Biochars prepared from rabbit manure for the adsorption of rhodamine B and Congo red: characterisation, kinetics, isotherms and thermodynamic studies

Wen Huang, Min Zhang, Yinhai Wang, Jiao Chen and Jianqiang Zhang

ABSTRACT

Biochar was prepared from rabbit faeces (RFB550) at 550°C through pyrolysis and was characterised using elemental analysis, scanning electron microscopy, Brunauer–Emmett–Teller analysis and Fourier transform infrared spectroscopy (FTIR). The related factors, kinetics, isothermal curves and thermodynamics of the adsorption behaviours were investigated by conducting batch experiments. The results revealed the adsorption equilibrium of rhodamine B (RhB) and Congo red (CR) onto RFB550 with initial concentrations of 30 mg·L⁻¹ at 25°C and 210 min, and the best adsorption was observed when the pH of the RhB and CR solutions was 3 and 5, respectively. Pseudo-second-order kinetics was the most suitable model for describing the adsorption of RhB and CR onto RFB550, indicating that the rate-limiting step was mainly chemical adsorption. The isotherm data were best described by the Freundlich model, and the adsorption process was multi-molecular layer adsorption. Thermodynamic parameters revealed the spontaneous adsorption of RhB and CR onto RFB550. According to the results of the FTIR analysis, the oxygen-containing functional groups and aromatic structures on the surface of RFB550 provided abundant adsorption sites for RhB and CR, and the adsorption mechanism was potentially related to the hydrogen bonds and π-π bonds.

Key words | biochar, isotherms, kinetics, rabbit faeces, thermodynamics

INTRODUCTION

Dyes are widely used in the textile, paper, medicine, food and plastic industries due to their low cost, stable nature and variety. Dyes are poorly biodegradable, highly toxic and have a complex composition and deep colours. At the same time, most dyes and their metabolic intermediates possess mutagenic and carcinogenic potential, as well as other characteristics (Khattri & Singh 2013). Wastewater that contains dyes does not easily meet the emission requirements after biological treatment. Thus, the extensive use of dyes causes a human health concern and water pollution. To date, several methods have been developed to remove dyes from aqueous solutions, such as adsorption (Cheng et al. 2018; Zhang et al. 2018), advanced oxidation (Dawood & Sen 2012) and membrane separation (Basilak et al. 2016). Activated carbon adsorption has exhibited good performance in removing dyes; however, its application has been restricted by its high cost. The identification of new adsorption materials that are cleaner, more efficient and inexpensive has therefore become a research hotspot in recent years.

Biochar is a carbonaceous material produced by pyrolysis of biomass under limited or absence of oxygen conditions. Its highly aromatic structure and abundance of oxygen-containing functional groups endow the biochar with good adsorption sites and stability. Recently, several studies examining the adsorption of dyes by biochar have been reported. However, these studies primarily used Korean cabbage (Sewu et al. 2017), straw (Lian et al. 2016), Pongamia glabra seed cover (Bordoloi et al. 2018) and other plants as raw materials to prepare biochar, but its preparation from animal manure as the source material for dye adsorption has rarely been reported. The adsorption properties and mechanism by which biochar adsorbs different types of dyes have not been clearly elucidated. This study therefore used rabbit faeces as the raw material to prepare a biochar for the adsorption rhodamine B (RhB) and Congo red (CR). The effects of the solution pH, biochar concentration, adsorption time and temperature on the adsorption effect were investigated. Based on this information, the adsorption...
mechanism was analysed using kinetic, isothermal and ther-

dynamic models to provide a theoretical basis for the
targeted selection of animal-derived biochar applications.

