The removal of rhodamine B dye from aqueous solution using *Casuarina equisetifolia* needles as adsorbent

Muhammad Raziq Rahimi Kooh1*, Muhammad Khairud Dahri1 and Linda B.L. Lim1

Abstract: *Casuarina equisetifolia* needle (CEN), a lignocellulosic-rich and sustainable material, was used in order to investigate its ability as an adsorbent to remove rhodamine B (RB) dye from aqueous solution. Fourier Transform Infrared spectrometer was used to characterise CEN functional groups and scanning electron microscope was used to study its surface morphology. Batch experiments were done in order to determine the effect of some parameters such as adsorbent dosage, initial pH, contact time, ionic strength, temperature and initial dye concentration. Kinetics, isotherm modelling and thermodynamics studies were also performed in order to explore an insight into the mechanism of the adsorption process. The study showed that the adsorption of RB by CEN is endothermic in nature and follows the pseudo-second-order kinetics model. The Langmuir isotherm model fitted the experimental data best with a maximum adsorption capacity of 82.34 mg g⁻¹.

Subjects: Environmental Chemistry; Environmental Sciences; Thermodynamics & Kinetic Theory

Keywords: *Casuarina equisetifolia* needle; rhodamine B; adsorption; kinetics; isotherm

1. Introduction

The rise of synthetic dyes in modern society replaced the natural dyes due to their high demands and economical feasibility. The dyes are mainly used as colouring agents for textile, paper printing, leather, food, pharmaceutical and microscopy. Dyes are also used as animal feed preservatives and as disinfectant in aquaculture industry due to their antifungal and antiseptic properties.

As synthetic dyes are usually designed to be chemically and thermally stable, dye wastewater needs to be disposed properly and should not be discharged directly into water bodies. However,
such practices are common in some developing countries (Ahmed, Sushil, & Krishna, 2012; Awomeso, Taiwo, Gbadebo, & Adenowo, 2010) and these led to severe ecological damages which can spread down to agricultural farmlands or aquaculture industry. Dye is also known to bioaccumulate in aquatic fauna and is able to transfer to higher food chain (Anliker & Moser, 1987), causing possible health liabilities of consumers. The high visibility of dye at low concentration reduces photosynthetic activities of aquatic plant and algae, leading to reduction in dissolved oxygen thereby harming aquatic life (Ahmed et al., 2012; Awomeso et al., 2010).

There are many methods to treat dye wastewater, and such methods include the use of oxidising/reducing agents, Fenton’s reagent, catalysis, photodegradation, electrodegradation, membrane filtration and adsorption methods. The advantages and disadvantages are widely discussed in the literature (Crini, 2006). Adsorption is the preferred method for treating dye wastewater which is simple and the cost of treatment mainly depends on the choice of adsorbent and the adsorption capacities of the adsorbent. The method can be easily learnt and applied by semi-skilled technician without the need of advanced knowledge, and can be adopted by industries with limited resources (Kooh, Lim, Lim, & Bandara, 2015b).

The choice of adsorbents ranged from abundant plant materials such as invasive weeds e.g. duckweed (Lim et al., 2014) and water fern (Kooh, Lim, Dahri, Lim, & Sarath Bandara, 2015; Kooh, Lim, Lim, et al., 2015), soil materials such as peat (Chieng, Lim, & Priyantha, 2014), carbonaceous materials, agricultural wastes such as sawdust (Hanafiah, Ngah, Zolkafly, Teong, & Majid, 2012) and walnut shell (Dahri, Kooh, & Lim, 2014), as well as biological culture materials such as Penicilium (Yang et al., 2011).

This study aimed to investigate the potential of Casuarina equisetifolia needle (CEN) as potential adsorbent for the removal of the hazardous dye rhodamine B (RB). The reason for choosing CEN is that Casuarina equisetifolia is a type of non-leguminous plant, where the root relied on bacteria, Frankia spp., for the nitrogenous resources for the growth of the host, thereby reducing the need of inputs (Diem, Gauthier, & Dommergues, 1982). The high leaf litter rate of Casuarina plant resulted in abundance of CEN covered the ground, and acidified the soil during the decaying process thereby preventing invasion of other plant species (Jamaludheen & Kumar, 1999). This CEN is of little economic value where the most common use is for landscaping garden. CEN can be easily processed into powder for adsorption due to its brittleness, and it also contains lignocellulosic material which is one of the materials known to be involved in adsorption of pollutants. Thus choosing CEN as an adsorbent for the removal of pollutant is a sustainable option. In previous studies, CEN was found to be effective in the removal of methyl violet 2B, malachite green and methylene blue (Dahri, Kooh, & Lim, 2013). This study focuses on carcinogenic xanthine dye, RB, because this dye is widely used in paint, textiles, paper and leather industries (Santhi, Prasad, & Manonmani, 2014). RB is known to be highly toxic to fish where LC50 of 83.9 mg L⁻¹ for Cyprinodon variegatus (sheepshead minnow) was reported (Sigma-Aldrich, 2014). Animal testing on rats reported tumours growth on the site of application, and also resulted in reproductive toxicity such as stunted foetuses (Sigma-Aldrich, 2014).

