and adsorbent dose on RB5 adsorption efficiency were not addressed in their work.

The objective of our work was to evaluate the potential of palm shell-based activated carbon for the removal of RB5 from an aqueous solution. Special attention was given to the evaluation of the influence of various parameters including contact time, solution pH, temperature, and adsorbent dose on RB5 removal. The equilibrium isotherms and adsorption kinetics modelling were studied, as they are important for the design of treatment processes.

EXPERIMENTAL

Materials and Analytical Methods

Reactive Black 5 dye (RB5) was purchased from Sigma-Aldrich, Malaysia and used as the adsorbate in this study. The dye solutions were freshly prepared using distilled water, and the pH was adjusted by 0.1 M H2SO4 or NaOH. Commercial granular palm shell activated carbon was supplied by Bravo Green Sdn Bhd, Sarawak. The adsorbent was crushed and sieved to a size of 350 to 710 μm and washed with distilled water several times to remove dust and suspended solids. The sieved activated carbon was then dried in an oven at 105 °C for 24 h to remove the moisture.

Prior to analysis, all samples collected during the experiments were filtered through a 0.22-μm filter membrane to remove the carbon fines that may affect the analysis process. The dye concentration was determined by Lambda 35 UV-Vis spectrophotometer (PerkinElmer, U.S.A) at a wavelength of 595 nm.

Characterization of Activated Carbon

The adsorbent surface was scanned by ultra-high resolution scanning electron microscopy (SU8000, Hitachi, Japan) at an accelerating voltage of 5000 V. The particle size distribution was determined using a Malvern 2000, United Kingdom.

Adsorption and desorption measurements were carried out by cold nitrogen gas at -196 °C on a Micrometrics ASAP 2020, United States. The average pore diameter was calculated using the Barrett-Joyner-Halenda (BJH) method, which was applied to the desorption isotherm.
Adsorption Equilibrium Isotherm Experiments

Adsorption isotherm tests were carried out using capped vials containing 30 mL of RB5 solution with various initial concentrations in the range of 20 to 140 mg/L and 0.09 g of activated carbon. Prepared samples were agitated in a temperature-controlled orbital shaker at 28 °C for 96 h to reach the equilibrium state. The experiments were performed at a constant pH of 2, 6 (original pH of the dye), or 10.

The Langmuir and Freundlich models were employed to estimate isotherm parameters, as expressed in Eqs. 1 and 2. Statistica software (StatSoft, Dell) was used to determine the parameters of the nonlinear isotherm models,

\[
q_e = \frac{q_m b C_e}{1 + b C_e} \quad (1)
\]

\[
q_e = K C_e^\frac{1}{n} \quad (2)
\]

where \(q_e\) is the equilibrium adsorption capacity (mg/g); \(q_m\) is the maximum monolayer adsorption capacity (mg/g); \(b\) is the Langmuir constant, which is related to the binding energy (L/mg); \(C_e\) is the equilibrium concentration of the adsorbate (mg/L); \(K\) is the Freundlich constant corresponding to adsorption capacity (mg/g)(L/mg); and \(n\) is the measurement of favorable adsorption.

The RB5 removal efficiency and adsorption capacity (\(q_{\text{exp}}\)) were calculated as follows:

\[
\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \cdot 100\% \quad \text{(3)}
\]

\[
q_{\text{exp}} = \frac{(C_0 - C_e)V}{m} \quad \text{(4)}
\]

where \(C_0\) and \(C_t\) denote the concentration of RB5 at time \(t = 0\) and \(t\), respectively; \(C_e\) is the equilibrium concentration of adsorbate (mg/L); \(V\) is the volume of the solution (L); and \(m\) is the mass of dry adsorbent used (g).

Adsorption Kinetics Studies

Adsorption kinetic tests were carried out at various RB5 concentrations (20, 40, and 60 mg/L) and temperatures (18, 28, and 38 °C) for 5 h. These experiments were conducted at initial solution pH 6 and adsorbent dose of 3 g/L, using a magnetic stirrer set at 250 rpm. A temperature-controlled water bath was used to maintain a constant temperature throughout the process.