**MATERIALS AND METHODS**

**Materials**

Biomass waste solids of rabbit faeces were collected from a
rabbit farm in Pixian, Chengdu. RhB and CR were pur-
chased from Tianjin Ruijin Special Chemical Co. Stock
solutions of 1,000 mg · L⁻¹ RhB and CR were prepared
diluted to the required concentration (5–250 mg · L⁻¹).
The initial pH of the RhB and CR solutions was adjusted
by adding 1 · L⁻¹ sodium hydroxide (NaOH) and 1 mol/L
hydrochloric acid (HCl) solutions. All the reagents used in
the experiment were analytically pure, and the water used
in this study was deionised water.

**Preparation of biochar**

The rabbit faeces were ground through an 80-mesh sieve after
drying and removing the impurities. Appropriate amounts of
sifted materials were weighed, placed into a crucible, com-
pacted and covered, and then placed in a stainless steel
cylinder. The air in the cylinder was removed by purging it
with nitrogen gas to ensure an oxygen-free atmosphere, and
the cylinder was then placed in the furnace. The temperature
was further increased to 550 °C at a rate of approximately
15 °C per minute and incubated for 150 min. After cooling
to room temperature, 20 mL of HCl (1.0 mol/L) was added
to the resulting material in 1:25 solid:liquid ratio (m:V), and
the solution was shaken at 150 rpm for 30 min. The products
were rinsed with deionised water to achieve a neutral pH and
the process was repeated three times to remove the ash.
Finally, the products were dried at 100 °C for 48 h and then
passed through a 100-mesh sieve. Based on the charring tem-
perature, the rabbit faeces biochar was labelled as RFB550.

**Biochar characterisation**

The contents of carbon (C), hydrogen (H), nitrogen (N) and
oxygen (O) were measured using an elemental analyser.
The surface physical morphology of RFB550 was observed
using a scanning electron microscope (SEM). The surface
area and porosity of RFB550 were determined using the
Brunauer–Emmett–Teller (BET) method. The functional
groups on the surface of RFB550 were determined using
Fourier transform infrared spectroscopy (FTIR).

**Adsorption experiments**

Adsorption experiments were conducted using a 250 mL
Erlenmeyer flask and 100 mL of 30 mg · L⁻¹ RhB and CR
solutions.

1. pH effect: For this experiment, 1 mol · L⁻¹ HCl or NaOH
was added to the RhB and CR solutions to adjust the pH
to 3–11. Then, 0.07 g of RFB550 was added to each sol-
ution with different pH values. The pH of the RhB and
CR solutions was adjusted to 3 and 5, respectively, in sub-
sequent experiments.

2. Effect of the biochar concentration: Different concen-
trations of RFB550 were added to prepare solutions with
liquid:solid ratios ranging from 0.7 to 2 g · L⁻¹.

3. Effect of the contact time: First, 0.09 g or 0.15 g RFB550
was added to RhB and CR solutions with a concentration
of 30 mg · L⁻¹. Next, samples were analysed at 10, 30, 50,
70, 90, 120, 150, 210, 300, 400 and 500 min.

4. Temperature effect: For this experiment, 0.09 g or 0.15 g
RFB550 was added to RhB and CR solutions. The samples
were placed in an oscillating shaker operated at 180 rpm
for 210 min. The experiment was conducted at 5 °C,
15 °C, 25 °C, 35 °C and 45 °C. After shaking, the suspensions
were centrifuged at 4,000 rpm for 5 min and the
absorbance of the clear solution was measured using a
spectrophotometer (the wavelengths were set to 554 nm
and 499 nm respectively, UV-1800PC, HITACHI, Japan).

**Adsorption kinetics**

Based on the parameters observed from the experiments
described above, the pH of the RhB and CR solutions was
adjusted to 3 and 5, respectively, and 0.09 g and 0.15 g
RFB550 were added to different initial concentrations (30
and 60 mg · L⁻¹) of RhB and CR. All samples were analysed
at 10, 30, 50, 70, 90, 120, 150, 210, 300, 400 and 500 min.
The other steps were the same as described above. The
amounts of adsorbed RhB and CR (qt, mg · g⁻¹) and removal
rates (η, %) were calculated using Equations (1) and (2),
respectively. The adsorption kinetic models are shown in
Equations (3)–(6) (Yang & Jiang 2014).

\[
q_t = (C_0 - C_t)V/m \quad (1)
\]

\[
\eta = \left(\frac{C_0 - C_t}{C_0}\right) \times 100%/C_0 \quad (2)
\]

where \(C_0\) and \(C_t\) are the initial and equilibrium concen-
trations of RhB and CR, respectively, in mg · L⁻¹; \(V\) is the
volume of the solution in mL; and \( m \) is the mass of the biochar in g.

