Adsorption properties of cationic rhodamine B dye onto metals chloride-activated castor bean residue carbons
Lee Lin Zhi and Muhammad Abbas Ahmad Zaini

ABSTRACT
This work was aimed to evaluate the feasibility of castor bean residue based activated carbons prepared through metals chloride activation. The activated carbons were characterized for textural properties and surface chemistry, and the adsorption data of rhodamine B were established to investigate the removal performance. Zinc chloride-activated carbon with specific surface area of 395 m²/g displayed a higher adsorption capacity of 175 mg/g. Magnesium chloride and iron(III) chloride are less toxic and promising agents for composite chemical activation. The adsorption data obeyed Langmuir isotherm and pseudo-second-order kinetics model. The rate-limiting step in the adsorption of rhodamine B is film diffusion. The positive values of enthalpy and entropy indicate that the adsorption is endothermic and spontaneous at high temperature.

Key words | adsorption, castor bean residue, chemical activation, metals chloride, rhodamine B

INTRODUCTION
About 1.3 million tons of dyes are produced and used in the textile industry annually. Of these, 10 to 25% of textile dyes are lost during the dyeing process, and 2 to 20% are discharged as effluent. Consequently, up to 260,000 tons of dyes are lost to the effluent every year due to inefficiency of the dyeing process. The dyes in water are highly stable to light, temperature, detergents, chemicals, soap and other parameters such as bleach and perspiration. Consequently, dyes resist biodegradation and remain in the environment for an extended period of time (Carmen & Daniela 2012). The main concern with the dyes wastewater issue is their absorption and reflection of sunlight entering the water that reduces the photosynthetic activities of the aquatic plants, hence impeding their growth and which subsequently affects the food chain (Abou-Gamra & Medien 2013).

The removal of dye pollutants from effluent can be divided into biological, chemical and physical methods. Adsorption is the most economical and attractive method due to the flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Robinson et al. 2001). Over the last few decades, activated carbon has been used in a wide number of industrial applications including water and wastewater treatment, air pollution control, catalytic process, electrolysis and so on (Moreno-Virgen et al. 2012). The application of AC is centred mostly in wastewater treatment as it is cheap and effective to removal trace pollutants.

The performance of AC in adsorption depends mainly on its surface chemistry and pore structure (Bhatnagar et al. 2015). Activated carbon can be prepared from a variety of carbon-rich materials. Among others, agricultural by-products such as pericarp of fruit, leaves, palm shells, etc., are the promising precursor of activated carbon (Mohammadi et al. 2010; Hayeeye et al. 2014; Jeyaraj et al. 2014). Castor oil derivatives are similar to petroleum derivatives, thus it is a perfect alternative to petroleum. Castor bean residue (CBR) is the by product of oil extraction that comprises about 50% of the castor bean weight. Because of its abundance, i.e. 1.1 tons for every 1 ton of castor oil production, CBR is foreseen as suitable substitute of activated carbon precursor (Santos et al. 2014). Generally, the abundance of agro-wastes can trigger a serious disposal problem in some nations. Therefore, converting them into activated carbon is a potential solution to the associated environmental issues. The production cost of agro-wastes-derived activated carbon through chemical activation is mainly contributed by the price of activating agent, which is about RM 7 per kg of activated carbon produced. This is nearly half the price of commercial activated carbon in Malaysia that is RM 14 per kg. Because the work is based on laboratory process,

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there should be a substantial decrease in costs as compared to industrial-scale production (Zaini 2010; Sun et al. 2016).

Zinc chloride (ZnCl2) is broadly used as dehydrating agent in activated carbon synthesis via chemical activation (Oliveira et al. 2009; Jeyaraj et al. 2014; Lee & Zaini 2015a). However, zinc cation is a hazardous water pollutant that is toxic and may cause long-term adverse effects to the aquatic environment. Other metals chloride such as KCl, FeCl3 and MgCl2 are less toxic, hence they opened up the possibility of replacing ZnCl2 in chemical activation (Lee & Zaini 2015b). To date, the reports on these metals chloride in activated carbon preparation are still lacking in much of published literature.

This study was carried out to give further understanding on the contribution of agricultural waste activated carbon to dye-containing wastewater treatment. A waste material of castor oil extraction, i.e. CBR, was used as the precursor of activated carbon. This paper aimed to investigate the effect of metals chloride, namely ZnCl2, KCl, FeCl3 and MgCl2 in chemical activation of CBR based activated carbons. The role of composite activating agent was also highlighted in this paper. The performance of activated carbons was established through adsorption of rhodamine B (RB) as model dye pollutant. The adsorption data were analyzed for isotherm, kinetics and thermodynamic parameters and the adsorptive mechanisms were also discussed.

**MATERIALS AND METHODS**

**Preparation of activated carbons**

Castor bean was obtained from Ancient GreenFields Pvt Ltd, India. CBR is the by product of oil extraction, and was used in the preparation of activated carbons. CBR was ground and sieved to a size of 212μm. RB dye (C.I. No. 45170, MW = 479.02 g/mol and λmax = 575 nm) was purchased from R&M Chemicals, Essex, UK. It was used as model dye (adsorbate) in this study. Zinc chloride (ZnCl2, 99.5%) and hydrochloric acid (HCl, 37.0%) were also purchased from R&M Chemicals. Potassium chloride (KCl, 99.5%) was purchased from Merck and sodium hydroxide pellet (NaOH, 96%) was obtained from Bensdosen. All chemicals used are of analytical-grade reagents.

Activated carbons were prepared using four activating agents at impregnation ratio (chemical agent(s) to CBR) of 1.0 as summarized in Table 1.