The objectives of this study include the characterisations of the adsorbent, the investigations of the dye removal at different adsorbent dosage, initial pH, dye initial concentration and contact time. Adsorption isotherm, kinetics, thermodynamics and regeneration experiments were also investigated.

2. Materials and methods

2.1. Preparation of adsorbent and adsorbate
CEN was collected from campus ground and was washed with distilled water prior to drying it in an oven at 70°C for few days. Dried CEN was blended, sieved to size below 355 μm and stored in a desiccator.
Rhodamine B (RB) \((C_{28}H_{31}ClN_2O_3; \text{HPLC grade, } M_r 479.01 \text{ g mol}^{-1})\), with a purity of 95% dye content, was purchased from Sigma-Aldrich and used without further purification. A RB stock solution was prepared by dissolving appropriate amount of dye powder in distilled water, and lower dye concentrations were obtained by diluting the stock solution.

2.2. Characterisations of adsorbent

Fourier transform infrared (FTIR) spectra were obtained by the KBr disc method using a Shimadzu Model IRPrestige-21 spectrophotometer, while the surface morphology analysis of CEN was carried out using Tescan Vega XMU scanning electron microscope (SEM) after sputter coated the adsorbent with gold using SPI-MODULE™ Sputter Coater for 60 s. SEM images were taken at 500× magnification.

The point of zero charge \((pH_{\text{pzc}})\) of the adsorbent was determined by the salt addition method using 0.1 mol L\(^{-1}\) KNO\(_3\) solutions (Zehra, Priyantha, Lim, & Iqbal, 2014). The pH of the KNO\(_3\) solutions was adjusted with dilute solution of HNO\(_3\) and NaOH to initial pH of 2.0–10.0. The pH was measured using a Thermo Scientific Orion 2 Star pH Benchtop meter. 0.04 g of adsorbent was added to 20 mL of pH-adjusted KNO\(_3\) and agitated for 24 h at 250 rpm using a Stuart orbital shaker, and the final pH was measured. The pH difference, \(\Delta pH\) (final pH – initial pH) vs. initial pH was plotted to determine the pH\(_{\text{pzc}}\).

2.3. Batch adsorption procedures

Batch experiment was carried out by mixing CEN (0.04 g) with dye solution (20 mL) in clean Erlenmeyer flasks and agitated at 250 rpm (unless otherwise stated). The quantity of the dye was analysed using a Shimadzu UV-1601PC UV–visible spectrophotometer at wavelength 555 nm.

Experimental parameters, such as dosage (0.01–0.06 g CEN), effect of contact time (5–240 min), effect of medium pH (2–10), effect of ionic strength (0–0.8 mol L\(^{-1}\) NaCl) effect of initial concentration (20–500 mg L\(^{-1}\) RB) and effect of temperature (25–65°C) were conducted by changing one parameter at a time, while other parameters being kept constant. The amount of dye adsorbed per gram of adsorbent at equilibrium, \(q_e\) (mg g\(^{-1}\)), is calculated using the following equation:

\[
q_e = \frac{(C_i - C_e)V}{m} \quad (1)
\]

where \(C_i\) is the initial dye concentration (mg L\(^{-1}\)), \(C_e\) is the dye concentration at equilibrium (mg L\(^{-1}\)), \(V\) is the volume of dye solution used (L) and \(m\) is the mass of adsorbent used (g).

The percentage removal is calculated by the following equation:

\[
\text{Percentage removal} = \frac{(C_i - C_e) \times 100\%}{C_i} \quad (2)
\]

2.4. Kinetics studies

Four kinetics models [pseudo-first-order (Lagergren, 1898), pseudo-second-order (Ho & McKay, 1999), Weber–Morris intraparticle diffusion (Weber & Morris, 1963) and Boyd (Boyd, Adamson, & Myers, 1947) models] were used for characterising the kinetics data.

The pseudo-first-order is typically expressed as:

\[
\log (q_e - q_t) = \log q_e - \frac{t}{2.303}k_1 \quad (3)
\]

where \(q_t\) is the amount of adsorbate adsorbed per gram of adsorbent (mg g\(^{-1}\)) at time \(t\), \(k_1\) is the pseudo-first-order rate constant (min\(^{-1}\)) and \(t\) is the contact time (min).

The pseudo-second-order is commonly expressed as:
where $k_2$ is the pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$).

The Weber–Morris intraparticle diffusion model is expressed as:

$$q_t = k_3 t^{1/2} + C$$  \hspace{1cm} (5)

where $k_3$ is the intraparticle diffusion rate constant (mg g$^{-1}$ min$^{-1/2}$) and $C$ is the intercept.

The Boyd model is expressed as:

$$B_t = 0.4977 - \ln(1 - F)$$  \hspace{1cm} (6)

where $F$ is equivalent to $\frac{q_t}{q_e}$ and $B_t$ is the mathematical function of $F$.

The rate constant and parameters of the pseudo-first-order, pseudo-second-order, Weber–Morris intraparticle diffusion and Boyd models were obtained from the linear plots of ln ($q_e - q_t$) vs. $t$, $\frac{q_t}{t}$ vs. $t$, $q_t$ vs. $t^{1/2}$ and $B_t$ vs. $t$, respectively.