Pseudo-first-order kinetic model:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(3)

Pseudo-second-order kinetic model:

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}
\]  

(4)

Intra-particle diffusion model:

\[
q_t = k_3 t^{0.5} + C
\]  

(5)

Elovich model:

\[
q_t = A + B \ln t
\]  

(6)

where \( q_e \) (mg · g\(^{-1}\)) is equilibrium amount of RhB and CR adsorbed; \( q_t \) (mg · g\(^{-1}\)) is the amount of RhB and CR adsorbed at time \( t \); \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g · (mg · min\(^{-1}\)) \(^{-1}\)) and \( k_3 \) (mg · (g · min\(^{0.5}\)) \(^{-1}\)) are the rate constants of the pseudo-first-order, pseudo-second-order and intra-particle diffusion models, respectively; \( t \) (min) is the contact time; and \( A, B \) and \( C \) are correlation constants.

Adsorption isotherm and thermodynamic models

In the present study, the pH of the RhB and CR solutions was adjusted to 3 and 5, respectively, and 0.09 g and 0.15 g RFB550 were added to different initial concentrations of RhB and CR (20, 30, 40, 50, 60 and 80 mg · L\(^{-1}\)). The flasks were agitated at 180 rpm for 210 min at 25°C, 35°C and 45°C. The other steps were the same as described above. The adsorption isotherm model is shown in Equations (7) and (8), and the adsorption thermodynamic model is shown in Equations (9) and (10) (Mandal et al. 2017).

Langmuir model: \( q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \)  

(7)

Freundlich model: \( q_e = K_F C_e^{1/n} \)  

(8)

where \( q_e \) (mg · g\(^{-1}\)) is the equilibrium amounts of RhB and CR adsorbed; \( q_m \) (mg · g\(^{-1}\)) is the theoretical maximum amount of RhB and CR adsorbed, respectively; \( C_e \) (mg · L\(^{-1}\)) is the RhB and CR concentration at equilibrium; \( K_L \) (L · mg\(^{-1}\)) and \( K_F \) (mg · g\(^{-1}\)(mg · L\(^{-1}\)) \(^{-n}\)) are equilibrium constants for the Langmuir and Freundlich model, respectively; and \( 1/n \) is the index of the Freundlich model.

\[
\Delta G^\theta = -RT \ln K_e
\]  

(9)

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

(10)

where \( R \) (8.314 J · (mol · K)\(^{-1}\)) is the ideal gas constant; \( T \) is the temperature in Kelvin(K); \( \Delta G^\theta \) (kJ · mol\(^{-1}\)) is the change in the Gibbs free energy; \( \Delta H^\theta \) (kJ · mol\(^{-1}\)) is the change in enthalpy; \( \Delta S^\theta \) (kJ · (mol · K)\(^{-1}\)) is the change in entropy; and \( K_e \) is the thermodynamic constant.