Activating agent(s) was dissolved in distilled water, and the CBR-activating agent mixture was heated at 90°C for 1.5 h. The mixture was oven-dried at 110°C for 24 h. The impregnated CBR sample was heated in a furnace at 550°C for 1.5 h. The resultant material was soaked in 0.1 M HCl overnight for partial demineralization and to remove excess activating agent(s). After that, the activated carbon was washed with hot distilled water to remove excess ash and acid to solution pH 4. All activated carbons were dried in an oven at 110°C overnight, and ready to use for characterization and RB adsorption.

**Characterization of activated carbons**

CBR was characterized for moisture content, volatile matter, fixed carbon and ash content. Thermogravimetric analysis (TGA) of CBR was carried out using a Perkin Elmer TGA 4000. Activated carbons were characterized for textural characteristics and surface chemistry. The Brunauer, Emmett and Teller (BET) specific surface area was determined using BET analyzer (model Thermo Surfer) at liquid N2 temperature of 77 K. The morphology of activated carbons was obtained using field emission scanning electron microscope (FESEM, model Hitachi SU8020).

A series of conical flasks filled with 50 mL of 0.1 M NaCl was prepared for the determination of the pH of the point of zero charge (pHpzc). The initial solution pH, pHf, was adjusted between 2 and 12 by adding 0.1 M HCl or 0.1 M NaOH. The pH value was measured using pH meter (model Hanna HI 8424). About 50 mg of activated carbon was added to each flask, and the mixture was agitated for 24 h. The final solution pH, pH, was measured and plotted against pHf. The pHpzc is the point of intersection, at which pHf is equal to pH.

The surface functional groups were analyzed according to the qualitative (Fourier transform infrared spectroscopy, FTIR) and quantitative (Boehm titration) methods. FTIR

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Designation of activated carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activating agent</td>
<td>Impregnation ratio (g/g)</td>
</tr>
<tr>
<td>ZnCl2</td>
<td>1.0:1.0</td>
</tr>
<tr>
<td>KCl</td>
<td>1.0:1.0</td>
</tr>
<tr>
<td>MgCl2</td>
<td>1.0:1.0</td>
</tr>
<tr>
<td>FeCl3</td>
<td>1.0:1.0</td>
</tr>
<tr>
<td>ZnCl2:KCl</td>
<td>0.5:0.5:1.0</td>
</tr>
<tr>
<td>ZnCl2:MgCl2</td>
<td>0.5:0.5:1.0</td>
</tr>
<tr>
<td>ZnCl2:FeCl3</td>
<td>0.5:0.5:1.0</td>
</tr>
</tbody>
</table>

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(model Shimadzu IR Tracer-100) was used to obtain the peaks of functional groups at specific wave number ranging from 400 to 4,000 cm$^{-1}$. The Boehm titration method was used to identify the oxygenated surface groups on the carbon surface. About 0.3 g of activated carbon was placed in 15 mL of 0.1 M NaOH, 0.05 M Na$_2$CO$_3$, 0.1 M NaHCO$_3$ and 0.1 M HCl solutions, and agitated for 48 h. 5 mL of each supernatant was pipetted out, and the excess of base or acid was titrated with 0.05 M HCl or 0.1 M NaOH, respectively. Phenolphthalein and methyl red were used as the pH indicators. The concentration of acidic sites was calculated with the assumption that NaOH neutralizes carboxylic, phenolic and lactonic groups, Na$_2$CO$_3$ neutralizes carboxylic and lactonic groups, and NaHCO$_3$ neutralizes only carboxylic groups. The concentration of basic sites was calculated from the amount of hydrochloric acid neutralized by the carbon.

**Adsorptive analysis**

About 0.05 g of activated carbon was brought into intimate contact with 50 mL of RB solution (pH = 4.1 ± 0.8) of varying concentrations (5 to 400 mg/L). The mixture was allowed to equilibrate on shaker (ST-WSZ100A) at 120 rpm and 25 °C for 72 h. The residual concentration was measured by visible spectrophotometer (HALO VIS-10) at a wavelength of 575 nm.

The adsorption capacity was calculated as

$$Q_e = \frac{(C_0 - C_e) V}{m}$$  \hspace{1cm} (1)

where $Q_e$ (mg/g) is the adsorption capacity, $C_0$ (mg/L) is the initial concentration of dye solution, $C_e$ (mg/L) is the equilibrium concentration of dye solution, $m$ (g) is the mass of activated carbon and $V$ (L) is the volume of dye solution.

Four isotherm models were used to analyze the adsorption data. The Langmuir isotherm as expressed in Equation (2) describes the formation of monolayer adsorbate on the outer surface of adsorbent (Dada et al. 2015)

$$Q_e = \frac{Q_m b C_e}{1 + b C_e}$$  \hspace{1cm} (2)

where $Q_e$ (mg/g) is the equilibrium adsorption capacity of dye by adsorbent, $C_e$ (mg/L) is the equilibrium concentration of dye solution, $Q_m$ (mg/g) is the maximum monolayer capacity of adsorbent, and $b$ (L/g) is the Langmuir adsorption constant. The separation factor, $R_L$ is the essential feature of the Langmuir isotherm

$$R_L = \frac{1}{1 + b C_o}$$  \hspace{1cm} (3)

where $C_o$ (mg/L) in Equation (3) is the maximum initial concentration. The $R_L$ value represents the adsorption nature either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The Freundlich isotherm model is applied to the non-ideal adsorption on heterogeneous surface, as well as in multilayer adsorption (Dada et al. 2012). The Freundlich equation is given as

$$Q_e = K C_e^{1/n}$$  \hspace{1cm} (4)

where $K$ and $n$ are the Freundlich constants. The Redlich-Peterson (RP) isotherm is a combination featuring both Langmuir and Freundlich models. It is applicable for a wide concentration range, either in homogeneous or heterogeneous system (Redlich & Peterson 1959). The RP model can be described as

$$Q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{\beta}}$$  \hspace{1cm} (5)

where $K_R$ (L/g) and $\alpha_R$ (L/mol) are the RP isotherm constants, and $\beta$ is the exponent lies between 0 and 1. The Dubinin-Radushkevich (DR) isotherm is generally applied to describe the mechanism of adsorption by the Gaussian energy distribution onto a heterogeneous surface (Dada et al. 2012). The DR equation is expressed as

$$Q_e = Q_s \exp(-K_{ad} \varepsilon^2)$$  \hspace{1cm} (6)

where $Q_s$ (mg/g) is the theoretical isotherm saturation capacity, $K_{ad}$ (mol$^2$/kJ$^2$) is the DR constant and $\varepsilon$ is the Polanyi potential as expressed in Equation (7)