### 2.5. Isotherm modelling

Three isotherm models: Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906) and Dubinin–Radushkevich (D–R) (Dubinin & Radushkevich, 1947) were used for modelling the adsorption data.

The Langmuir isotherm is one of the commonly used isotherm model, which assumes monolayer coverage of adsorbate molecules onto the adsorbent surface.

The Langmuir equation is generally expressed as:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m}$$  \hspace{1cm} (7)

where $q_m$ is the maximum monolayer adsorption capacity of the adsorbent (mg g$^{-1}$), and $k_L$ is the Langmuir adsorption constant (L mg$^{-1}$) which is related to the free energy of adsorption.

The separation factor ($R_L$) is a dimensionless constant which is an essential characteristic of the Langmuir model. The equation of $R_L$ is expressed as:

$$R_L = \frac{1}{1 + k_L C_o}$$  \hspace{1cm} (8)

where $C_o$ (mg L$^{-1}$) is the highest initial dye concentration ($C_o = 500$ mg L$^{-1}$). $R_L$ indicates if the isotherm is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable (0 < $R_L < 1$), or irreversible ($R_L = 0$).

The Freundlich isotherm model assumes multilayer coverage of adsorbate onto the adsorbent surface and the equation is typically expressed as:

$$\ln q_e = \frac{1}{n_F} \ln C_o + \ln k_F$$  \hspace{1cm} (9)

where $k_F$ (mg$^{1/n_F}$ L$^{1-n_F}$ g$^{-1}$) is the adsorption capacity of the adsorbent and $n_F$ (Freundlich constant) indicates the favourability of the adsorption process. The adsorption process is considered favourable if $1 < n_F < 10$. 

$$\frac{t}{q_t} = \frac{1}{q_e k_2} + \frac{t}{q_e}$$  \hspace{1cm} (4)
The D–R isotherm assumes no homogenous surface of the adsorbent and is temperature-dependent. The equation is as followed:

\[ \ln q_e = \ln q_m - k_{DR} \varepsilon^2 \]  

(10)

where \( q_m \) is the saturation capacity (mg g\(^{-1}\)), \( k_{DR} \) is a D–R constant (mol\(^2\) kJ\(^{-2}\)), and \( \varepsilon \) is the D–R isotherm constant which is also known as the Polanyi potential.

The D–R isotherm constant, \( \varepsilon \), is expressed as:

\[ \varepsilon = RT \ln \left[ 1 + \frac{1}{C_s} \right] \]  

(11)

where \( R \) is the gas constant (8.314 \times 10\(^{-3}\) kJ mol\(^{-1}\) K\(^{-1}\)) and \( T \) is temperature (K).

The mean free energy, \( E \) (kJ mol\(^{-1}\)), of the sorption per molecule of adsorbate is obtained from \( k_{DR} \) and the equation is expressed as:

\[ E = \frac{1}{\sqrt{2k_{DR}}} \]  

(12)

The parameters of the isotherm models: Langmuir, Freundlich and D–R isotherm were obtained from the linear plot of: \( Ce/q_e \) vs. \( Ce \), \( \ln q_e \) vs. \( \ln Ce \), and \( \ln q_e \) vs. \( \varepsilon^2 \), respectively.

The kinetics and isotherm models that best fit the equilibrium data were determined by the values of the coefficient of determination (R\(^2\)). In addition, the predicted \( q_e \) (\( q_e,\text{cal} \)) were calculated from either the kinetics or isotherm models and error analysis was applied. Best fit of experimental data (\( q_e,\text{exp} \)) was determined by the smallest values Chi-square test error analysis function which indicates the least error (Tsai & Juang, 2000).

\[ \text{Chi - square test(} \chi^2 \text{): } \sum_{i=1}^{n} \frac{(q_e,\text{exp} - q_e,\text{cal})^2}{q_e,\text{exp}} \]  

(13)

where \( q_e,\text{exp} \) is the experimental value while \( q_e,\text{cal} \) is the calculated value, \( n \) is the number of data points in the experiment and \( p \) is the number of parameters of the isotherm model.

### 2.6. Thermodynamics study

The thermodynamics parameters were studied from temperature 25 to 65°C.

The Van’t Hoff equation was used for the thermodynamics studies, expressed as follow:

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  

(14)

where \( \Delta G^\circ \) is the Gibbs free energy, \( \Delta H^\circ \) is the change in enthalpy, \( \Delta S^\circ \) is the change in entropy and \( T \) is the temperature (K).

The Gibbs free energy is expressed as:

\[ \Delta G^\circ = -RT \ln k \]  

(15)

\[ k = \frac{C_s}{C_e} \]  

(16)
where \( k \) is the distribution coefficient for adsorption, \( C_s \) is the concentration of dye adsorbed by the adsorbent at equilibrium (mg L\(^{-1}\)), \( C_e \) is the concentration of dye remains in solution at equilibrium (mg L\(^{-1}\)) and \( R \) is the gas constant (J mol\(^{-1}\) K\(^{-1}\)).