RESULTS AND DISCUSSION

Biochar characterisation

The elemental composition of RFB550 is presented in Table 1. RFB550 contains a large amount of C and lower levels of H, O and N. Generally, the aromaticity and carbonisation level of the adsorbate are determined according to the H/C ratio, and adsorbate polarity is generally determined by the O/C and (O + N)/C ratios. (Schimmelpfennig & Glaser 2012). A lower H/C ratio indicates a higher carbonation level and aromaticity, and higher O/C and (O + N)/C ratios indicate an increase in the polarity of the biochar. In this study, H/C < 0.6 and O/C < 2.0, indicating that RFB550 had high aromaticity and stability. The BET surface area, total pore volume and average pore diameter of RFB550 were 42.66 m\(^2\) · g\(^{-1}\), 0.138 cm\(^3\) · g\(^{-1}\) and 9.91 nm, respectively. The SEM images of RFB550 are shown in Figure 1. The surface of RFB550 was rough and

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass composition</td>
<td>Ash content/%</td>
</tr>
<tr>
<td></td>
<td>C/%</td>
</tr>
<tr>
<td></td>
<td>H/%</td>
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<tr>
<td></td>
<td>O/%</td>
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<tr>
<td></td>
<td>N/%</td>
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<tr>
<td>Atomic ratio</td>
<td>H/C</td>
</tr>
<tr>
<td></td>
<td>O/C</td>
</tr>
<tr>
<td></td>
<td>(O + N)/C</td>
</tr>
<tr>
<td>Surface area (m(^2) · g(^{-1}))</td>
<td>42.66</td>
</tr>
<tr>
<td>Total pore volume (cm(^3) · g(^{-1}))</td>
<td>0.138</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>9.91</td>
</tr>
</tbody>
</table>
uneven, with a large number of irregular pores per unit area. As a result, the stronger aromaticity and polarity, large specific surface area and rich pore structure of RFB550 provides favourable conditions for RhB and CR adsorption onto RFB550.

**Preliminary adsorption studies**

**Effect of pH on adsorption**

The pH of the solution is an important factor affecting the adsorption process because it not only alters the surface protonation state of the adsorbent but also affects the speciation of the adsorbate. The effects of different initial solution pH values on the adsorption of RhB and CR onto RFB550 are shown in Figure 2(a). The removal rate of RhB by RFB550 decreased as the pH increased. Under acidic conditions, the surface functional groups of RFB550 were highly protonated and the adsorption effect was increased by ion exchange with RhB quaternary ammonium cations or molecules in solution. Under alkaline conditions, RFB550 was deprotonated and the RhB in the solution underwent carboxyl ionisation, resulting in the production of an amphoteric compound containing both a quaternary ammonium cation and carboxyl anion. The mutual polymerisation or precipitation between RhB leads to poor adsorption (Li et al. 2010; Almasi et al. 2012). At pH5, the sulfonic acid group of CR (−SO3Na) will be hydrolysed into a...
negatively charged ion (\(-\text{SO}_3^-\)) and the surface functional groups of RFB\(_{550}\) become protonated (Ahmad & Kumar 2010; Zhang et al. 2011), Therefore, the best adsorption effect was mediated by electrostatic attraction. However, as the pH increased the protonation of RFB\(_{550}\) and electrostatic attraction gradually decreased, resulting in a decrease in the removal rate. Therefore, the optimal pH values for RhB and CR adsorption by RFB\(_{550}\) are 3 and 5, respectively.

**Effect of the biochar concentration**

The effects of different RFB\(_{550}\) concentrations on RhB and CR adsorption are shown in Figure 2(b). According to the results, the RhB and CR removal rates of RFB\(_{550}\) increased and then tended to plateau as the RFB\(_{550}\) concentration increased, which was related to the increases in the specific surface area and active adsorption sites for RhB and CR as the biochar concentration increased. In contrast, the RhB and CR adsorption capacity of RFB\(_{550}\) decreased as the RFB\(_{550}\) concentration increased. When the concentration of RFB\(_{550}\) increased from 0.7 to 2 g·L\(^{-1}\), the adsorption capacity for RhB and CR decreased from 34.87 to 15.00 mg·g\(^{-1}\) and 21.92 to 9.65 mg·g\(^{-1}\), respectively. An excess concentration of RFB\(_{550}\) decreased the equilibrium concentrations of RhB and CR in the liquid phase, and the amounts of RhB and CR adsorbed decreased per unit mass of RFB\(_{550}\).