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$  \hspace{1cm} (7)

where $R$ (=8.314 J/mol. K) is the gas constant and $T$ (K) is the absolute temperature. The physical adsorption and chemical adsorption are distinguished by the mean free energy, $E$ per molecule of adsorbate as expressed in Equation (8)

$$E = \frac{1}{\sqrt{2K_{ad}}}$$  \hspace{1cm} (8)
For instance, the magnitude of $E$ between 8 and 16 kJ/mol suggests that the adsorption may involve ion exchange reaction (Subha & Namasivayam 2008).

For kinetics study, 0.05 g of CBR-based activated carbons was brought into intimate contact with 50 mL of RB solution of different initial concentrations. The mixture was equilibrated at 25 °C and 120 rpm. A small volume of the solution was withdrawn at varying time intervals to evaluate the rate of adsorption. The adsorption capacity at time $t$, was computed as

$$Q_t = \frac{(C_0 - C_t) V}{m}$$

(9)

where $Q_t$ (mg/g) is the amount of dye adsorbed at time $t$, and $C_t$ (mg/L) is the dye concentration in solution at time $t$.

The rate of adsorption data were fitted in the kinetics models to describe the adsorption mechanisms of RB dye. The pseudo-first-order and pseudo-second-order models as shown in Equations (10) and (11), respectively, were used to explain the adsorption reaction

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$$

(10)

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} - \frac{1}{Q_e} t$$

(11)

where $k_1$ (h$^{-1}$) and $k_2$ (g/mg.h) are the rate constants of pseudo-first-order and pseudo-second-order, respectively. The intraparticle diffusion model was used to identify the diffusion mechanism. The model is expressed as

$$Q_t = k_d t^{1/2} + c$$

(12)

where $k_d$ (mg/g.h$^{0.5}$) is the rate constant for intraparticle diffusion and $c$ (mg/g) is the intercept to the y-axis. The pore diffusion is the rate-limiting step if the $Q_t$ vs. $t^{1/2}$ is linear and passes through the origin. The kinetic data were also analyzed for the rate-controlling step based on the Boyd model, where the particle diffusion is the rate-limiting step when $Bt$ vs. $t$ is linear and passes through the origin. A non-linear or linear but does not pass through the origin indicates that the film diffusion as the rate-limiting step. The $Bt$ value was calculated by Reichenberg relation as expressed in Equations (13) and (14) (Suteu & Malutan 2013)

$$Bt = -0.4977 - \ln(1 - F) \text{ for } F > 0.85$$

(13)

where $F$ represents the fraction of solute adsorbed at time $t$ (h)

$$F = \frac{Q_t}{Q_e}$$

(15)

The adsorption thermodynamics was performed as follows. About 0.05 g of activated carbon was brought into intimate contact with 50 mL of RB solution at concentrations of 20, 50 and 100 mg/L. The temperature was varied between 30 and 50 °C, and the mixture was allowed to equilibrate at 120 rpm for 72 h. The Gibbs energy, $\Delta G^o$, enthalpy, $\Delta H^o$ and entropy, $\Delta S^o$ were determined using the van ’t Hoff equation

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

(16)

where $K_d$ is the distribution coefficient that can be calculated as

$$K_d = \frac{Q_{ae}}{C_e}$$

(17)

where $Q_{ae}$ (mg/L) is the amount of dye adsorbed on solid at equilibrium.

RESULTS AND DISCUSSION

Characteristics of activated carbons

Figure 1 shows the TGA profile of CBR.

The initial weight loss, which is less than 10% at the temperature range of 35 to 225 °C could be attributed to the removal of molecular bound water and some volatile organic compounds. A weight loss of 58% from 225 to 550 °C may be related to the thermal decomposition of hemicellulose and cellulose. Volatile products such as CO$_2$ and CO are probably generated at this stage. The weight loss above 550 °C was slowed down, at which a considerable decomposition of 17% could be associated with the degradation of lignin that is almost completed. As a result, the appropriate temperature for the carbonization of CBR was found to be 550 °C to ensure the volatile matters are...
removed, while fixed carbon and ash remained (Rajeshwar et al. 2012).

The ash content of CBR is 0.035%, substantiating that it has less inorganic constituents. It is supported by the energy-dispersive X-ray (EDX) analysis in which the inorganic content is negligible. The moisture content of 8.7% points out that CBR has poor affinity towards water. A higher moisture content of raw material may give a low product yield after activation. The findings are comparable with the TGA analysis. Some variation in the ash content and moisture content is expected because of the physical and environmental conditions, and the oil extraction methods involved (Bansal et al. 1988).

Table 2 shows the effect of activating agents on the yield and textural properties of activated carbons. ZCBR displays a higher yield, suggesting the role of ZnCl₂ as superior dehydrating agent to inhibit the formation of tar during the pyrolytic decomposition, consequently reduces the excessive char burning-off and production of other volatile products (Sunanda et al. 2013).