Substitution of Equation 14 into Equation 15 yields the following equation:

\[
\ln k = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} 
\]  

(17)

The linear plot of \( \ln k \) vs. \( T^{-1} \) was used for obtaining the thermodynamics parameters.

2.7. Regeneration experiment

The adsorption capability of CEN was regenerated using three solvents (distilled water, 0.1 mol L\(^{-1}\) HNO\(_3\) and 0.1 mol L\(^{-1}\) NaOH). The detailed procedure of regeneration experiment was described in our previous work (Dahri et al., 2014). Briefly, 0.04 g of CEN was treated with 50 mg L\(^{-1}\) RB and the 2 h of contact time, the dye-treated adsorbent was washed thoroughly using distilled water to desorb the dye. Adsorbent was filtered and dried at 70°C for 24 h, for the next cycle. For acidic and basic washing, dye-treated adsorbents were initially agitated in respective solvents for 30 min, followed by repeated distilled water washing until the washed solution become near neutral. The regeneration experiments were repeated up to the fifth cycle.

3. Result and discussion

3.1. Characterisations of adsorbent

The CHNS analysis and XRF elemental analysis of untreated CEN were reported in our previous work (Dahri, Kooh, & Lim, 2015). The surface morphology of the CEN particle (Figure 1) showed high irregularity, with many observable cavities which may contribute surface area for interaction with dye molecules. The specific surface area of the untreated CEN was also determined in previous work and reported to be 351 m\(^2\) g\(^{-1}\) (Dahri et al., 2015).

FTIR is important to investigate the functional groups present on the adsorbent and is also useful in checking on the loading of dye onto the adsorbent. The FTIR spectra of both untreated CEN and RB-treated CEN were as shown in Figure 2. In the untreated CEN, the following bands were observed: broad adsorption band due to the vibration of –OH and –NH functional groups (3,404 cm\(^{-1}\)), C–H bond in methyl group stretching vibration (2,920 cm\(^{-1}\)), C=O bending (1,620 cm\(^{-1}\)) and C-O-C stretching band (1,049 cm\(^{-1}\)). In the spectrum of CEN after treatment with RB, the bands depicting the OH and NH group (3,412 cm\(^{-1}\)) and C-H (2,922 and 2,852 cm\(^{-1}\)) shifted indicating possible involvement of these functional groups in the adsorption process.
3.2. Effect of dosage

It is important to determine the optimum dosage of adsorbent of CEN–RB adsorption system. The effect of adsorbent dosage is summarised in Figure 3. It can be observed that the increase in adsorbent dosage from 0.01 to 0.04 g led to a gradual increase in the removal of RB dye, and eventually insignificant increase beyond the dosage of 0.04 g. This trend is due to the increase in active sites for the adsorption of RB with increasing adsorbent dosage. High adsorbent dosage results in little improvement in dye adsorbent. This may be due to higher collision rate between the adsorbent particles, resulting in less vacant sites per unit mass of adsorbent available for adsorption, and such collisions may lead to overlapping or aggregation of active sites. Hence, the amount of 0.04 g was chosen as the optimised dosage of adsorbent and was used for the rest of the experiment.

3.3. Effect of pH and ionic strength

Dye molecules mainly interacted with the adsorbent particles by electrostatic interaction, hydrophobic–hydrophobic interaction and hydrogen bonding.

The effect of pH is important because it directly influences the electrostatic interaction of the adsorption system. The effect of pH is summarised in Figure 4(A). The removal of RB was the highest when the initial pH was at pH 2.1 and 2.9. As the pH increases, the removal started to decrease and no further significant decrease was observed beyond pH 6. At solution pH < 4.0, the RB molecules exist in cationic and monomeric forms and it forms dimer at solution pH > 4.0 due to RB molecule exists in zwitterionic form. Despite RB molecule being positively charged in pH 2.1 and 2.9, the
removal of RB was higher than the rest of the pH range. This suggested that electronic interaction might not be the major force in the interaction between the adsorbate and adsorbent. Also, the smaller monomeric RB may diffuse into the micropores of the adsorbent particle more readily than the dimer form (Deshpande & Kumar, 2002; Gad & El-Sayed, 2009).

The point of zero charge (pHpzc) is defined as the solution pH at which the net surface charge of the adsorbent particle is zero. If solution pH > pHpzc, then the adsorbent surface will be predominant negatively charged, while solution pH < pHpzc resulted in predominant positively charged surface. The pHpzc of CEN was determined to be at 4.4, which suggests that optimum adsorption should be above solution pH > 4.4. However, the experimental data disagreed with the concept of pHpzc thereby suggesting the possibility of other attraction forces such as hydrophobic–hydrophobic interaction could be more dominant than electrostatic interaction.