**Effect of contact time**

The effects of contact time on RhB and CR removal are shown in Figure 2(c). The adsorption process was divided into three stages: I, rapid adsorption phase (10–50 min); II, slow diffusion phase (50–180 min) and III, adsorption equilibrium phase (180–500 min). In the rapid adsorption phase, the adsorption sites of RFB\(_{550}\) were abundant and the highest concentrations of RhB and CR were adsorbed. RhB and CR quickly occupied the active sites through the action of mass transfer, and thus the highest removal rates were achieved. At this stage, the amounts of RhB and CR adsorbed onto RFB\(_{550}\) reached 29.22 and 10.72 mg·g\(^{-1}\), respectively. In the slow diffusion phase, with an increase in the contact time, the surface active sites of RFB\(_{550}\) and the residual RhB and CR concentrations in the solution decreased; thus, the removal rate increased slowly with the reduction in the mass transfer driving force. In the adsorption equilibrium phase, the adsorption tends to be saturated, and the amount adsorbed and removal rate change little over time. At 180 min, the adsorption reached equilibrium and the amounts of RhB and CR adsorbed onto RFB\(_{550}\) were 30.99 and 12.50 mg·g\(^{-1}\), respectively.

**Effect of temperature**

The dye-containing wastewater, which is directly discharged from the actual printing and dyeing process, reaches temperatures greater than 80 °C. After heat recovery, the residual temperature is approximately 40 °C. An analysis of the characteristics of the adsorption of organic dyes onto biochar at higher temperatures is therefore crucial. Figure 2(d) shows the adsorption performance for RhB and CR onto RFB\(_{550}\) at different temperatures. When temperature increased from 5 to 45 °C, the amounts of RhB and CR adsorbed onto RFB\(_{550}\) increased from 28.36 to 31.84 mg·g\(^{-1}\) and 11.59 to 13.93 mg·g\(^{-1}\), respectively. Meanwhile, the corresponding removal rates increased from 85.09% to 95.53% and 57.93% to 69.63%, respectively. Based on these results, when the temperature increased, the porosity and total pore volume of the RFB\(_{550}\) and diffusion rate of RhB and CR increased, resulting in increases in the amounts of RhB and CR adsorbed and removal rates (Hameed & Ahmad 2009).

**Adsorption kinetics**

The kinetics of the adsorption of different initial concentrations of RhB and CR solutions (50 and 60 mg·L\(^{-1}\), respectively) were analysed using a pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich models to further study the mechanism by which RFB\(_{550}\) adsorbs RhB and CR. The kinetic curves of RhB and CR adsorption onto RFB\(_{550}\) are presented in Figure 3 and the parameters are shown in Table 2. RhB and CR adsorption fitted best to the pseudo-second-order model with coefficient of correlation \((R^2)\) greater than 0.90. The values of \(q_e\) calculated by fitting the equation were very close to the experimental \(q_e\) values, and the relative error was less than 4.67%. The pseudo-second-order kinetic model reflected the entire adsorption process, namely liquid film diffusion, surface adsorption and intra-particle diffusion (Fan et al. 2016). RhB and CR therefore probably adsorbed onto RFB\(_{550}\) through multiple mechanisms. The rate-limiting step was mainly chemical adsorption (Sun et al. 2014). The rate constant \(k_2\) decreased with increasing initial concentrations of RhB and CR, indicating that mass transfer was more likely to occur at higher RhB and CR concentrations. Considering the results of the intra-particle diffusion model, the coefficient of correlation \((R^2)\) increased as the
RhB and CR concentrations increased, indicating that a high initial concentration was favourable for the RhB and CR molecules to diffuse inside the RFB550 particles, but $R^2 < 0.71$ and $C \neq 0$, indicating that intra-particle diffusion was not the only rate-limiting step. The Elovich model fit well to the kinetic data, indicating that the adsorption of RhB and CR onto RFB550 was not a simple first-order reaction and adsorption was an integrated process controlled by the reaction rate and diffusion (Wu et al. 2009), as consistent with the results of the fits to the pseudo-second-order kinetic and intra-particle diffusion models.