The textural characteristics were analyzed based on the effect of different activating agents on the specific surface area and pore size. The CBR char has a poor surface area (27.4 m²/g) compared to the other metals chloride-activated carbons (118.4 to 494.0 m²/g) because some of the pores are not well-developed and filled or partially blocked with tar. For metals-chloride activated carbons, the decomposition of metals chloride at 550 °C may leave metal oxide particles within the carbon matrix and create new pores. Decomposition of MgCl₂ to MgO happened at temperature higher

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**Table 2** | Yield and textural properties of activated carbons

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Yield (%)</th>
<th>BET surface area (m²/g)</th>
<th>Micro/meso area</th>
<th>Pore volume (cm³/g)</th>
<th>Mesoporosity (%)</th>
<th>Pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZCBR</td>
<td>50.6</td>
<td>395</td>
<td>11.5</td>
<td>0.269</td>
<td>34.4</td>
<td>17.8</td>
</tr>
<tr>
<td>KCBR</td>
<td>30.9</td>
<td>494</td>
<td>8.11</td>
<td>0.436</td>
<td>51.1</td>
<td>27.5</td>
</tr>
<tr>
<td>MCBR</td>
<td>40.7</td>
<td>118</td>
<td>2.02</td>
<td>0.234</td>
<td>75.5</td>
<td>15.1</td>
</tr>
<tr>
<td>FCBR</td>
<td>28.6</td>
<td>379</td>
<td>7.64</td>
<td>0.297</td>
<td>45.0</td>
<td>13.7</td>
</tr>
<tr>
<td>KZCBR</td>
<td>35.9</td>
<td>335</td>
<td>6.08</td>
<td>0.292</td>
<td>51.2</td>
<td>19.3</td>
</tr>
<tr>
<td>MZCBR</td>
<td>47.0</td>
<td>399</td>
<td>11.5</td>
<td>0.293</td>
<td>40.7</td>
<td>25.6</td>
</tr>
<tr>
<td>FZCBR</td>
<td>45.1</td>
<td>411</td>
<td>13.7</td>
<td>0.280</td>
<td>35.2</td>
<td>37.2</td>
</tr>
</tbody>
</table>

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**Figure 1** | TGA curve of CBR.
than 500 °C, while decomposition of FeCl₃ to Fe₂O₃ happened at around 400 °C (Rufford et al. 2010). Metal oxide particles could act as catalyst to enhance the gasification of carbon. Such mechanism can increase the pore volume of activated carbon by creating new pores. This explains why FCBR exhibits a higher pore volume and specific surface area than MCBR.

Figure 2 depicts the effect of ionic radius of metals chloride on the pore size of activated carbons. A proportional correlation was observed for activated carbons with impregnation ratio of 1.0.

Oliveira et al. (2009) reported that a small size metal ion used in activation may result in activated carbon with smaller pores, higher surface area and better dyes adsorption capacity. The remaining activating agent deposited on the surface of carbon matrix can be removed with HCl solution, thus aiding to the evolution of additional pores. Therefore, smaller size metal ions may act as the template for creating smaller pores (Viswanathan et al. 2009; Angin et al. 2013). For metals chloride used in this work, Fe³⁺ (55 pm) has the smallest ionic radius, followed by Zn²⁺ (72 pm), Mg²⁺ (74 pm) and K⁺ (138 pm). However, this may not be the case when the activating agent acts as the catalyst to enhance the carbon gasification. Hence, the evolution of porosity due to carbon-activator reaction also explains that small ionic radius may cause larger pores. Nevertheless, the pore size does not represent the true value of specific surface area. A large ionic radius may contribute to high surface area as it is able to create a bigger pore volume.

Figure 3 shows the morphology of CBR char, ZCBR, MZCBR and FZCBR.

Rough and dented structure is usually generated on the surface of raw material during the carbonization process. A
distribution of shallow pores and cavities on the surface of CBR char is likely due to the absence of chemical activation in the carbonization process that results in small depth of pores. Different activating agents used in the chemical activation result in diverse sizes and shapes of pore structure. From Figure 3(b) and 3(d), ZCBR and FZCBR show irregular and highly porous surface texture with plenty of pits, crevices and scales, indicating the possibility of good adsorption properties. The pore development was caused by the breakdown and release of volatile materials in CBR due to thermal expansion during chemical activation. The carbon-chemical reaction enhanced the breakdown process, leading to the well-developed porous structure of activated carbon (Sun & Webley 2014). The honeycomb-like structure formed by the tunnel-shaped pores could be observed on the surface of MZCBR as shown in Figure 3(c). The larger pores may be related to a bigger size of Mg²⁺ as compared to Zn²⁺ and Fe³⁺. However, the nano-sized pores may inhibit the adsorption of bigger dye molecules (Jeyaraj et al. 2017).

Figure 4 shows the FTIR spectrum of CBR.

CBR is a potential precursor of activated carbon due to high lignin and low cellulose content as depicted from the peaks in Figure 4. Lignin is particularly important in the formation of cell walls as it is rigid and does not rot easily. Chemically, lignin is a cross-linked phenol polymer which consists of many aromatic compounds such as O–H (3,400 to 3,200 cm⁻¹), C–O (1,050 cm⁻¹), C–H (2,910 and 2,850 cm⁻¹) and C = O (1,720 cm⁻¹). Hydrogen bonding, O–H (broad 3,400 to 3,200 cm⁻¹) can also be found in cellulose (Pavia et al. 2013). Peaks that represent leftover fatty acids include hydrocarbon chain: C–H (2,950 cm⁻¹), C = C (1,640 cm⁻¹) and C≡C (2,170 cm⁻¹), and carboxylic acid groups: O–H (broad 3,400 to 2,400 cm⁻¹), C = O (1,720 cm⁻¹) and C–O (1,050 cm⁻¹) (Alslaibi et al. 2014). The carboxylic acid and amine groups with peaks centred at 1,360 cm⁻¹ (C–N) and 3,200 cm⁻¹ (N–H) are mainly associated with the presence of ricin (Pavia et al. 2013).