The effect of ionic strength is important to verify the existence of the hydrophobic–hydrophobic interaction which is the attraction between the non-polar groups of the dye with non-polar group of the adsorbent. The data of the effect of ionic strength are summarised in Figure 4(B). It can be observed that an increase in ionic strength (0.1 mol L⁻¹ NaCl) of the solution led to higher adsorption of dye as compared to solution without addition of NaCl. Any further increase in ionic strength did not further improve adsorption of dye. This verified that hydrophobic–hydrophobic interaction may be the dominant attraction force for the CEN–RB adsorption system. This is because in solution of high ionic strength, the electrostatic attraction mechanism is suppressed due to the competition between the cationic dye molecule with the Na⁺ present for the active sites on adsorbent surface, leading to electrostatic repulsion (Hu et al., 2013). High ionic strength can also enhance the hydrophobic–hydrophobic interaction by the compression of the electrical double layer that moves...
particles much closer together, which leads to increase in dye adsorption as observed in Figure 4(B) (Hu et al., 2013; Maurya, Mittal, Cornel, & Rother, 2006). Moreover, the adsorption capability of CEN was enhanced in solution of high ionic strength which is perceived as an advantage in real-life application, where salt content in textile dye wastewater is usually high due to the present of ionic salts in electrolyte, detergent and surfactant used in pre-treatment or post-treatment of fabrics.

3.4. Effect of concentration and isotherm modelling

The effect of dye concentrations on the adsorption capacity of CEN is shown in Figure 5. As the concentration increases, the $q_e$ value increased from 7.3 to 68.1 mg g$^{-1}$. The $q_e$ value steadily increased from 20 to 300 mg L$^{-1}$, reaching a plateau at concentration beyond 300 mg L$^{-1}$. The force of concentration gradient between the RB solution and CEN drove the mass transfer rate (Rehman et al., 2013), hence higher $q_e$ at higher concentration. The amount of active sites on CEN was limited, therefore at lower dye concentration the number of active sites was enough to accommodate the number of dye molecules but then became saturated with dye molecules as the concentration increased. Reaching a plateau signified that the maximum adsorption of dye has been attained, hence no further increase in the $q_e$ value beyond dye concentration of 300 mg L$^{-1}$.

Adsorption isotherm is crucial in the design of adsorption systems in wastewater treatment as it provides insight into interaction between the adsorbate and adsorbent. The equilibrium data obtained for RB onto CEN was fitted to the Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. The best-fit model for the adsorption isotherm was chosen based on the coefficient of determination ($R^2$) value and smallest value of the Chi-square test ($\chi^2$). Table 1 summarised the parameters of the three isotherm models and the Chi-square test error function analysis. It can be observed that the $R^2$ value is the highest for Langmuir isotherm when compared with Freundlich and Dubinin–Radushkevich isotherm models. Furthermore, the chi-square test of the Langmuir isotherm displayed the smallest value, which indicates that the $q_{e,\text{cal}}$ of the Langmuir isotherm is closest to the $q_{e,\text{exp}}$. Therefore with consideration of the $R^2$ and the error functions, it is concluded that the Langmuir isotherm best fitted

| Langmuir | Freundlich | Dubinin–Radushkevich |
|----------|------------|-----------------------|
| $q_m$ (mg g$^{-1}$) | 82.34 | 3.73 | 1.23 |
| $k_L$ (L mg$^{-1}$) | 0.02 | $n_f$ | 1.90 | $q_m$ (mg g$^{-1}$) |
| $R_L$ | 0.11 | | | $E$ (kJ mol$^{-1}$) |
| $R^2$ | 0.99 | $R^2$ | 0.95 | $R^2$ |
| $\chi^2$ | 2.68 | $\chi^2$ | 9.59 | $\chi^2$ | 425.99 |
the experimental data. The $R_L$ and $n_F$ values from the experiment indicate that the adsorption process is favourable.

The maximum monolayer adsorbent capacity predicted by the Langmuir model for CEN is 82.3 mg g$^{-1}$, which is higher than some adsorbents reported in the literature such as the diatomite (21.4 mg g$^{-1}$) (Badii, Ardejani, Saberi, Limaee, & Shafaei, 2010) and base-treated Shorea dasphylla sawdust (24.4 mg g$^{-1}$) (Hanafiah et al., 2012), while comparable to peat (85.5 mg g$^{-1}$) (Chieng et al., 2014) and lower than Penicillium (90.1 mg g$^{-1}$) and Cetlpyridinium-chloride-modified Penicillium (106.4 mg g$^{-1}$) (Yang et al., 2011).

3.5. Effect of contact time and kinetics modelling
The determination of the contact time is important for investigating time taken for the adsorption process to reach equilibrium. The results of the contact time effect are summarised in Figure 6(A). Rapid dye adsorption was observed within the first 20 min, and thereafter gradually slow down to a plateau. Rapid adsorption is due to high availability of active sites for dye interaction, which gradual decreases with time. The plateau signified the attainment of the equilibrium process and contact time of 180 min is seemed sufficient and was applied to all the experiments.

In order to understand the adsorption mechanism, the four mentioned kinetics models were used. The data of various kinetics models are summarised in Table 2. In all the concentrations used, the coefficient of determination, $R^2$, is higher for the pseudo-second-order (>0.99) as shown in Figure 6(B) than the pseudo-first-order (<0.94). This shows that the pseudo-second-order model is a better fit for the experimental data than the pseudo-first-order model. This is further supported by the close values between the predicted values of $q_e$ from pseudo-second-order model to the experimental $q_e$, whereas the pseudo-first-order predicted $q_e$ values greatly deviated from experimental $q_e$. This indicates that the adsorption process follows pseudo-second-order model and appeared to be controlled by chemical process.