### Adsorption isotherms and thermodynamics

The sorption equilibrium data obtained at different temperatures were analysed using the Langmuir and Freundlich models. The results are shown in Figure 4 and Table 3. The adsorption reached equilibrium when the initial concentrations of RhB and CR were 30 mg · L$^{-1}$ and 20 mg · L$^{-1}$, respectively. Coefficient of correlation indicated that the Freundlich model ($R^2 > 0.95$) described the adsorption process well. The adsorption of RhB and CR onto RFB550 was therefore a multi-molecular layer adsorption

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**Figure 3** | Adsorption kinetics curves of RhB and CR onto RFB550: (a) pseudo-first-order model, (b) pseudo-second-order model, (c) intra-particle diffusion model, and (d) Elovich model.

**Table 2** | Kinetic parameters for the adsorption of RhB and CR onto RFB550

<table>
<thead>
<tr>
<th>Initial concentration (~ L$^{-1}$)</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
<th>Intra-particle diffusion model</th>
<th>Elovich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$</td>
<td>$k_1$</td>
<td>$R^2$</td>
<td>$q_e$</td>
</tr>
<tr>
<td>20 RhB</td>
<td>30.182</td>
<td>0.193</td>
<td>0.6888</td>
<td>30.850</td>
</tr>
<tr>
<td>20 CR</td>
<td>11.738</td>
<td>0.108</td>
<td>0.5911</td>
<td>12.392</td>
</tr>
<tr>
<td>60 RhB</td>
<td>47.608</td>
<td>0.122</td>
<td>0.6313</td>
<td>49.932</td>
</tr>
<tr>
<td>60 CR</td>
<td>21.905</td>
<td>0.033</td>
<td>0.7858</td>
<td>23.611</td>
</tr>
</tbody>
</table>
process, and the amount adsorbed would continue to increase when the concentration of adsorbate was high (Delle Site 2001). This finding was consistent with the results of the fits to the kinetic models. In addition, the constant $K_F$ positively reflected the adsorption capacity. In this study, the $K_F$ value of RhB was higher than CR, indicating that the adsorption capacity of RFB550 for RhB was greater than CR. The factor $1/n$ reflected the surface homogeneity of adsorption. Values of $1/n < 0.5$ indicate that the adsorption process was easily completed, whereas values of $1/n > 2$ indicate that the adsorption process was more difficult to complete (Shi et al. 2014). In the present study, the values of $1/n$ for RhB and CR were all lower than 0.33, indicating that the adsorption of RhB and CR onto RFB550 readily occurred.

Thermodynamic fitting results are shown in Figure 4 and Table 4. The negative values for $\Delta G$ at different temperatures suggested that the adsorption of RhB and CR onto RFB550 occurred in a spontaneous process. In

![Figure 4](image_url)