Figure 5 shows the FTIR spectra of CBR char and metals chloride-activated carbons.

CBR char demonstrates fewer peaks compared to other metals chloride-activated carbons which signifies the presence of functional groups on the surface of activated carbons. Metals chloride activation is likely to reduce the release of volatile products so as to preserve some of the functional groups (Sun & Webley 2010). Activation at high temperature also enhances the elimination of light and volatile matters by breaking the aliphatic and aromatic bonds (Yorgun et al. 2009). Cellulose may be converted into aromatic carbon due to the decomposition of hemicellulose, splitting off cellulose and the breaking down of lignin structure at high temperature (Byrne & Nagle 1997). Thus, it is expected that considerable fractions of peaks are eliminated at 550°C. The peaks left after activation represent O–H, C≡C, C = C, C–O and C–Cl bonds. Besides, the peaks belong to ricin centred at 3,200 and 1,560 cm⁻¹ were diminished as well. According to Pohanish (2012), ricin begins to decompose at 60°C and almost completely eliminated.

Figure 4 | FTIR spectrum of CBR.
after 30 min at 80 °C. The presence of C–Cl is suspected due to the use of metals chloride in the activation process. In view of functional groups, the adsorption of RB may be possible due to chemical or electrostatic interaction between hydroxyl groups and electronegative groups of RB, and hydrogen bonding between hydroxyl groups and oxygen of the xanthene ring of RB molecule (Mohammadi et al. 2010).

Table 3 shows the concentration of functional groups of ZCBR, MZCBR and FZCBR. The pH_{PZC} values for ZCBR, MZCBR and FZCBR are 6.4, 6.9 and 3.4, respectively. The result shows that the adsorbents possess different surface chemistry as a result of different metals chloride-activation. The pH of the system may affect the surface functional groups by dissociating the active sites on the activated carbon surface. The change in pH can also influence the adsorption performance. For instance, the cationic dye adsorption is more favourable in solution that has pH greater than pH_{PZC} for activated carbon with negatively charged surface sites (Zanella et al. 2015).

Figure 5 | FTIR spectra of (a) CBR char, (b) ZCBR, (c) KCBR, (d) FCBR, (e) MCBR, (f) FZCBR and (g) MZCBR.

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>pH_{PZC}</th>
<th>Carboxylic</th>
<th>Lactonic</th>
<th>Phenolic</th>
<th>Total acidic</th>
<th>Basic</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZCBR</td>
<td>6.4</td>
<td>1.050</td>
<td>0.075</td>
<td>1.600</td>
<td>2.725</td>
<td>0.052</td>
</tr>
<tr>
<td>MZCBR</td>
<td>6.9</td>
<td>0.700</td>
<td>0</td>
<td>1.625</td>
<td>1.625</td>
<td>0.729</td>
</tr>
<tr>
<td>FZCBR</td>
<td>3.4</td>
<td>1.625</td>
<td>0.025</td>
<td>1.325</td>
<td>1.325</td>
<td>0.052</td>
</tr>
</tbody>
</table>
slightly higher pH_{PZC} due to high concentration of basic groups (Fu et al. 2013). The surface functional groups can give significant contribution towards the adsorption ability. The development of surface functional groups is dependent upon type of activating agent, type of precursor and operating conditions. Surface oxygen groups are usually formed when the activated carbon is prepared under oxidizing environment. However, metals chloride are not oxidizers. Thus, the evolution pattern of surface oxygen groups could not be clearly observed. Also, the concentration of functional groups is not much influenced by the increase in impregnation ratio (Yang et al. 2013).

**Adsorptive analysis**

**Equilibrium adsorption**

Figures 6 and 7 show the RB adsorption performance by different metals chloride-activated carbons at impregnation ratio of 1.0.

All activated carbons demonstrate an increasing trend in the equilibrium adsorption capacity, $Q_e$ and achieved a saturation point known as maximum uptake. Equilibrium at any concentration is achieved when the rate of adsorption is equal to the rate of desorption. At lower concentration, there are plenty available sites for adsorption, so the percentage of adsorption is independent of concentration. While the adsorption becomes concentration-dependent at higher concentration until the active sites are completely occupied, at which no further increase in adsorption with increasing concentration, and the maximum adsorption is achieved (Hema & Arivoli 2007). ZCBR exhibits a better RB adsorption among all activated carbons studied. This could be attributed to high BET surface area of 395 m$^2$/g. However, KCBR possesses a higher BET surface area (494 m$^2$/g) but a lower removal of RB. The average pore diameter of activated carbon should be two to three times that of the adsorbate for smooth diffusion to happen. The molecular size of RB is around 1.8 nm, thus the micropores are not favourable to capture RB molecules (Mohammadi et al. 2010). Moreover, RB molecules are usually combined into dimer form at higher pH between 5 and 8 (Setiawan et al. 2010). The equilibrium pH of KCBR is slightly higher than that of ZCBR, whereas the pore size of KCBR is smaller than that of ZCBR. The bigger size of RB in dimer form and smaller pore size might be the reason for a lower RB adsorption by KCBR (Arivoli et al. 2009). Certainly, it may also be caused by other factors such as microporosity, temperature, size, etc.

Table 4 summarizes the constants of Langmuir, Freundlich, RP and DR models for RB adsorption by metals chloride-activated carbons.

