Effective adsorption of Direct Red 23 by sludge biochar-based adsorbent: adsorption kinetics, thermodynamics and mechanisms study
Ruqing Jiang, Guangwei Yu, Pamphile Ndagijimana, Yu Wang, Futian You, Zhenjiao Xing and Yin Wang

ABSTRACT
Using solid adsorbents, such as biochar, has been a potential practice to remove the pollutants from water bodies to render the water safer for potential usage. A potential application of sludge biochar-based adsorbent (SBA), obtained by pyrolysis with hydrothermal treatment, was developed to adsorb Direct Red 23 (DR23) from wastewater. The results showed that for the synthesized SBA (0.5 g/L) in the adsorption of DR23 at low concentration (<20 mg/L), the DR23 was totally removed from the aqueous solution. pH had a limited effect on the adsorption, while an increase in temperature was shown to have a large enhancing effect. The adsorption kinetics were best fitted by the pseudo-second-order kinetic model, while the equilibrium data were best fitted by the Langmuir isotherm. A maximum saturation adsorption capacity of SBA of 111.98 mg/g was achieved. SBA could then be regenerated by pyrolysis, and after three cycles, SBA still retained good adsorption ability for DR23, a removal rate exceeding 97% was achieved. Functional groups, pores, π-π bond, and electrostatic interactions are the key to the adsorption mechanisms. The results proved that SBA would be a promising material in the application of removing dyes in printing and dyeing wastewater.

Key words | adsorption kinetics, Direct Red 23, mechanism, sludge biochar-based adsorbent, thermodynamic

HIGHLIGHTS
- An adsorbent was synthesized from sludge by pyrolysis with hydrothermal treatment.
- The adsorbent presented high removal efficiency for DR23 with 111.98 mg/g.
- Physicochemical interactions are key factors for the adsorption mechanism.
- The new adsorbent could be regenerated to obtain awesome adsorption performance.

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INTRODUCTION

The textile industry development nowadays is contributing much to the pollution of the aquatic environment. Recently, various pollutants such as dyes, pesticides, heavy metals, antibiotics, and many others are detected in the water environment from sewage and wastewater treatment and have been proved very harmful to aquatic and terrestrial life (Zhang et al. 2011; Lu et al. 2012; Chen et al. 2014). Dyes were mostly reported as dominant in the aquatic environment (Noroozi & Sorial 2013) because of their ultimate and gradual applications in the textile industry such as tanning, paper and cellulose, ink, food, cosmetics, and pharmaceuticals. The manufacturing of those associated products produces a huge amount of organic matter containing deep color and high chemical oxygen demand in the water environment (Zhang 2000). Their colors in the water environment block the light to the aquatic life and decrease the transparency of water bodies, which lead to serious negative effects on biological functions such as photosynthesis, bacterial growth, and degradation of biological wastes in the water environment (Luan et al. 2016). For example, Direct Red 23 (DR23, C_{35}H_{25}N_{7}S_{2}O_{10}Na_{2}, C.I.29160), which is a popular anionic diazo dye in printing and dyeing split fabrics featuring a complex and stable aromatic core, was reported to be abundant in wastewater. Thus, the treatment of DR23 from the water environment is highly required. The recent reports showed that the treatment of DR23 from a water environment especially in wastewater is still challenging (Ardejani et al. 2008; Kallel et al. 2016). Therefore, finding suitable methods for treating organic dye wastewater is required for solving a difficult issue in environmental pollution control. Various techniques for DR23 removal from wastewater have been applied (Szpyrkowski et al. 2001; Kim et al. 2004; Alventosa et al. 2012; Ahmed et al. 2018); among them, adsorption has been selected as a promising method owing to its low-cost, fast reaction, and sensitivity to remove dye from wastewater treatment (Noroozi & Sorial 2013; Sadegh et al. 2017). In this perspective, biochar is a preferable adsorbent presenting good physiochemical properties such as high surface area and important functional groups to enhance the adsorption of targeted pollutants. The biochar is sourced from various types of biomass including from agriculture, food, and animal waste. Recently, it was publicized that sludge was converted to biochar, which is a positive way of turning sludge into a valuable material (Otero et al. 2003; Smith et al. 2009). In our group, lots of researches on the sludge pyrolysis and carbonization process were carried out, while a demonstration of 50 t/d urban sludge pyrolysis carbonization was built in Xiamen. Based on this, the migration and transformation of heavy metals in sludge biochar, the residual characteristics of effective elements such as nitrogen, phosphorus, and potassium, and the ecological risks of biochar application have been studied (Wang et al. 2016a, 2016b; Li et al. 2018; Xie et al. 2019). At present, most studies on sludge carbonization focus on reducing sludge treatment costs, reducing energy consumption, and using biochar as a soil amendment. However, there are few reports on sludge biochar resource utilization for dyes.