**Figure 4** Isothermal and thermodynamic adsorption curves of RhB and CR onto RFB550.

| Table 3 | Langmuir and Freundlich isotherm parameters for RhB and CR adsorption |
| --- | --- | --- | --- |
| | Langmuir model | Freundlich model |
| | $q_m$ | $K_L$ | $R^2$ | $K_F$ | $1/n$ | $R^2$ |
| T/K | | | | | |
| RhB | 298 | 58.698 | 0.521 | 0.7994 | 22.990 | 0.305 | 0.9642 |
| | 308 | 61.829 | 0.642 | 0.6966 | 27.095 | 0.283 | 0.9709 |
| | 318 | 65.029 | 0.748 | 0.7305 | 30.080 | 0.275 | 0.9803 |
| CR | 298 | 27.969 | 0.127 | 0.8024 | 7.297 | 0.325 | 0.9632 |
| | 308 | 28.559 | 0.137 | 0.8058 | 7.806 | 0.316 | 0.9607 |
| | 318 | 28.372 | 0.157 | 0.7505 | 8.396 | 0.302 | 0.9553 |
addition, as the temperature increased a greater decrease was observed in the $\Delta G$ values, implying that higher temperatures favour RhB and CR adsorption. The values of $\Delta S^\theta$ and $\Delta H^\theta$ were positive, indicating that adsorption was an endothermic process characterised by an increase in entropy. Generally, when $4 < \Delta H^\theta < 10$ kJ·mol$^{-1}$, the acting force was the van der Waals force; when $2 < \Delta H^\theta < 40$ kJ·mol$^{-1}$, the acting force was the hydrogen bond force. We speculated that the adsorption of RhB onto RFB$_{550}$ was primarily mediated by dipole forces and hydrogen bonds. RFB$_{550}$ mainly adsorbs CR through van der Waals forces, dipole forces and hydrogen bonds.

**FTIR analysis before and after adsorption**

The FTIR spectra of RFB$_{550}$ showed changes in the functional groups on the surfaces of the biochar samples (Figure 5(a)). The absorption peaks at 2,939–2,878 cm$^{-1}$ were assigned to the C–H stretching vibration of methyl groups. The peaks at 3,322, 1,552 and 1,075 cm$^{-1}$ were assigned to the stretching vibration of the phenolic –OH, C–C and C–O bonds in the aromatic ring, and C–O bonds in ester and ether groups, respectively, and the peak at 834 cm$^{-1}$ was assigned to the C–H bond in aromatic and heterocyclic groups (Steinbeiss et al. 2009; Zheng et al. 2013). The abundance of functional groups and aromatic structures on the surface of RFB$_{550}$ provided a good substrate for the adsorption of RhB and CR.

According to Figure 5(b), some positions of the peaks and peak heights were shifted in the samples containing RhB and CR compared with the FTIR spectra of the biochar alone. The band at 3,522 cm$^{-1}$ in the RFB$_{550}$ spectrum shifted to 3,574 and 3,562 cm$^{-1}$, suggesting that hydrogen bonds might form through the interactions of –CH$_3$, –COOH, and N-containing heterocyclic ring in the adsorbate and the oxygen-containing functional groups on RFB$_{550}$. Therefore, we speculated that hydrogen bonds played an important role in the adsorption process. The characteristic C–H, C=O, C=C and C–O peaks shifted, indicating that the C=O, C=C and C–O groups were all involved in the adsorption process. In addition, the C–H absorption peaks at approximately 834 cm$^{-1}$ exhibited a blueshift to a lower wave number, which may be associated with the formation of $\pi$–$\pi$ bonds through the interactions of –COOH and the aromatic structure of the adsorbate and the C–H and C=C functional groups on RFB$_{550}$. After adsorption, the peaks of RhB at 3,500 and 750 cm$^{-1}$ were obviously stronger than the peaks of CR, and this phenomenon might be one of the explanations for the stronger adsorption of RhB onto RFB than CR.

**CONCLUSIONS**

RFB$_{550}$ was produced from rabbit faeces through pyrolysis and displayed high specific surface area, well-developed
porous structure and abundant surface functional groups. The adsorption process of RhB and CR onto RFB550 was more accurately described by the pseudo-second-order model and the Freundlich model, and the fitting results showed that the adsorption process was not a single mechanism. The entire process was jointly controlled by liquid film diffusion, surface adsorption and intra-particle diffusion. The calculated thermodynamic parameters indicated that the adsorption of RhB and CR onto RFB550 was a spontaneous and endothermic process. According to the FTIR analysis, hydrogen bonds and π-π bonds were intimately involved in the adsorption process. The present study shows the promise of rabbit faeces-derived biochar as an effective adsorbent for the removal of atrazine from aqueous solutions.

REFERENCES