From Table 4, it was found that the correlation of determination ($R^2$) of Langmuir model are close to 1. This indicates the applicability of Langmuir isotherm to describe the adsorption of RB by activated carbons. The adsorption can be assumed as monolayer coverage of RB on homogeneous surface of activated carbon (Dada et al. 2012). The
active sites are presumed to exhibit the same affinity for adsorption, by which no further adsorption can take place once the sites are occupied and no interaction amongst the adsorbed molecules (Vijayakumar et al. 2010; Dada et al. 2012). Furthermore, the $n$ values of Freundlich model are greater than 1 for all activated carbons. It indicates that the adsorption follows ordinary Langmuir isotherm (Tan et al. 2012).

ZCBR shows the highest $Q_m$ of 175 mg/g. It is in agreement with the highest $K$ constant of Freundlich model that also indicates the highest adsorption capacity (Azizi et al. 2012). For composite activated carbons, MZCBR and FZCBR display adsorptive capacity higher than MCBR and FCBR, but slightly lower than ZCBR. The activation of these composite activated carbons could be less hazardous because less ZnCl$_2$ was used, in which the usage was reduced by half. It shows that the mixture of ZnCl$_2$ with either MgCl$_2$ or FeCl$_3$ could be a promising substitute and alternative to hazardous ZnCl$_2$. Nevertheless, KZCBR displays a poor performance of RB adsorption as compared to the KCBR series. The performance of the KCBR series is almost the same as that of CBR char. In other words, KCl is not an attractive option of activating agent to activate CBR.

The Langmuir constant, $b$ is related to the energy of adsorption. FCBR has the highest $b$, suggesting a favourable RB adsorption at low dye concentration. It signifies a high affinity between RB molecules and FCBR sites as depicted in Figure 7 (Alslaibi et al. 2014). The $R_L$ values in the range of 0 to 1 show that the adsorption is favourable and reversible (Dada et al. 2012). Hence, ZCBR, MZCBR and FZCBR are more favourable and possess better adsorption performance than KCBR series ($R_L$ values between 0.143 and 0.475) (Ahmad et al. 2014).

The RP isotherm is the hybrid of both Langmuir and Freundlich models. For $\beta = 1$, the RP equation reduces to Langmuir isotherm. Accordingly, $K_R$ is equal to $Q_m b$, and $\alpha_R$ represents Langmuir constant, $b$. From Table 4, the RP constants agreed well with the Langmuir isotherm for $\beta$ approaching unity (Redlich & Peterson 1959).

The DR model was used to evaluate the porosity and apparent adsorption capacity. For $K_{aw}$ less than unity, the activated carbon is microporous and the surface heterogeneity may be attributed to the pore structure and adsorbate–adsorbent interaction (Kim et al. 1995). $E$ is the mean free energy of adsorption, and it is assumed that $E < 8$ is due to physical adsorption, $E$ between 8 and 16 is due to electrostatic adsorption, and $E > 16$ is due to chemical adsorption (Jeyaraj et al. 2014). From Table 4, it is suggested that RB

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Isotherm constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>pH$_{eq}$</td>
</tr>
<tr>
<td>CBR char</td>
<td>6.0 ± 1.2</td>
</tr>
<tr>
<td>ZCBR</td>
<td>5.6 ± 0.4</td>
</tr>
<tr>
<td>KCBR</td>
<td>6.8 ± 0.5</td>
</tr>
<tr>
<td>MCBR</td>
<td>6.6 ± 0.5</td>
</tr>
<tr>
<td>FCBR</td>
<td>4.2 ± 0.6</td>
</tr>
<tr>
<td>KZCBR</td>
<td>4.2 ± 0.6</td>
</tr>
<tr>
<td>MZCBR</td>
<td>5.1 ± 0.2</td>
</tr>
<tr>
<td>FZCBR</td>
<td>3.3 ± 0.1</td>
</tr>
</tbody>
</table>

pH$_{eq}$ = Equilibrium solution pH.
adsorption by CBR-based activated carbons is due to physi-
sorption. The maximum adsorption capacity, \( Q_s \), obtained by DR model are slightly different from \( Q_m \) of Langmuir model. The poor \( R^2 \) values reveals that DR model did not fit well to the adsorption data.

Table 5 summarizes the performance of RB removal by different activated carbons in literature.

In general, the adsorption performance of ZCBR, MZCBR and FZCBR are comparable with some of the listed adsorbents/activated carbons. ZCBR is similar to activated carbon studied by Jeyaraj et al. (2014), both demonstrate a specific surface area about 400 m\(^2/g\) and maximum adsorption capacity of around 170 mg/g. While KCBR and KZCBR are identical to palm shell-based activated carbon reported by Mohammadi et al. (2010), these activated carbons possess high specific surface area but low adsorption capacity.

Table 5 | Maximum adsorption capacity of RB by various activated carbons

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Activating agent</th>
<th>BET surface area (m(^2/g))</th>
<th>( Q_m ) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial AC</td>
<td>–</td>
<td>1,317</td>
<td>429</td>
<td>Hayeeye et al. (2014)</td>
</tr>
<tr>
<td>Pericarp of rubber fruit</td>
<td>ZnCl(_2)</td>
<td>921</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Peltophorum pterocarpum leaf</td>
<td>H(_2)PO(_4)</td>
<td>409</td>
<td>170</td>
<td>Jeyaraj et al. (2014)</td>
</tr>
<tr>
<td>Palm kernel shell</td>
<td>H(_2)SO(_4)</td>
<td>1,086</td>
<td>556</td>
<td>Panneerselvam et al. (2012)</td>
</tr>
<tr>
<td>Palm shell</td>
<td>NaOH</td>
<td>477</td>
<td>1.40</td>
<td>Mohammadi et al. (2010)</td>
</tr>
<tr>
<td>CBR</td>
<td>ZnCl(_2)</td>
<td>395</td>
<td>175</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>KCl</td>
<td>494</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>KCl + ZnCl(_2)</td>
<td>335</td>
<td>6.61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MgCl(_2) + ZnCl(_2)</td>
<td>399</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FeCl(_3) + ZnCl(_2)</td>
<td>411</td>
<td>115</td>
<td></td>
</tr>
</tbody>
</table>

Figure 8 shows the effect of pH on RB adsorption by ZCBR. The initial concentration was fixed at 400 mg/L.

