Adsorption of Congo red with hydrothermal treated shiitake mushroom

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Adsorption of Congo red with hydrothermal treated shiitake mushroom

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Abstract
The shiitake mushroom was treated by hydrothermal method to obtain a novel biosorbent. Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) Spectroscopy and Brunauer–Emmett–Teller (BET) method have been used to characterize the physico-chemical properties of the novel biosorbent. Factors affecting the adsorption properties of Congo red onto biosorbent such as pH, dose, time and temperature were investigated respectively. The experimental data more suitable for the langmuir model than the Freundlich model. The maximum adsorption capacity of the biosorbent obtained by the Langmuir model at 293 K was 217.86 mg g⁻¹. The kinetic study illustrated that the adsorption fit the pseudo–first–order model. Thermodynamic analysis indicated that the adsorption reaction was a spontaneous endothermic reaction.

1. Introduction
While the development of industry has brought a rapidly developing economy, it has also brought problems of water pollution that cannot be ignored (Neoh et al 2016). Toxic wastewater is produced in electricity, pharmacy, printing and Papernaking, textiles, and other chemical industries. The various heavy metals and organic pollutants contained in the wastewater are mostly incapable or need hundreds or thousands of years to degrade by nature (Chen et al 2015, Khatri et al 2015).

Traditional sewage treatment methods such as chemical precipitation (Mao–Xu et al 2007), membrane separation (Hou et al 2019), adsorption (Pang et al 2013), activated sludge (Devi and Saroha 2017), etc can treat sewage effectively. The use of adsorbents to treat sewage is a promising method of wastewater treatment, and there’s more and more intellectuals have begun research work on new adsorbents such as graphene (Liu et al 2012), magnetic composites (Foroutan et al 2019, Foroutan et al 2019, Shafiee et al 2019), aluminosilicate monoliths (El–Safty et al 2011), eggshell (Foroutan et al 2019). Biomass materials like cashew nut shell (Senthil Kumar et al 2016), Populus alba (Bonyadi et al 2019), Jujuba seeds (Reddy et al 2012), spent tea leaves (Hameed 2009b), pine sawdust and wheat straw biochars (Yang et al 2018), pomelo peel (Hameed et al 2008), olive mill residues (F et al 2003), rice husk (Han et al 2008), Jute stick powder (Panda et al 2009), canola stalks (Yahya et al 2012), activated palm ash (Hameed et al 2007) have already been studied as adsorbent by researchers. These materials were all some kind of wastes from agriculture that containing lignin, cellulose and hemicellulose (Salleh et al 2011), and because of their biological factors, loose and porous structures, a large number of functional groups like carboxyl group and hydroxyl group can be found on the materials, which gives them good potentials to become adsorbent. Unlike other adsorbents have features of high cost, high energy consumption, and difficult to degrade, there will be better research prospects because of the biomaterials’ efficient, green, renewable and low cost characteristics.

Shiitake mushrooms are widely distributed in southern China, and are popular among people because they are not only edible but also have certain medicinal value (Tian et al 2016). However, expired mushrooms are...
inedible and can only be thrown away as garbage, so the reuse of expired mushrooms is a problem that must be solved.

Congo red, a typical disazo dye with four color-assisting groups (amino and sodium sulfonate), an anionic dyes widely used in the papermaking, textiles and plastic industries (Du 2014). This dye can be discharged with sewage and poses a great environmental problem because of poor degradation. This study completed the secondary use of shiitake mushrooms to treat Congo red in aqueous solution as an adsorbent.

2. Material and method

2.1. Materials
The shiitake mushrooms were provided by a supermarket and the culture medium is similar to the article (Naeimi et al 2018). KOH and other chemicals and reagents used in this experiment are of analytical grade, no further purification and purchased from Sinopharm Chemical Reagent Co. Ltd, China.