The pseudo-first-order kinetic model (Eq. 5), the pseudo-second-order kinetic model (Eq. 6), and the Elovich model (Eq. 7) were applied to investigate the adsorption kinetics of RB5 onto activated carbon. The diffusion mechanism was identified by the intra-particle diffusion model (Eq. 8) proposed by Weber and Morris (Bulut and Aydin 2006; Jiwalak et al. 2010). All the adsorption kinetic parameters were estimated using a non-linear regression by Statsoft Statistica software,

\[
q = q_e (1 - e^{-k_1 t}) \quad \text{(5)}
\]

\[
q = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t} \quad \text{(6)}
\]
\[ q = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \]  
(7)

\[ q = k_{\text{ind}} t^{0.5} + I \]  
(8)

where \( q \) and \( q_e \) are the amount of RB5 adsorbed at time \( t \) and at equilibrium (mg/g), respectively; \( t \) is the contact time (min); \( k_1 \) is the rate constant of pseudo-first-order adsorption (min\(^{-1}\)); \( k_2 \) is the rate constant of pseudo-second-order adsorption (g/mg min); \( b \) is the desorption constant (g/mg); \( a \) is the initial adsorption rate (mg/g min); \( k_{\text{ind}} \) is the intra-particle diffusion rate constant (mg/g min\(^{0.5}\)); and \( I \) is the constant of boundary layer thickness (mg/g).

**Effect of Variables on Adsorption**

To determine the influence of solution pH and adsorbent dose on adsorption efficiency, the set of tests were conducted using an orbital shaker at 28 °C for 96 h. The effect of pH on RB5 adsorption was investigated at a fixed adsorbent dose of 3 g/L and dye concentration of 40 mg/L. The pH range was varied from 2 to 11 and kept constant throughout the experiments.

The influence of adsorbent dose on RB5 adsorption was conducted with various adsorbtion doses ranging from 2 to 10 g/L. The concentration of RB5 was 40 mg/L, and the pH solution was set at 6 and maintained throughout the tests.

**RESULTS AND DISCUSSION**

**Characteristics of Palm Shell-based Activated Carbon**

The activated carbon used in this study is a highly porous material with a specific surface area of 759.78 m\(^2\)/g. Pores in various sizes in nanometers scale (micropores, mesopores) were identified by the analysis of nitrogen gas adsorption isotherm. The volume of micropores (< 2 nm) was 0.299 cm\(^3\)/g, which corresponds to 71% of the total volume of pores. The average pore diameter calculated using the BJH method was 4.96 nm. By means of scanning electron microscopy extrinsic large-size pores on the surface of activated carbon were also recognized. The distinct pores of micrometers in size are readily found on the surface, as shown in Fig. 1.

The properties of palm shell-based activated carbon are summarized in Table 1.

**Table 1. Properties of Palm Shell-based Activated Carbon**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brunauer, Emmett and Teller (BET) surface area (m(^2)/g)</td>
<td>759.78</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>4.96</td>
</tr>
<tr>
<td>Micro-pore volume (cm(^3)/g)</td>
<td>0.299</td>
</tr>
<tr>
<td>Meso-pore volume (cm(^3)/g)</td>
<td>0.122</td>
</tr>
<tr>
<td>Particle size (µm)</td>
<td>563.68</td>
</tr>
</tbody>
</table>
Equilibrium Isotherms

The adsorption isotherm describes the distribution of dye molecules between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. The Langmuir and Freundlich models were used to evaluate the equilibrium data, as shown in Fig. 2. The selection of the isotherm model is based on the highest value of the coefficient of determination, $R^2$. Each of the isotherm parameters was calculated and is expressed in Table 2.
The typical adsorption capacity ascended progressively to a plateau region at a higher equilibrium adsorbate concentration. The uptake of RB5 was highest at the lowest solution pH because of electrostatic integrations between the adsorbent surface and the dye molecules present in the solution (the RB5 pH-dependency is explained below).