In the attention of our work, we prepared sludge biochar-based adsorbent (SBA) by pyrolysis with hydrothermal treatment from sludge obtained from the Xiamen Tong’an wastewater treatment plant. The synthesized SBA was then used as an adsorbent for DR23 under different batch adsorption conditions. The removal effects, adsorption isotherm, kinetics, and mechanisms of DR23 adsorption onto SBA
were investigated. Moreover, the reusability of the material was evaluated to determine the viability of the produced material. This research demonstrates the potential application of SBA in dye wastewater treatment and inspires using SBA in other industrial applications.

**MATERIALS AND METHODS**

**Materials**

A centrifugally dewatered sludge collected from Xiamen Tong’an Wastewater Treatment Plant was used as raw material to prepare SBA. DR23, which was used as the adsorbate, was purchased from Tianjin Chemical Station Co., Ltd. A simulated printing and dyeing wastewater was prepared by dissolving DR23 in distilled water. The physico-chemical properties of DR23, sludge, and SBA are presented in **Tables 1** and **2**, respectively.

**Preparation of SBA**

The sludge was hydrothermally pretreated at 180 °C for 50 min, dewatered by vacuum filtration, and dried to a moisture content of less than 0.5%. The dried sludge was then pulverized to 100-mesh particle size and pyrolyzed in a tube furnace under flowing N₂ (80 mL/min) at 600 °C for 1 h with a heating ramp of 10 °C/min. After cooling at room temperature, the sample was ground and then sieved with 100-mesh to obtain SBA. The particle diameter of SBA is seen in Figure S1 (Supporting Information). The sample was stored in a sealed desiccator for further adsorption experiments. The flow chart of SBA preparation is shown in Figure S2.

**Experimental conditions on DR23 adsorption**

Batch adsorption experiments were carried out by adding a certain amount of SBA to 80 mL DR23 solution in a 150 mL Erlenmeyer flask, which was then sealed. The sealed Erlenmeyer flasks were then placed in an orbital shaker for 24 h with a speed of 200 RPM.

To evaluate its further reuse in the adsorption process, the spent SBA after adsorption (SBA_{ad}) was regenerated at 600 °C for 1 h under the N₂ atmosphere to obtain regenerated SBA (SBA_{re}). The DR23 removal rate η(%) and adsorption amount q_{e} (mg/g) were calculated using Equations (1) and (2), respectively.

\[
\eta = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (1)
\]

\[
q_e = \frac{(C_o - C_e)}{V/W} \quad (2)
\]

where C_{o} and C_{e} (mg/L) were the initial and equilibrated DR23 concentrations, respectively; V (L) was the volume of DR23 solution and W (g) was the weight of SBA.

**Adsorption isotherm and kinetics studies**

Adsorbent capacity was investigated by adsorption isotherms. The maximum DR23 adsorption and equilibrium isotherm constants were also determined. To determine the isotherm parameters, the linearized forms of the adsorption isotherm models were used. The adsorption experiment results were fitted by the Freundlich model (Witalius & Balin 1958) and the Langmuir model (Langmuir 1916) to provide further insight into the adsorption mechanisms of DR23 onto SBA.