As the previous two models are not applicable in identifying the diffusion mechanism, Weber–Morris model and Boyd models were used instead. As the particles are vigorously agitated during the process, it is assumed that mass transfer from the bulk liquid to the particle external surface is not the rate limiting factor but may be film or intraparticle diffusion (Hameed, 2008). According to the Weber–Morris model, the plot of $q_t$ vs. $t^{1/2}$ has to pass through the origin for intraparticle diffusion to be the rate-limiting step.

Intraparticle diffusion model is divided into three phases: the fast external surface adsorption, intraparticle diffusion phase and the slow equilibrium phase due to low adsorbate concentration left in solution resulting in the slowing down of the intraparticle diffusion (Özacar & Şengil, 2004; Zhao et al., 2012). As seen in Figure 6(C), the plots are multi-linear with the first linear section indicating the intraparticle diffusion stage while the other section represents the slow equilibrium stage. The external surface adsorption was not observed and may have rapidly occurred within the first 5 min of the agitation. Similar observation was reported by Özacar and Şengil in the adsorption of disperse dye into alunite (Özacar & Şengil, 2004). As shown in Table 2 and Figure 6(C), none of the regions has $C$ values equal to zero which indicates that these lines do not pass through the origins which suggests that intraparticle diffusion is not the rate-limiting step. The Boyd model also can be used to investigate whether the adsorption is controlled by particle diffusion, where the adsorbate transport occurs within the pores or controlled by film diffusion, in which the transport occurs at the external surface (Tavlieva, Genieva, Georgieva, & Vlaev, 2013). According to the Boyd model, if the plot $B_t$ against $t$ (not shown) is a straight line passing through the origin then the process is controlled by particle diffusion. Otherwise, the process is controlled by film diffusion. From Table 2, the intercepts of all three dye concentrations were not zero, which indicates that the adsorption process might be controlled by film diffusion.
3.6. Effect of temperature and thermodynamics studies

The effect of temperature was investigated from 25 to 65°C with 50 mg L⁻¹ RB. The adsorption capacities of CEN at 25, 35, 45, 55 and 65°C were 18.1, 19.5, 21.2, 21.2 and 21.2 mg g⁻¹, respectively. The increase of $q_e$ with an increasing temperature indicated that adsorption process is endothermic in nature.

Thermodynamics studies are useful for the determination of the change of Gibbs free energy ($\Delta G^\circ$), change in enthalpy ($\Delta H^\circ$) and the changes in entropy ($\Delta S^\circ$). These thermodynamic parameters were calculated from the linear plot of ln $K$ against $T^{-1}$ which yielded $R^2$ of 96.8%. The $\Delta G^\circ$ was found to be $-2.25$, $-3.08$, $-4.18$, $-5.01$ and $-5.33$ kJ mol⁻¹ at temperature 25, 35, 45, 55 and 65°C, respectively. The $\Delta G^\circ$ becomes less positive with an increasing temperature indicated the spontaneity of
CEN–RB adsorption system. The value of \( \Delta H^\circ \) was determined to be 20.1 kJ mol\(^{-1}\). The positive value of \( \Delta H^\circ \) indicates that CEN–RB adsorption system is endothermic in nature. The low value of \( \Delta H^\circ \) suggested that this adsorption system may operate mainly by physical adsorption, which is backed by the experimental data in the effect of pH and ionic strength. The \( \Delta S^\circ \) was determined to be at 75.0 J mol\(^{-1}\) K\(^{-1}\). The positive value of \( \Delta S^\circ \) is resulted from the increased randomness at the solid–liquid interface during the adsorption of RB dye molecules on the active sites of the adsorbent surface. The positive value of \( \Delta S^\circ \) also suggests good affinity of RB towards the adsorbent.

### 3.7. Regeneration experiment

Spent adsorbents that contained hazardous dye must be disposed properly and cannot be dumped to landfill as the dye may leach out. The conventional way of disposing dye hazardous waste is by incineration. However, the release of poisonous gases and other side products is always possible. The cost of fuel also increases the total cost of treatment. Regeneration experiment explored an alternative way to incineration of spent adsorbent, and the reusability of the adsorbent provides added value to this adsorbent as a more sustainable option.

The data of regeneration experiment are summarised in Figure 7. Among the three studied solvents, 0.1 mol L\(^{-1}\) HNO\(_3\) is the most effective in regenerating the spent adsorbent. Data showed that
the adsorbent was able to adsorb dye at an amount close to unused sample at the first washed cycle (approximately 19 mg g\(^{-1}\)), and decreased by half on the second wash cycle. The adsorption capacity remained almost the same at approximately 10 mg g\(^{-1}\) from second washed cycle to the fifth.