The Langmuir model assumes monolayer adsorption onto an adsorbent surface containing a finite number of adsorption sites, with no transmigration of adsorbate in the plane surface (Desta 2013). The constant $b$ in the Langmuir isotherm model indicates the adsorption energy and strength of binding sites (Aljeboree et al. 2014). A higher $b$ value is the reason for a steeper isotherm, which indicates higher RB5-activated carbon bond stability.

On the other hand, the Freundlich isotherm is an empirical model describing the adsorption characteristics of a heterogeneous surface. The value of the parameter $n$ within the range of 1 to 10 represents a good adsorption. From Table 2, the magnitudes of $n$ were 2.938, 2.807, and 2.542 for solution pH values of 2, 6, and 10, respectively. These results indicate that the adsorption of RB5 onto palm shell-based activated carbon was favorable.

Moreover, the Langmuir isotherm model resulted in a higher $R^2$ value, suggesting that the model fit well with the adsorption data. This revealed that the accessible surfaces of palm shell-based activated carbon could be modeled as a monolayer occupancy of RB5 molecules in equivalent sites.

The essential features of the Langmuir isotherm parameter can be used to estimate the affinity of absorbate and absorbent in terms of dimensionless equilibrium parameters, $R_L$ (Eq. 9). The $R_L$ value determines if the Langmuir isotherm is either favorable ($0<R_L<1$), unfavorable ($R_L>1$), linear ($R_L=1$), or irreversible ($R_L=0$) (Data et al. 2012). The $R_L$ for pH 2, 6, and 10 was 0.060, 0.081, and 0.074, respectively, which affirms that the Langmuir isotherm model was favorable for RB5 adsorption onto palm shell-based activated carbon (see Eq. 9),

$$R_L = \frac{1}{1 + bC_0}$$

where $b$ is the Langmuir constant and $C_0$ is the initial dye concentration (mg/L).

In general, the amount of RB5 adsorbed by the material used in this study was comparable to adsorption capacities of other agricultural waste-based activated carbons, as shown in Table 3.

Analyzing the results obtained for the activated carbons made of the same waste material, it was found that the adsorption capacity of tested adsorbent was lower than this reported by Nourouzi et al. (2009). The lower adsorption of RB5 observed in the study may be related to differences in pore size distribution of palm shell-based activated carbons.

### Table 2. Langmuir and Freundlich Isotherm Model Parameters and Correlation Coefficients for RB5 Adsorption

<table>
<thead>
<tr>
<th>pH</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>$b$ (L/mg)</td>
</tr>
<tr>
<td>----</td>
<td>-------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>2</td>
<td>25.12</td>
<td>0.112</td>
</tr>
<tr>
<td>6</td>
<td>23.61</td>
<td>0.081</td>
</tr>
<tr>
<td>10</td>
<td>24.86</td>
<td>0.089</td>
</tr>
</tbody>
</table>
Table 3. Comparison of Adsorption Capacity of RB5 Adsorption by Various Agricultural Waste-based Activated Carbons

<table>
<thead>
<tr>
<th>Agricultural waste-based activated carbon</th>
<th>Adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walnut wood</td>
<td>19.34</td>
<td>Heibati et al. (2014)</td>
</tr>
<tr>
<td>Carob</td>
<td>36.90</td>
<td>Güzel et al. (2015)</td>
</tr>
<tr>
<td>Bamboo</td>
<td>39.02</td>
<td>Ahmad and Hameed (2010)</td>
</tr>
<tr>
<td>Bamboo</td>
<td>286</td>
<td>Ip et al. (2010)</td>
</tr>
<tr>
<td>Palm shell</td>
<td>40</td>
<td>Nourouzi et al. (2009)</td>
</tr>
<tr>
<td>Palm shell</td>
<td>25.12</td>
<td>This work</td>
</tr>
</tbody>
</table>

Adsorption Kinetics

Effect of contact time

Figure 3 depicts the experimental and modeled data of RB5 adsorption by palm shell-based activated carbon at various initial dye concentrations, i.e., 20, 40, and 60 mg/L. The adsorption of RB5 increased progressively with contact time. For the lowest dye concentration (20 mg/L), the adsorption achieved a plateau region within 4 h, which corresponds to a removal efficiency and adsorption capacity of 96.7% and 6.45 mg/g, respectively. In the case of 40 and 60 mg/L of RB5, dye removal was 76.4% and 64.9% after 5 h, respectively. This means that when a higher amount of dye is present in the solution, a longer time is required to reach the equilibrium state. The obtained data are in good agreement with the results presented by Osma et al. (2007) and Heibati et al. (2014), who used walnut wood and sunflower seed, respectively, for RB5 removal.