**Table 1 | Physicochemical properties of DR23**

<table>
<thead>
<tr>
<th>Organic dye</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Ionicity</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR23</td>
<td>C_{35}H_{25}N_{7}Na_{2}O_{10}S_{2}</td>
<td>813.72</td>
<td>Anionic</td>
<td><img src="image" alt="Molecular Structure" /></td>
</tr>
</tbody>
</table>

**Table 2 | Physicochemical properties of sludge and SBA**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate (wt.%, air-dried)</th>
<th>Ultimate (wt.%, air-dried)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ash</td>
<td>VM</td>
</tr>
<tr>
<td>Sludge</td>
<td>44.71</td>
<td>48.23</td>
</tr>
<tr>
<td>SBA</td>
<td>82.65</td>
<td>5.62</td>
</tr>
</tbody>
</table>

O* = 100 – (C + H + N + S + ash); VM: volatile matter; FC: fixed carbon.
For further studying the adsorption characteristics, four kinetics models were applied, including the pseudo-first-order (PFO) (Aksu 2001), pseudo-second-order (PSO) (Ho & McKay 1999), intra-particle diffusion (IPD) (Cheung et al. 2007), and Elovich model (EM) (Siddiqui et al. 2018). The equations were applied to fit the kinetics data.

Characterization of SBA

The ash, volatile matter, and fixed carbon of sludge and SBA were measured by the method of proximate analysis (GB8731-2012). The ultimate analysis was performed with an elemental analyzer (VARIO EL III, Elementar, Inc., Germany). The surface area of SBA was determined by an N₂ multipoint Brunauer-Emmett-Teller (BET) isotherm which was obtained using a Micromeritics ASAP 2020M + C (USA). The total pore volume was determined from a single N₂ adsorbed point. A portion of the SBA, SBA_{ad}, and SBA_{re} were deposited onto Cu plates, sputter-coated with an Au film, and the surface morphology was characterized by scanning electron microscopy (SEM) using a Hitachi S-4800 (Japan). Some samples were also mixed with KBr (1:200, w/w), finely ground, and then pressed into pellets. The mixed pellets were then analyzed by Fourier transform infrared spectrometry (FTIR) using a Thermo Fisher Scientific iS10 (USA) to identify the surface functional groups. Spectra were obtained between 2,000 and 400 cm⁻¹. X-ray diffraction (XRD) (X’Pert Pro, The Netherlands) was applied to study the crystal structure of the elements of SBA, SBA_{ad}, and SBA_{re}. The surface species of the samples were measured by X-ray photoelectron spectroscopy (XPS) (Axis Supra, UK).

Statistical analysis

All treatments were performed in triplicate. Data were analyzed using one-way analysis of variance and then a mean test was performed. The minimum significant difference was set to $P < 0.05$ to test the differences in the unique properties.

RESULTS AND DISCUSSION

Basic characteristics of SBA

Physicochemical properties of sludge and SBA are presented in Table 2. When sludge was pyrolyzed to SBA, the ash content increased significantly, and the O, H, and N element content decreased. The decrease in O and H content was mainly due to the dehydration of sludge during pyrolysis. The decrease in N content was attributed to the loss of volatile nitrogen-containing substances (NH₄/NO₃) at high temperatures (Tang et al. 2019).

The BET results showed that SBA presents a relatively high surface area of 53.28 m²/g, and the total pore volume and average pore sizes (average pore diameter) of SBA were 0.09 cm³/g and 8.96 nm, respectively. This classified the biochar as a mesoporous material, which typically has an average pore size between 2 and 50 nm (Chen et al. 2011). A similar type V isotherm with an H1-type hysteresis loop in a P/P₀ range of 0.60–0.98 (Figure 1(a)) was observed and this is evidence of the presence of mesopores (Kang et al. 2019), which may play an important role in the adsorption process of DR23. The presence of mesoporous structure as shown in Figure 1(b) is the potential evidence of adsorption of DR23 by SBA.