4. Conclusions

In the study, CEN was applied successfully applied for the removal of RB from aqueous solution making it as a potential low-cost adsorbent. The process has considerably fast kinetic which achieve equilibrium at 2 h. Of the three isotherm models, the Langmuir best fitted with the experimental data with \(q_e\) value of 82.34 mg g\(^{-1}\). The studies on the effect of pH and ionic strength provide insights that hydrophobic–hydrophobic interaction may be more dominant than electrostatic interaction. The presence of salt and increase in temperature enhanced the adsorption process of RB onto CEN. These observations can introduce CEN as a potential adsorbent as dye wastewater usually contain high ionic strength and extreme pH.

Acknowledgement

The authors would like to thank the Government of Brunei Darussalam and the Universiti Brunei Darussalam for their supports.

Funding

The authors received no direct funding for this research.

Author details

Muhammad Raziq Rahimi Kooh\(^1\)
E-mail: chernyuan@hotmail.com
Linda B.L. Lim\(^1\)
E-mail: linda.lim@ubd.edu.bn

\(^1\) Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, Pengkalang Gadong, Bandar Seri Begawan, BE 1410, Brunei Darussalam.

Citation information

Cite this article as: The removal of rhodamine B dye from aqueous solution using CEN at equilibrium at 2 h. Of the three isotherm models, the Langmuir best fitted with the experimental data with \(q_e\) value of 82.34 mg g\(^{-1}\). The studies on the effect of pH and ionic strength provide insights that hydrophobic–hydrophobic interaction may be more dominant than electrostatic interaction. The presence of salt and increase in temperature enhanced the adsorption process of RB onto CEN. These observations can introduce CEN as a potential adsorbent as dye wastewater usually contain high ionic strength and extreme pH.

References

Ahmed, T. F., Sushil, M., & Krishna, M. (2012). Impact of dye industrial effluent on physicochemical characteristics of Kshira River, Ujjain City, India. International Research Journal of Environmental Sciences, 1, 41–45.

Anilker, R., & Moser, P. (1987). The limits of bioaccumulation of organic pigments in fish: Their relation to the partition coefficient and the solubility in water and octanol. Ecotoxicology and Environmental Safety, 13, 43–52. http://dx.doi.org/10.1016/0013-9341(87)90041-8

Aworneso, J. A., Toiwo, A. M., Gbadebo, A. M., & Adenowo, J. A. (2010). Studies on the pollution of water body by textile industry effluents in Lagos, Nigeria. Journal of Applied Sciences in Environmental Sanitation, 5, 353–359.

Bodli, K., Arefijani, F. D., Sabeti, M. A., Lirmoe, N. Y., & Shafoei, S. (2010). Adsorption of acid blue 25 dye on diatomite in aqueous solutions. Indian Journal of Chemical Technology, 17, 7–16.

Boyd, G. E., Adamson, A. W., & Myers Jr., L. S. M. (1947). The exchange adsorption of ions from aqueous solutions by organic zeolites. II. kinetics. 1. Journal of the American Chemical Society, 69, 2836–2848. http://dx.doi.org/10.1021/ja01030a066

Cheng, H. I., Lim, L. B. L., & Priyanta, N. (2014). Sorption characteristics of peat from Brunei Darussalam for the removal of rhodamine B dye from aqueous solution: adsorption isotherms, thermodynamics, kinetics and regeneration studies. Desalination and Water Treatment. doi:10.1080/19443994.2014.919609

Crittenden, R., & Moser, P. (1987). The limits of bioaccumulation of organic pigments in fish: Their relation to the partition coefficient and the solubility in water and octanol. Ecotoxicology and Environmental Safety, 13, 43–52. http://dx.doi.org/10.1016/0013-9341(87)90041-8

Diem, H. G., Gauthier, D., & Dommergues, Y. (1982). Isolation of Frankia from nodules of Casuarina equisetifolia. Canadian Journal of Microbiology, 28, 526–530. http://dx.doi.org/10.1139/m82-079

Dubinin, M. M., & Radushkevich, L. V. (1947). Equation of the characteristic curve of activated charcoal. Proceedings of the National Academy of Sciences, 55, 331–337.

Freundlich, H. M. F. (1906). Über die Adsorption in Lösung. The Journal of Physical Chemistry, 57, 385–471.

Gad, H. M., & El-Sayed, A. A. (2009). Activated carbon from agricultural by-products for the removal of rhodamine-B from aqueous solution. Journal of Hazardous Materials, 168, 1070–1081. http://dx.doi.org/10.1016/j.jhazmat.2009.02.155

Hameed, B. H. (2008). Equilibrium and kinetic studies of methyl violet sorption by agricultural waste. Journal of Hazardous Materials, 154, 204–212. http://dx.doi.org/10.1016/j.jhazmat.2007.10.010

Hanafiah, M. A. K. M., Ngah, W. S. W., Zolkafly, S. H., Teong, L. C., & Majid, Z. A. A. (2012). Acid blue 25 adsorption on base treated Shorea dasyphylla sawdust: Kinetic, isotherm, thermodynamic and spectroscopic analysis. Journal of Environmental Sciences, 24, 261–268. http://dx.doi.org/10.1016/j.jes.2011.01.007

Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. Process Biochemistry, 34, 451–465. http://dx.doi.org/10.1016/S0031-9422(98)00112-5
Hu, Y., Guo, T., Ye, X., Li, Q., Guo, M., Liu, H., & Wu, Z. (2013). Dye adsorption by resins: Effect of ionic strength on hydrophobic and electrostatic interactions. Chemical Engineering Journal, 228, 392–397. http://dx.doi.org/10.1016/j.cej.2013.04.116

Jamiludheen, V. & Kumar, B. M. (1999). Litter of multipurpose trees in Kerala, India: Variations in the amount, quality, decay rates and release of nutrients. Forest Ecology and Management, 115, 1–11. http://dx.doi.org/10.1016/S0378-1127(98)00439-3

Kooh, M. R. R., Lim, L. B. L., Dahri, M. K., Lim, L. H., & Bandara, J. M. R. (2013). Azolla pinnata: An efficient low cost material for removal of methyl violet 2B by using adsorption method. Waste and Biomass Valorization, 6, 547–559. http://dx.doi.org/10.1007/s12649-015-9369-0

Kooh, M. R. R., Lim, L. B. L., Lim, L. H., & Bandara, J. M. R. S. (2015). Batch adsorption studies on the removal of malachite green from water by chemically modified Azolla pinnata. Desalination and Water Treatment. doi:10.1080/19443994.2015.1065450

Lagergren, S. (1898). Zur Theorie der Sogenannten Adsorption gel ster Stoffe. Kgl. Svenska Vetenskaps Akademiens Handlingar, 24, 1–39.

Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. Part I. Solids. Journal of the American Chemical Society, 38, 2221–2295. http://dx.doi.org/10.1021/ja02280b002

Lim, L. B. L., Priyantha, N., Chan, C. M., Matassan, D., Chieng, H. I., & Kooh, M. R. R. (2014). Adsorption behavior of methyl violet 2B using duckweed: Equilibrium and kinetics studies. Arabian Journal for Science and Engineering, 39, 6757–6765.

Maurya, N. S., Mittal, A. K., Cornell, P., & Rother, E. (2006). Biosorption of dyes using dead macro fungi: Effect of dye structure, ionic strength and pH. Bioresource Technology, 97, 512–521. http://dx.doi.org/10.1016/j.biortech.2005.02.045

Özacar, M., & Şengil, İ. A. (2004). Application of kinetic models to the sorption of disperse dyes onto alunite. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 242, 105–113.

Rehman, M. S. U., Munir, M., Ashfaq, M., Roshid, N., Nazar, M. F., Danish, M., & Han, J.-I. (2013). Adsorption of brilliant green dye from aqueous solution onto red clay. Chemical Engineering Journal, 228, 54–62. http://dx.doi.org/10.1016/j.cej.2013.04.094

Santhi, T., Prasad, A. L., & Manonmani, S. (2014). A comparative study of microwave and chemically treated Acacia nilotica leaf as an eco friendly adsorbent for the removal of rhodamine B dye from aqueous solution. Arabian Journal of Chemistry, 7, 494–503. http://dx.doi.org/10.1016/j.arabjc.2010.11.008

Sigma-Aldrich. (2014). Rhodamine B [Material Safety Data Sheet] Version 5.4. Retrieved September 21, 2015, from http://www.sigmaaldrich.com/MSDS/MSDS05006/PrintMSDSAction.do?name=msdsidxf_150379221603834

Tavlieva, M. P., Genieva, S. D., Georgieva, V. G., & Vlaev, L. T. (2013). Kinetic study of brilliant green adsorption from aqueous solution onto white rice husk ash. Journal of Colloid and Interface Science, 409, 112–122. http://dx.doi.org/10.1016/j.jcis.2013.07.052

Tsai, S. C., & Jiang, K. W. (2000). Comparison of linear and nonlinear forms of isotherm models for strontium sorption on a sodium bentonite. Journal of Radioanalytical and Nuclear Chemistry, 243, 741–746. http://dx.doi.org/10.1023/A:10102510.10253.10

Weber, W., & Morris, J. (1963). Kinetics of adsorption on carbon from solution. Journal of the Sanitary Engineering Division, 89, 31–60.

Yang, Y., Jin, D., Wang, G., Liu, D., Jia, X., & Zhao, Y. (2011). Biosorption of acid blue 25 by unmodified and CPC-modified biomass of penicillium YM01: Kinetic study, equilibrium isotherm and FTIR analysis. Colloids and Surfaces B: Biointerfaces, 88, 521–526. http://dx.doi.org/10.1016/j.colsurfb.2011.07.047

Zehra, T., Priyantha, N., Lim, L. B. L., & Iqbal, E. (2014). Sorption characteristics of peat of Brunei Darussalam V: Removal of Congo red dye from aqueous solution by peat. Desalination and Water Treatment, 54, 2592–2600.

Zhao, Y., Yue, Q., Li, Q., Xu, Y., Yang, Z., Wang, X., … Yu, H. (2012). Characterization of red mud granular adsorbent (RMGA) and its performance on phosphate removal from aqueous solution. Chemical Engineering Journal, 193–194, 161–168. http://dx.doi.org/10.1016/j.cej.2012.04.040