![Fig. 3. Kinetics for adsorption of RB5 by palm shell-based activated carbon at various dye concentrations and a constant temperature of 28 °C](image-url)
To evaluate the adsorption rate and reaction mechanisms, the kinetic experimental data were fitted with three models: the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, and the Elovich model. All calculated kinetic parameters are presented in Table 4.

The pseudo-first-order model showed the best fit to the kinetic data, as the highest \( R^2 \) values were obtained for each tested initial dye concentration. Moreover, the calculated \( (q_e) \) and experimental equilibrium adsorption capacities \( (q_{exp}) \) were in good agreement. This confirms that the pseudo-first-order model is sufficient to interpret the kinetics of RB5 adsorption onto palm shell-based activated carbon. The adsorption rate constant \( (k_1) \) was the highest \( (0.010 \text{ min}^{-1}) \) at a low initial concentration \( (20 \text{ mg/L}) \), as the available number of adsorption sites on the activated carbon surface was high enough to remove over 90% of RB5 from the solution.

### Table 4. Kinetic Model Parameters for Various Initial Dye Concentrations at 28°C

<table>
<thead>
<tr>
<th>( C_0 ) (mg/L)</th>
<th>( q_{exp} ) (mg/g)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Elovich equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( k_1 ) (min)</td>
<td>( q_e ) (mg/g)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>20</td>
<td>6.45</td>
<td>0.010</td>
<td>6.95</td>
<td>0.999</td>
</tr>
<tr>
<td>40</td>
<td>10.18</td>
<td>0.005</td>
<td>12.48</td>
<td>0.995</td>
</tr>
<tr>
<td>60</td>
<td>12.99</td>
<td>0.006</td>
<td>15.64</td>
<td>0.992</td>
</tr>
</tbody>
</table>

A diffusion model proposed by Weber and Morris was applied to determine the rate-limiting step of the adsorption process. Adsorption kinetics are typically controlled by different diffusion mechanisms: (i) film diffusion, in which the mass transfer of the bulk phase to the adsorbent surface is across the boundary layer and is represented by the curve portion; and (ii) intra-particle diffusion (gradual adsorption stage), where diffusion of the adsorbate occurs within the pores of material, binding the pores and capillary spaces. The plateau region (final stage) means that the intra-particle diffusion starts to decrease as low concentrations of adsorbate and fewer available adsorption sites are present (Samiey and Ashoori 2012). In cases where a plot of \( q \) versus \( t^{0.5} \) gives a straight line and passes through the origin, this means that intra-particle diffusion is the rate-limiting step. If the plot is linear but does not pass through the origin, the adsorption process involves intra-particle diffusion, but it is not the only limiting step; a multi-linear plot indicates the adsorption process is influenced by two or more processes (Cestari et al. 2005; Szlachta and Chubar 2013).

Figure 4 shows a multi-linear plot that has two different linear regions. The initial region corresponds to the RB5 molecules that diffuse across the boundary layer of palm shell-based activated carbon. The second region is the region of intra-particle diffusion, where the RB5 molecules gradually diffuse into surface pores and are retained by the micropores of adsorbent. In the case of 20 mg/L dye, a third region of the equilibrium (plateau) was reached, but this did not occur for the 40 and 60 mg/L concentrations of RB5. Thus, this region is not considered to be part of the diffusion mechanism. The first region was formed by the first three points (up to 1 min), while the second region comprised 3 to 300 min. The molecular size of RB5 is 2.99 nm x 0.875 nm (Ip et al. 2010), which is slightly greater than the micropores (diameter less than 2 nm); thus, a longer time is required for intra-particle diffusion.
The intra-particle diffusion rate constants \( (k_{\text{ind1}} \text{ and } k_{\text{ind2}}) \) were achieved from the slope of the linear plot \( q \text{ versus } t^{0.5} \), as listed in Table 5. The values of \( k_{\text{ind1}} \) and \( k_{\text{ind2}} \) increased from 0.063 to 0.390 mg/g min\(^{-0.5}\) and 0.454 to 0.795 mg/g min\(^{-0.5}\), respectively, as the initial dye concentration was increased from 20 to 60 mg/L. This could be explained by the high amount of dye molecules that diffuse rapidly to easily available adsorption sites.