2.2. Preparation of adsorbent
The shiitake mushrooms was thoroughly rinsed with water, then freeze-dried for 24 h to remove the water and pulverized into particles having a maximum side length of no more than 5 mm. 25 g of KOH was dissolved in 100 ml of deionized water, 4 g of the pulverized shiitake mushroom was immersed in the KOH solution and sealed 24 h for completely infiltration. After that, the shiitake mushroom was transferred together with the remaining solution into a Teflon-lined stainless steel autoclave. When the oven was heated to 180 °C, placed in the autoclave and remained for 1 h, then the autoclave was taken out and cooled in the air. The mushrooms was soaked several times in deionized water to neutrality, and lyophilized for 12 h to obtain shiitake mushroom biosorbent (SMB).

2.3. Characterization of the SMB.
The adsorbent was characterized by SEM (TM-3000, HitachiSU-70, Japan), and gold spray treatment was carried out to improve the SEM quality. The surface functional groups of the adsorbent were determined using a FTIR spectrometer (Nicolet iS10, Thermo Scientific, USA). After degassing at 383 K for 24 h, the BET surface area of the adsorbent was measured by nitrogen adsorption and desorption in liquid nitrogen using ASAP 2460 system (Micrometric, Shanghai).

2.4. Adsorption experiments
All adsorption experiments were performed in a water bath temperature controlled shaker (SHZ-82A). 0.5 g of Congo red was dissolved in a 500 ml volumetric flask to prepare a 1000 mg l⁻¹ Congo red stock solution. In the experiment, different concentrations of Congo red solution were diluted from the stock solution. The concentrations of the solution after adsorption were measured by a UV-visible spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd, Beijing). The adsorption capacity of adsorbent was evaluated using the following equation:

\[ q_e = \left( \frac{C_0 - C_e}{m} \right) V \]  \hspace{1cm} (1) 

\[ q_t = \left( \frac{C_0 - C_t}{m} \right) V \]  \hspace{1cm} (2)

\( q_e (\text{mg g}^{-1}) \) is the equilibrium adsorption capacity of the adsorbent at a specific initial concentration, meanwhile \( q_t (\text{mg g}^{-1}) \) is the adsorption capacity of the adsorbent at a specific time. \( C_0 (\text{mg/L}) \) called the solution’s initial concentration. \( C_e \) and \( C_t \) are used to present the concentrations of the solutions when the adsorption process was at the adsorption equilibrium and the adsorption time \( t \), respectively \( V (\text{L}) \) and \( m (\text{g}) \) are two factors representing the solution volume and the adsorbent mass.

To study the thermodynamic properties, adding 0.01 g adsorbents to 20 ml Congo red solutions with different initial concentrations (60–180 mg l⁻¹), shake them at 293, 308 and 323 k, respectively. Different doses (0.005–0.025 g) of adsorbents were added to 20 ml 100 mg l⁻¹ Congo red solutions to test how different doses can affect the adsorption capacity. The pH value (4–10) of the Congo red solutions was adjusted with different concentrations of nitric acid and sodium hydroxide solution to test the effect of the initial pH value on the adsorption capacity.

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3. Results and discussion

3.1. Characterization of adsorbents
SEM is used to reveal the microstructure of the SMB. Figure 1(a) is lyophilized shiitake mushroom, and figure 1(b) is the SMB. It can be seen in the image that the freeze-dried shiitake mushroom has a dense micro-structure. A lot of collapsed folds can be found in the picture. The SMB has a more inattentive structure. The folded structure has been stretched out. The gap becomes larger and presents a sheet structure. It is more conducive to the adsorption process.

FTIR is used to characterize the functional group of the adsorbent. In the infrared image (figure 2), it can be seen that the infrared absorption peaks of all the samples are basically the same, 3295 cm\(^{-1}\) (3339 cm\(^{-1}\), 3357 cm\(^{-1}\), 2917 cm\(^{-1}\) (2918 cm\(^{-1}\), 2919 cm\(^{-1}\)), 1636 cm\(^{-1}\) (1630 cm\(^{-1}\), 1632 cm\(^{-1}\)), 1412 cm\(^{-1}\) (1375 cm\(^{-1}\), 1373 cm\(^{-1}\)) and 1041 cm\(^{-1}\) (1040 cm\(^{-1}\)) belong to O–H, CH\(_2\) opposes vibration, C=O, C–H in-plane bending vibration and C–O stretching vibration, respectively, indicating the presence of abundant functional groups on the surface which may be beneficial to the adsorption capability. Compared with the dried shiitake mushroom, the intensity of some adsorbent characteristic peaks is weakened or even disappeared, representing a decrease in
these groups. After adsorption process, there are many peaks appeared between 1600 cm$^{-1}$ and 1200 cm$^{-1}$, which is supposed to be brought by Congo red. The nitrogen adsorption desorption isotherm is shown in figure 3. The specific surface area of the freeze-dried shiitake mushroom was 2.9596 m$^{2}$ g$^{-1}$, meanwhile the SMB is 4.3850 m$^{2}$ g$^{-1}$, which proved that the KOH hydrothermal treatment increased the specific surface area of the adsorbent.