The surface element composition and valence state of SBA was analyzed by X-ray photoelectron spectroscopy (XPS), and the result is displayed in Figure 1(c)–1(f). As illustrated in Figure 1(c), the XPS results exhibited the coexistence of large C 1 s, O 1 s, and a small number of N 1 s in SBA, corresponding to the peaks at around 285.09, 531.12, and 404.10 eV, respectively. The peaks (C 1 s spectrum) presented in Figure 1(d) at 284.73, 285.05 and 286.31 eV were related to C=C=C in aromatic rings, C=O/C=O, and C–O–C, respectively (Duan et al. 2015). Figure 1(e) also illustrates the peaks (O 1 s XPS spectrum) at 530.01, 532.79, and 533.30 eV, which were also attributed to C=O, C–C=O, and C=O, respectively. The N 1 s XPS spectrum (Figure 1(f)) showed that two types of nitrogen configurations including graphitic N (401.01 eV), and oxidized N (402.28 eV) were present in SBA (Ma et al. 2019). Furthermore, a recent report proposed that the nitrogen configurations would alter the electronic structure of the original carbon plane to increase defects, boost catalytic performance, and accelerate the electron transfer (Shi et al. 2016; Yao et al. 2017). Therefore, the active sites such as different nitrogen configurations, hybridized carbons, and C=O species were successfully observed in the SBA sample as confirmed by XPS results. The existence of these functional groups could facilitate the adsorption of DR23.

Effect of adsorption conditions

Effect of SBA amount

The amount of adsorbent required not only affects the removal efficiency but also determines the cost of the overall treatment. The $q$ (%) of DR23 increased from 70.47% to
98.64%, when the amount of adsorbent increased from 0.01 g to 0.04 g, or 0.125 g/L to 0.5 g/L, respectively (Figure 2(a)). All DR23 in a 20 mg/L dye solution was completely removed when the amount of SBA increased, which indicated an η(%) of 100%, and no release of DR23 back into the water was detected.

Since the η(%) was 98.64% when 0.04 g SBA was used, and only minor increases in the η(%) were observed with the further addition of SBA, the most economical amount of adsorbent for treating a 20 mg/L DR23 solution was 0.5 g/L. Any further increase in adsorption rate with additional SBA was attributed to a corresponding increase in the available surface area and adsorbent active sites.

**Effect of solution pH**

It is also known that the pH of the pollutant solution affects the performance of the adsorbent. Our results show that the absorption effect of DR23 is better under acidic and neutral conditions. When the pH is greater than 8, the η(%) of DR23 by SBA drops sharply.
For economic considerations, the pH of the solution was set to 6.5 in subsequent experiments, which is the neutral and representative pH of the wastewater.

**Effect of the initial concentration of DR23**

The effect of initial concentration for DR23 dye adsorption was evaluated at different concentrations including 20, 40, 60, 80, 100, and 120 mg/L. The results (Figure 2(c)) showed that the removal efficiency increased with low initial concentration, which should be attributed to the possible available active sites for low concentrations on SBA. However, the removal efficiency decreased with the increase in the initial concentration of DR23; this should be attributed to the low number of active sites to accommodate the large amount of DR23 (Nautiyal et al. 2016).

**Effect of contact time**

The adsorption of DR23 from solutions of different concentrations by SBA at a fixed amount of 0.5 g/L was also investigated at a fixed interval of time. The equilibrium η(%) decreased as the concentration increased. The amount of dye adsorbed increased with contact time at each initial DR23 concentration (Figure 3). For example, when the initial DR23 solution concentration was 20 mg/L, the η(%) was 86.16% after 5 min, but further increases η(%) at extended times were limited. The η(%) during the adsorption process should be attributed to the sufficiency of active sites of SBA for a low concentration of DR23. Conclusively, after 240 min, equilibrium was reached regardless of the initial DR23 concentration. Accordingly, 240 min was selected as a fixed contact time in further experiments.