The intercepts \( (I_1 \text{ and } I_2) \) from the plot provide information about the boundary layer thickness. A larger intercept value represents a greater boundary layer effect. The extrapolated lines did not pass through the origin, showing that RB5 adsorption was involved in intra-particle diffusion and was not the only rate-limiting step (Fig. 4). In this study, the negative intercept values suggest that the boundary layer effect was close to a minimum value (Samiey and Ashoori 2012).

![Weber and Morris intra-particle diffusion plot 28 °C](image)

**Table 5.** Parameters of Intra-Particle Diffusion Model

<table>
<thead>
<tr>
<th>( C_0 ) (mg/L)</th>
<th>( k_{\text{ind1}} )</th>
<th>( I_1 )</th>
<th>( R^2 )</th>
<th>( k_{\text{ind2}} )</th>
<th>( I_2 )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.063</td>
<td>0.024</td>
<td>0.825</td>
<td>0.454</td>
<td>-0.645</td>
<td>0.981</td>
</tr>
<tr>
<td>40</td>
<td>0.478</td>
<td>-0.176</td>
<td>0.998</td>
<td>0.633</td>
<td>-1.037</td>
<td>0.996</td>
</tr>
<tr>
<td>60</td>
<td>0.390</td>
<td>-0.078</td>
<td>0.932</td>
<td>0.795</td>
<td>-1.182</td>
<td>0.995</td>
</tr>
</tbody>
</table>

**Effect of temperature**

Figure 5 shows the removal of RB5 by the palm shell-based activated carbon at three different solution temperatures (18, 28, and 38 °C). An increase in solution temperature from 18 to 38 °C yielded an increase in adsorption capacity from 7.29 to 10.61 mg/g, indicating that the adsorption was endothermic in nature (Hsueh et al. 2007). The obtained data are in good agreement with the results presented by Al-Degs et al. (2008), who reported higher reactive dyes adsorption by activated carbon as the temperature was increased from about 25 to 55 °C. The higher surface coverage at higher solution temperature was attributed to increased penetration of reactive dyes inside micropores of the activated carbon or the creation of new active sites on adsorbent surface (Al-Degs et al. 2008).

The pseudo-first-order model and the pseudo-second-order model were used to calculate the adsorption rate constant to evaluate the activation energy. Both models fit...
well with the experimental data, as the coefficients of determination ($R^2$) were close to unity (Table 6). However, according to the literature the adsorption kinetics for reactive dyes by activated carbons is usually described by pseudo-second-order equation (Schimmel et al. 2010; Isah et al. 2015; Qu et al. 2008). The calculated rate constant ($k_2$) increased progressively from 0.00033 to 0.00046 g/mg min as the temperature increased from 18 to 38 ºC. Thus, adsorption of RB5 occurred more rapidly with higher temperature.

These rate constants were then used for the calculation of activation energy ($E_a$) (Eq. 10). The $E_a$ value was found from the slope of the plot $\ln k_2$ against $1/T$, as presented in Fig. 6. The value of $E_a$ is an indicator of either physical or chemical adsorption. In physical adsorption, the reaction is easily reversible and equilibrium is achieved rapidly. Hence, it involves a weak intermolecular force and small energy requirements (5 to 40 kJ/mol). Chemical adsorption, on the other hand, involves stronger bonding forces and has a greater $E_a$ value, ranging from 40 to 800 kJ/mol (Jiwalak et al. 2010; Szlachta and Chubar 2013). In this study, the $E_a$ was 12.619 kJ/mol, indicating that RB5 adsorption onto palm shell-based activated carbon is a physical adsorption process,

$$\ln k_2 = \ln A - \left(\frac{E_a}{RT}\right)$$

where $A$ is the temperature-independent factor (g/mg min); $E_a$ is the activation energy (kJ/mol); $R$ is the gas constant (8.314 J/mol.K), and $T$ is the temperature (K).