3.2. Water treatment comparison
SMB has a good adsorption effect on Congo red. 10 mg shiitake mushroom particles and SMB were added to 20 ml of Congo red solution with an initial concentration of 100 mg l$^{-1}$ to study the effect of hydrothermal treatment on adsorption capacity. The adsorption capacity measured after the adsorption equilibrium is shown in the figure 4. It is obviously that hydrothermal treatment greatly enhances the adsorption capacity of SMB. The untreated mushroom had an adsorption capacity of 23.19 mg l$^{-1}$, while the adsorption capacity of SMB increased to 158.23 mg l$^{-1}$. This significant change may because the hydrothermal treatment increases the specific surface area of the SMB and changes the surface functional groups of the adsorbent.

3.3. Effect of initial pH
The solution pH is one of the important parameters affecting the adsorption process. It can affect ionization degree of dye molecules, as well as the surface of the adsorbent (Bhattacharyya and Ray 2014, Kerkez et al. 2014, Foroutan et al. 2018, 2018). The effect of the initial pH on the adsorbent is shown in figure 5(a). As the pH decreases, the adsorbent’s adsorption capacity increases significantly from 113.65 mg g$^{-1}$ to 168.11 mg g$^{-1}$, which demonstrate a better adsorption capacity in an acidic environment. This phenomenon may be explained
by the active center and surface charge of the adsorbent. At alkaline pH, the hydrogen-containing functional groups on SMB may combine with \( \text{OH}^- \) to negatively charge the surface, causing the adsorbent and Congo red to generate electrostatic repulsion to reduce the adsorption capacity. At acidic pH, the active center is not occupied by \( \text{OH}^- \), the surface of adsorbent is positively charged, and the electrostatic attraction with Congo red increases the adsorption capacity (Purkait et al 2007, Wang and Wang 2007, Chatterjee et al 2009, 2009).

3.4. Effect of adsorbent dosage
One of the important parameters affecting the adsorption efficiency is adsorbent dose. Figure 5(b) shows the result of the removal with different dosages. With the dosage increase, the Congo red removal percentage increase significantly. It is because the surface area and adsorption active sites increase as the adsorbent dose increase, resulting in a rising removal percentage (Hameed 2009a, Esmaeili and Foroutan 2018). It also can be seen from the picture that there is a decrease of adsorption capacity with the dose increase, which may because of the excessive active sites cannot be occupied by Congo Red.

3.5. Effect of contact time
The figure 5(c) shows how contact time affecting on the adsorption of Congo red. Obviously, it can be concluded that the slope of the curve is decreasing continuously, which proves that the adsorption rate decreases with time, that is, the adsorption effect is continuously weakened. Similar phenomena have been reported before (Toor and Jin 2004, Amin 2009, Zhu et al 2011, Dawood and Sen 2012, Hou et al 2012, Reddy et al 2012, Munagapati and Kim 2017). This may be because the active center is constantly occupied by Congo red over time. when the adsorption process begin, a large quantity of active centers on the adsorbent’s surface are in contact with Congo red and adsorbed together, so that the Congo red in the solution is rapidly reduced. As time passing by, the active center is continuously consumed, making the adsorption process slower and slower until equilibrium.