RB is in cationic form in acidic polar solvent (such as water), while it becomes zwitterion in basic polar solvent (Figure 9). At pH 2, the surface of ZCBR is positively charged because the solution pH is lower than \( p_{pzc} \) of ZCBR is 6.1. Poor RB removal at this pH is due to competition between H\(^+\) ions and RB cations. At pH 3.5–7.5, the presence of zwitterions in water increases the aggregation between dye molecules to form dimer. It is due to attractive electrostatic interaction between the carboxyl and xanthane groups of RB. Because of its larger size, dimer is unable to lodge into the pore structure of ZCBR. Meanwhile, OH\(^-\) ions interrupt the interaction between the carboxyl and xanthane groups at pH higher than 7.5, which subsequently decreases the aggregation of RB molecules. As a result, the adsorption capacity increased.

Figure 8 | Equilibrium adsorption of RB by ZCBR at different solution pH (solution volume – 50 mL, adsorbent mass – 0.05 g, concentration – 400 mg/L, temperature – 25 °C, contact time – 72 h).
as RB molecules are able to enter the pore again. The surface of activated carbon is negatively charged at pH higher than pH_{PZC}, at which the adsorption performance can be enhanced through electrostatic attraction (Arivoli et al. 2013; Abou-Gamra & Medien 2015).

Adsorption kinetics

Figures 10–12 show the rate of adsorption of RB by metals chloride-activated carbons.

Rapid adsorption at initial contact time can be attributed to large number of available surface sites. After a lapse of time, the remaining sites are unoccupied because of repulsion between the adsorbed RB molecules on activated carbon surface and bulk phase (Viswanathan et al. 2009; Abou-Gamra & Medien 2013). The repulsive lateral interaction among neighbouring RB molecules reduces the bond energy of RB-activated carbon surface, resulting in the desorption of RB molecules from the adsorption layer at which the equilibrium is attained (Mohammadi et al. 2010). A rapid adsorption happened at the outer surface, followed by a slower adsorption inside the pores. Adsorption increased gradually with time suggesting the formation of monolayer on the surface of activated carbon (Arivoli et al. 2009). Figures 11 and 12 show that the adsorption capacity of RB increases with time, and time taken to reach equilibrium becomes longer when initial concentration increases due to the decreasing number of sites with time for higher concentration that reduces the rate of adsorption (Khan et al. 2014).

The pseudo-first-order and pseudo-second-order models were employed to discuss the rate of RB adsorption by CBR-activated carbons while the intraparticle diffusion and Boyd
models were used to evaluate diffusion mechanisms. The kinetics constants are tabulated in Table 6.

The \( R^2 \) values for pseudo-first-order model are lower than that of pseudo-second-order model for all activated carbons studied, indicating the applicability of the latter to describe the rate of adsorption. Ho (1995) proposed the pseudo-second-order model for chemical adsorption. It means that the overall adsorption rate of RB is chemically controlled through sharing or exchange electron between RB molecules and activated carbon surface (Alfaro-Cuevas-Villanueva et al. 2014). The pseudo-second-order is a suitable kinetics model to predict the adsorption behaviour of solid–liquid system based on the assumption that the rate-limiting step is chemisorption (Huang & Zhang 2014). According to Arrhenius equation, high rate constant indicates very spontaneous reaction due to lower activation energy. The \( k_2 \) value is higher at lower \( C_o \) because of rapid RB adsorption due to less repulsion between RB molecules (Viswanathan et al. 2009).

The initial adsorption rate, \( h \) (mg/g.h) can be calculated by the following expression:

\[
h = k_2q_e^2
\]  

(18)

ZCBR shows the highest \( h \) value, whereas FCBR possesses the lowest. The \( h \) value is greater at high \( C_o \) because of the decrease in solid-phase mass transfer resistant, rendering a greater driving force for dye removal (Arivoli et al. 2009). Adsorption is generally governed by four sequential steps: (1) bulk diffusion – diffusion of dye molecules from bulk solution to the surface of adsorbent; (2) film diffusion – diffusion of dye molecules through the boundary layer; (3) pore diffusion or intraparticle diffusion – diffusion of dye molecules from the adsorbent surface into the pores; and (4) adsorption – binding of dye molecules to the active sites (Suteu & Malutan 2013).

The intercept, \( c \) of intraparticle diffusion model, indicates that pore diffusion is not the sole rate-limiting step (Qi et al. 2011). The \( c \) value gives an idea about the thickness of the boundary layer. A larger \( c \) signifies a greater contribution of film diffusion in the rate-limiting step (Arivoli et al. 2009; Khan et al. 2011). Figure 13 shows the intraparticle diffusion model for ZCBR at different RB concentrations. The first sharp region represents a strong electrostatic attraction between RB molecules and the outer surface of activated carbon. The second region indicates a gradual adsorption stage of pore diffusion. The third region shows a slow diffusion of RB molecules.