---

**Fig. 5.** Kinetics for RB5 adsorption at various temperatures with a constant dye concentration of 40 mg/L

**Table 6.** Kinetic Model Parameters for Different Temperatures with a RB5 Concentration of 40 mg/L

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$q_{exp}$ (mg/g)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1 \times 10^3$ (min)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>18</td>
<td>7.29</td>
<td>6.23</td>
<td>12.73</td>
</tr>
<tr>
<td>28</td>
<td>10.01</td>
<td>8.05</td>
<td>15.97</td>
</tr>
<tr>
<td>38</td>
<td>10.61</td>
<td>10.54</td>
<td>15.95</td>
</tr>
</tbody>
</table>
Effect of pH

Solution pH has been recognized as a crucial factor influencing adsorption performance. Figure 7 shows the pH effects on RB5 removal using palm shell-based activated carbon. The adsorption is highly dependent on the pH, as the removal efficiency decreased with increasing pH. This could be ascribed to the electrostatic interaction between RB5 and the adsorbent surface. At low pH, the activated carbon surface is predominantly positively charged and a strong electrostatic attraction between anionic RB5 and the adsorbent surface can be expected to enhance the process. This led to a maximum uptake of RB5 from the solution. As pH increases, OH\textsuperscript{-} ions become more prevalent in the solution and compete with anionic RB5 for active sites on the adsorbent surface. Moreover, repulsion occurred between the adsorbent and RB5 when the solution pH was higher, may contribute to a reduction of removal efficiency (Nekouei et al. 2015).

A slight increase in RB5 removal at pH 4 to 7 was found, indicating that other processes are involved in RB5 removal. There are (i) hydrophobic interactions between hydrophobic parts of the RB5 molecule and the activated carbon surface and (ii) hydrogen bonding between the alcohol group of the RB5 molecule and the carbon surface (Newcombe and Drikas 1997).

In the tested pH range from 2 to 11, the adsorption capacity decreased from 11.95 to 9.3 mg/g, respectively. In the alkaline zone, the surface of activated carbon was more negatively charged, and a strengthening force of electrostatic repulsion between RB5 and the adsorbent occurred, reducing the adsorption capacity.
**Fig. 7.** Effect of pH on RB5 removal by palm shell-based activated carbon

**Effect of adsorbent dose**

The adsorption is influenced by the availability of binding sites on the adsorbent surface. Therefore, to determine the effect of the activated carbon dose on RB5 adsorption, a series of tests were conducted, with the obtained results presented in Fig. 8. As expected, the RB5 removal efficiency increased with an increasing adsorbent dose. A complete depletion was reached for an adsorbent dose greater than 6 g/L. However, the removal only increased slightly, by 5.4%, when the adsorbent dose increased from 4 to 6 g/L. This is attributed to RB5 being almost completely adsorbed by the 4 g/L adsorbent dose.

**Fig. 8.** Effect of adsorbent dose on RB5 removal by palm shell-based activated carbon
CONCLUSIONS

1. Palm shell-based activated carbon derived from biomass waste was used as an adsorbent to remove Reactive Black 5 dye (RB5).
2. The variables of contact time, pH, adsorbent dose, and temperature had noticeable effects on RB5 adsorption.
3. Equilibrium data were best represented by the Langmuir isotherm model, and the pseudo-first-order kinetic model fit well with the kinetic data.
4. RB5 adsorption was found to be endothermic in nature, with a low activation energy.
5. The maximum adsorption capacity of the adsorbent was 25.12 mg/g at pH 2.
6. The palm shell-based activated carbon is a very promising material to remove RB5 and is comparable to other adsorbents derived from agricultural waste, as reported in literature studies.

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