3.6. Effect of temperature
Temperature is a very important factor of adsorption process. The effects of temperature on the adsorption process were investigated at 293 K, 308 K, and 323 K (figure 5(d)). It can be seen that the increase in temperature at the same initial concentration causes a decrease in the adsorption effect. When the initial concentration is
160 mg L$^{-1}$ and the temperature rises from 293 K to 323 K, the adsorption capacity decreases from 196.86 mg g$^{-1}$ to 172.97 mg g$^{-1}$. It can be concluded that the adsorption process is an exothermic process from above.

### 3.7. Adsorption isotherms

Many mathematical models have explained the adsorption process, and Freundlich and Langmuir models can better explain the adsorption process and are widely recognized. The experimental data obtained at different temperatures (293 K, 308 K, 323 K) is used to detect whether the adsorption process of the biosorbent conforms to the models introduced above. The Langmuir model assumes that the adsorption process is adsorption of a monolayer, and the active center of the adsorbent is evenly distributed on the surface. Langmuir equation is shown below (Langmuir 1918):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}} k_L}$$

$q_{\text{max}}$ is the maximum adsorption capacity of the adsorbent, and $k_L$ is the Langmuir constant. A straight line can be fitted by plotting $C_e / q_e$ and $C_e$ as dependent variables and independent variables (figure 6(a)). The slope and the intercept correspond to $q_{\text{max}}$ and $k_L$. The maximum adsorption capacity of the adsorbent for Congo red was 217.86 mg g$^{-1}$ at 293 K (table 1), which is greater than the previously reported graphene oxide composite (103.54 mg g$^{-1}$) (Wei et al 2019), egg shell membrane (117.65 mg g$^{-1}$) (Parvin et al 2019) and eucalyptus leaf powder (29.68 mg g$^{-1}$) (Kumari et al 2019). $R^2$ represents the degree of fit between the experimental data and the langmuir model. It can be seen from the table 1 that the experimental data perfectly fits the model.

$R_L$ is a dimensionless equilibrium parameter in the langmuir model, which can be obtained by the following formula (Bulut et al 2008):

$$R_L = \frac{1}{1 + k_L C_0}$$

Figure 6. Equilibrium isotherms for Congo red adsorbed by SMB: (a) the Langmuir isotherm, (b) the Freundlich isotherm, (c) the Scatchard isotherm, (d) the D-R isotherm.
Table 1. Adsorption isotherm model parameters of SMB adsorb Congo red

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>293k</th>
<th>308k</th>
<th>323k</th>
</tr>
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<tbody>
<tr>
<td>Langmuir</td>
<td>$q_{max}$ (mg g$^{-1}$)</td>
<td>217.86</td>
<td>211.86</td>
<td>209.44</td>
</tr>
<tr>
<td></td>
<td>$k_L$ (L mg$^{-1}$)</td>
<td>0.149</td>
<td>0.100</td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9938</td>
<td>0.9880</td>
<td>0.9495</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.04–0.10</td>
<td>0.05–0.14</td>
<td>0.09–0.22</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$k_F$ (L mg$^{-1}$)</td>
<td>71.38</td>
<td>58.28</td>
<td>44.44</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>3.88</td>
<td>3.55</td>
<td>3.16</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9360</td>
<td>0.9215</td>
<td>0.9042</td>
</tr>
<tr>
<td>Scatchard</td>
<td>$q_{max}$ (mg g$^{-1}$)</td>
<td>217.80</td>
<td>212.90</td>
<td>202.69</td>
</tr>
<tr>
<td></td>
<td>$K_F$ (L mg$^{-1}$)</td>
<td>0.165</td>
<td>0.109</td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.979</td>
<td>0.990</td>
<td>0.931</td>
</tr>
<tr>
<td>D–R</td>
<td>$E$ (kJ mol$^{-1}$)</td>
<td>9.479</td>
<td>9.203</td>
<td>9.000</td>
</tr>
<tr>
<td></td>
<td>$q_{max}$ (mg g$^{-1}$)</td>
<td>263.29</td>
<td>251.66</td>
<td>232.07</td>
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<tr>
<td></td>
<td>$\beta$ (mol$^2$ kJ$^{-2}$)</td>
<td>0.0056</td>
<td>0.0059</td>
<td>0.0062</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.965</td>
<td>0.949</td>
<td>0.901</td>
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</tbody>
</table>

The langmuir isotherms are irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$) with different $R_L$ values (Chen et al 2010). All $R_L$ (table 1) in this experiment were between 0 and 1, indicating that the adsorption of Congo red by the adsorbent is favorable.