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Co (mg/L)</th>
<th>Qe ( \exp ) (mg/g)</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
<th>Intraparticle diffusion</th>
<th>Boyd model</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZCBR</td>
<td>400</td>
<td>165</td>
<td>0.759</td>
<td>0.444</td>
<td>0.796</td>
<td>0.0044</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>151</td>
<td>0.791</td>
<td>0.211</td>
<td>0.825</td>
<td>0.0042</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>46.1</td>
<td>0.991</td>
<td>0.113</td>
<td>0.995</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15.6</td>
<td>0.995</td>
<td>0.152</td>
<td>0.985</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5.91</td>
<td>0.979</td>
<td>0.188</td>
<td>0.985</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.31</td>
<td>0.985</td>
<td>0.382</td>
<td>0.985</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2.20</td>
<td>0.995</td>
<td>0.723</td>
<td>0.995</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>7.80</td>
<td>0.964</td>
<td>0.857</td>
<td>0.995</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>22.0</td>
<td>0.964</td>
<td>0.857</td>
<td>0.995</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>145</td>
<td>0.964</td>
<td>0.857</td>
<td>0.995</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>7.80</td>
<td>0.964</td>
<td>0.857</td>
<td>0.995</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>130</td>
<td>0.964</td>
<td>0.857</td>
<td>0.995</td>
<td>0.0043</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>104</td>
<td>0.964</td>
<td>0.857</td>
<td>0.995</td>
<td>0.0043</td>
</tr>
</tbody>
</table>

Table 6: Kinetics constants
approaching equilibrium. The third region also signifies that equilibrium is attained earlier for low RB concentration (Hameed & El-Khaiary 2013).

The intercept of the Boyd model implies that pore diffusion is not the rate-limiting step, but can be either film diffusion or chemical reaction (Hameed & El-Khaiary 2013). Effective diffusion coefficient is expressed as

$$B = \frac{\pi^2 D_i}{r^2}$$

(19)

where $B$ is the slope of $Bt$ vs. $t$, $D_i$ (cm$^2$/s) is the effective diffusion coefficient and $r$ (cm) is the radius of adsorbent particle (particle radius = 106 µm). The calculated values of $D_i$ from Equation (19) are summarized in Table 6. Film diffusion could be the rate-limiting step if $D_i$ are in the range of $10^{-6}$ to $10^{-8}$ cm$^2$/s (Karthikeyan & Sivakumar 2012). Thus, the rate-limiting step in the adsorption of RB by CBR-activated carbons could be more than one step.

Adsorption thermodynamics

Figure 14 shows the effect of temperature on RB adsorption by ZCBR.

The diffusion rate of dye molecules from the outer layer into internal pores is accelerated due to the decrease in solution viscosity at high temperature. Besides, the change in solution temperature may interfere the equilibrium between adsorbate and adsorbent (Ahmad et al. 2014). From Figure 14, the adsorption of RB increased with increasing temperature from 20 to 55 °C. It indicates that the adsorption is endothermic in nature. At higher temperature, more heat (energy) is supplied to facilitate the adsorption of RB onto activated carbon (Mohammadi et al. 2010). A better adsorption performance at high temperature may also be due to affinity improvement of adsorption sites (Khan et al. 2011).

Table 7 shows the thermodynamic properties of ZCBR at various RB concentrations and temperatures between 20 and 55 °C.

The positive $\Delta H^0$ suggests that adsorption is endothermic, i.e. heat is absorbed during the process. The adsorption capacity increased with temperature as heat is needed to overcome the repulsive force on the activated carbon surface (Mohammadi et al. 2010). Moreover, $\Delta H^0$ decreased with increasing concentration because of greater repulsion among neighbouring RB molecules, hence weakening the RB-activated carbon bonds (Mohammadi et al. 2010). Generally, $\Delta H^0$ less than 84 kJ/mol indicates that adsorption is likely due to physisorption.

The positive $\Delta S^0$ infers the dispersal of energy that causes more disorder of the matter. At the beginning of
adsorption, the RB molecules at the boundary layer are more ordered than in the adsorbed state. Likewise, the ratio of free RB molecules to the interacted ones is bigger than in the adsorbed state. As a result, the distribution of translational and rotational energy increased due to decreasing amount of RB molecules during adsorption, thus allowing the prevalence of randomness in the system (Arivoli et al. 2009; Alfaro-Cuevas-Villanueva et al. 2014). Moreover, a higher $\Delta S^0$ indicates a weaker bond between RB molecules and activated carbon, which becomes more disordered at lower RB concentration.

The Gibbs free energy, $\Delta G^0$, is the amount of energy available to do work. A more negative or less positive $\Delta G^0$ reveals the increasing degree of spontaneity and favourable adsorption. For all initial concentrations studied, the adsorption is more favourable at higher temperature. This is also supported by positive $\Delta H^0$ and $\Delta S^0$, indicating that the adsorption process is spontaneous at high temperature (Alfaro-Cuevas-Villanueva et al. 2014). Physiosorption is dominant if $\Delta G^0$ are in the range of 0 to 20 kJ/mol. Consistent findings of $\Delta H^0$ and $\Delta G^0$ as well as $E$ of DR isotherm, suggest that the adsorption of RB onto ZCBR is physisorption. Based on the adsorption kinetics, neither fully physical nor fully chemical, but probably some complex mechanisms can be proposed for the adsorption of RB onto CBR-based activated carbons (Huang & Zhang 2013).

CONCLUSION

This study was carried out to investigate the performance of metals chloride-activated carbons prepared from CBR for RB adsorption. The specific surface area of activated carbons are in the order of KCBR > FZCBR > MZCBR > ZCBR > MCBR > FCBR > KZCBR > MCBR. ZCBR showed a greater RB adsorption of 175 mg/g. The composite activated carbons, i.e. MZCBR and FZCBR also displayed a reasonably high adsorptive capacity of 114 and 115 mg/g, respectively. Less hazardous metals chloride, i.e. magnesium chloride and iron(III) chloride are promising agents in chemical activation. The physisorption may play a dominating role in RB adsorption with film diffusion as a possible rate-limiting step. For ZCBR, the adsorption process is spontaneous at high temperature.

CONFLICT OF INTEREST

All authors declare that they have no conflict of interest.

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