The Freundlich model assumes that adsorption occurs on the heterogeneous surface and allows multilayer adsorption, the presence of solute intermolecular forces. The Freundlich model formula is as follows (Freundlich 1906):

$$
\ln q_e = \ln k_F + \frac{1}{n} \ln C_e
$$

$k_F$ and $n$ are the Freundlich constants corresponding to the adsorption capacity parameters and the adsorption strength empirical parameters. $K_F$ and $n$ can be obtained by plotting $\ln C_e$ against $\ln q_e$ (figure 6(b)). table 1 shows all values belong to $n$ greater than 1, which demonstrates that adsorption is prone to occur, which is consistent with the conclusions obtained by the langmuir model. From $R^2$, the experimental data is more suitable for the langmuir model than the Freundlich model.

To further investigate the adsorption behavior of SMB, the Scatchard and Dubinin–Radushkevich (D–R) isotherm model were used. The Scatchard model (Shafiee et al 2019) was used to analyze the active site of the adsorbent. In general, the linear fitting means the adsorbent has one type of active site, otherwise multiple active sites can be found on the adsorbent. Scatchard model can be expressed by the following formula:

$$
\frac{q_e}{C_e} = K_F q_{max} - K_F q_e
$$

Where $K_F$ is the Scatchard constant, and can be obtained by plotting $q_e/C_e$ versus $q_e$ (figure 6(c)). The value of $R^2$ (table 1) showed a well linear relationship between $q_e/C_e$ and $q_e$, which indicates one type of active site in the adsorption process.

The D–R model (Ali et al 2018) is an empirical model which is commonly used to determine the type of adsorption process (physisorption or chemisorption). The following is the formula:

$$
\ln q_e = \ln q_{max} - \beta e^2
$$

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

Where $\beta$ is D–R constant obtained by plotting $lnq_e$ versus $e^2$ (figure 6(d)) and $\varepsilon$ is Polanyi potential. $R$ and $T$ are gas constant (8.314 J mol$^{-1}$ K) and absolute temperature (K), respectively. $\beta$ is closely related to mean free energy $E$ (kJ mol$^{-1}$) and can be derived from:

$$
E = \frac{1}{\sqrt{2\beta}}
$$

If the value of $E$ is less than 8 kJ mol$^{-1}$, it is proved that the adsorption process is physisorption. As can be seen from table 1, the value of $E$ obtained by D–R model is 9.49 kJ mol$^{-1}$, 9.20 kJ mol$^{-1}$, 9.00 kJ mol$^{-1}$, suggesting that the adsorption is a chemisorption process.
3.8. Kinetic studies

The pseudo-first-order kinetic equation and pseudo-second-order kinetic equation were used to analyze the adsorption kinetics of the experimental data. The formula is as follows (Ho and Mckay 1998, Doğan et al 2006):

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

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

$q_e$ is the adsorption amount at the time of adsorption equilibrium, $q_t$ is the adsorption amount at the adsorption time $t$ (min). $k_1$ and $k_2$ (1/min) are rate constants of pseudo-first-order kinetic model and pseudo-second-order kinetic model, respectively. After linear fitting (figures 7(a), (b)), $k_1$, $k_2$ and $q_e$ can be obtained from the slope and intercept (table 2), respectively. The $R^2$ indicates that the experimental data is more in line with the pseudo-first-order kinetic model. Furthermore, the $q_e$ obtained from the pseudo-first-order model (125.16 mg g$^{-1}$) is closer to the experimental data (129.54 mg g$^{-1}$), which proves that the adsorption of Congo red by the adsorbent is more consistent with the pseudo-first-order model (Esvandi et al 2018, Foroutan et al 2019).

In order to study the diffusion mechanism of Congo red on SMB, Intra-particle diffusion model was introduced (Foroutan et al 2019). According to the empirically derived theory of Weber and Morris, the amount of adsorption is proportional to $t^{1/2}$, and the equation is as follows:

\[
q_t = k_{id}t^{1/2} + C_i
\]

$k_{id}$ is the Intra-particle diffusion constant (mg g$^{-1}$ min$^{1/2}$), and $C_i$ is the intercept of i-stage (table 2). The figure 7(c) shows that the adsorption process is divided into two stages. In the first stage, there are a large number of active sites on the surface of the adsorbent available for the MB molecule causing a high efficiency adsorption. The second stage of adsorption is gradually happened, which indicate the internal process of MB entering the adsorbent becomes the main factor controlling the adsorption rate.

Figure 7. Adsorption kinetics of Congo red adsorbed by SMB: (a) pseudo-first-order model, (b) pseudo-second-order model, (c) Intra-particle diffusion model.
3.9. Adsorption thermodynamic

Thermodynamic parameters such as enthalpy (ΔH) and entropy (ΔS) can be obtained from the Van’t Hoff formula (Neghlani et al 2011). Gibbs free energy (ΔG) can be obtained from ΔH and ΔS. The formula is as follows:

$$
\ln \left( \frac{q_e}{C_e} \right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
$$

(13)

$$
\Delta G = \Delta H - T \Delta S
$$

(14)

In the formula, R is the universal gas constant (8.314 J mol\(^{-1}\) K), T is the absolute temperature (K). The thermodynamic parameters obtained after calculation are shown in the table 3. The negative values of ΔG indicate that the adsorption reaction is a spontaneous reaction in the test temperature range. In general, the value of ΔG ranges from 0–20 kJ mol\(^{-1}\), indicating that the adsorption process is physisorption (Weng et al 2009, Fernandes et al 2010). The values of ΔG suggest the adsorption is a physisorption process. The negative value of ΔH indicates that the adsorption reaction is an endothermic reaction. The lower the temperature, the more likely the reaction occurs, which is consistent with the experimental data and phenomena.

4. Conclusion

The novel biosorbent is obtained by Hydrothermal treatment of shiitake mushrooms with KOH, and has good ability to adsorb Congo red. Adsorption experiments show that the pH of the solution, the dose of the adsorbent, the contact time and the temperature all have an effect on the adsorption progress. With the temperature rises, the adsorption capacity of the biosorbent decreases, when the pH of the solution, the dose of the adsorbent and the time increase, the ability of the biosorbent to adsorb Congo red increases. The langmuir model fits the experimental data very well and the calculated maximum adsorption capacity is 217.86 mg g\(^{-1}\) (293 k). The experimental data is in accordance with the pseudo-first-order kinetic model. Thermodynamic analysis shows that the adsorption reaction is an exothermic spontaneous reaction.

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<th>Kinetic model</th>
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<td>1.03 \times 10^{-3}</td>
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<td>( q_e ) (mg g(^{-1}))</td>
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<td></td>
<td>( R^2 )</td>
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<tr>
<td>Pseudo-second-order</td>
<td>( k_2 ) (g/mg·min)</td>
<td>3.84 \times 10^{-7}</td>
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<td>( q_e ) (mg g(^{-1}))</td>
<td>137.58</td>
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<td></td>
<td>( R^2 )</td>
<td>0.9676</td>
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<tr>
<td>Intra-particle diffusion</td>
<td>( k_{d1} ) (mg g(^{-1})·min(^{-1/2}))</td>
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<td>( C_1 ) (mg g(^{-1}))</td>
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<tr>
<td></td>
<td>( R^2 )</td>
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<td></td>
<td>( k_{d2} ) (mg g(^{-1})·min(^{-1/2}))</td>
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<td>( C_2 ) (mg g(^{-1}))</td>
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<tr>
<th>Temperature (K)</th>
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<th>ΔH (kJ mol(^{-1}))</th>
<th>ΔS (J Kmol(^{-1}))</th>
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<tr>
<td>293</td>
<td>−4.69</td>
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<tr>
<td>308</td>
<td>−3.96</td>
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<tr>
<td>323</td>
<td>−3.24</td>
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Table 2. Kinetic constants of SMB adsorb Congo red.

Table 3. Thermodynamic parameters of SMB adsorb Congo red.
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