**Adsorption isotherm**

The Freundlich adsorption isotherm is more suitable for heterogeneous or multilayer adsorption, while the Langmuir adsorption isotherm is more suitable for homogeneous or monolayer adsorption (Nautiyal et al. 2016). The experimental data were tested by both models (Figure 4). Parameters derived from both isotherms showed that the Langmuir isotherm showed better fit for the experimental adsorption data ($R^2 > 0.99$) (Table 3). It was concluded that the adsorption of DR23 onto SBA occurred mainly by single-molecule adsorption. Heterogeneity factors, potential energy heterogeneity, and adsorption strength can be reflected by the ‘$1/n$’ factor in the Freundlich isotherm model. When the value of $1/n$ is less than 0.5, it indicates that the adsorbate is easily adsorbed (Fan et al. 2017). In contrast, when the value of $1/n$ is greater than 2, it indicates the adsorption of adsorbate is difficult. In this study, $1/n$ values for DR23 adsorption onto SBA were less than 0.5 at all three temperatures, which indicated that an increase in temperature enhanced the adsorption process.
According to Langmuir isotherm, the values of equilibrium factor ($R_L$) were all less than 1 (Figure S3, Supporting Information), which indicated that the adsorption of DR23 onto SBA was favorable (Li et al. 2017). Additionally, the changes in the increase of the adsorption capacity resulted from the increase of the initial DR23 concentration. The increase of the temperature leads to the decrease of the viscosity of the DR23 solution, which enhances the rate of mass diffusion of the solution from the bulk solution to the inner pores of SBA. Furthermore, the decrease in $R_L$ resulting from the increase of the temperature was indicative of the favorable adsorption of DR23 on SBA.

The adsorption capacity (Table 4) of SBA used in this study is good to compare to certain adsorbents reported in a recent study (Ardejani et al. 2018; Akgul 2014; Kallel et al. 2016; Liu et al. 2016).

### Adsorption kinetics

Adsorption kinetics plots of DR23 onto SBA were obtained at different initial DR23 concentrations and pH = 6.5 and 25 °C (Figure 5). The rate of increase of the amount of

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**Table 3** Isotherm fitting parameters of DR23 adsorption by SBA at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_f$</th>
<th>$1/n$</th>
<th>$R^2$</th>
<th>$b$</th>
<th>$q_m$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4.91</td>
<td>0.26299</td>
<td>0.56</td>
<td>0.39</td>
<td>110.50</td>
<td>0.99</td>
</tr>
<tr>
<td>35</td>
<td>6.81</td>
<td>0.07526</td>
<td>0.74</td>
<td>11.70</td>
<td>108.70</td>
<td>0.99</td>
</tr>
<tr>
<td>45</td>
<td>6.83</td>
<td>0.08253</td>
<td>0.60</td>
<td>6.82</td>
<td>111.98</td>
<td>0.99</td>
</tr>
</tbody>
</table>

According to Langmuir isotherm, the values of equilibrium factor ($R_L$) were all less than 1 (Figure S3, Supporting Information), which indicated that the adsorption of DR23 onto SBA was favorable (Li et al. 2017). Additionally, the changes in the increase of the adsorption capacity resulted from the increase of the initial DR23 concentration. The increase of the temperature leads to the decrease of the viscosity of the DR23 solution, which enhances the rate of mass diffusion of the solution from the bulk solution to the inner pores of SBA. Furthermore, the decrease in $R_L$ resulting from the increase of the temperature was indicative of the favorable adsorption of DR23 on SBA.

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### Adsorption kinetics

Adsorption kinetics plots of DR23 onto SBA were obtained at different initial DR23 concentrations and pH = 6.5 and 25 °C (Figure 5). The rate of increase of the amount of

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**Table 4** Comparison of adsorption capacities of some adsorbents

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Red 23</td>
<td>SBA</td>
<td>111.98</td>
<td>This work</td>
</tr>
<tr>
<td>Direct Red 23</td>
<td>Fig manure biochar</td>
<td>17.82</td>
<td>Liu et al. (2016)</td>
</tr>
<tr>
<td>Direct Red 80</td>
<td>Garlic straw</td>
<td>107.53</td>
<td>Kallel et al. (2016)</td>
</tr>
<tr>
<td>Direct Red 80</td>
<td>Mixture almond shells</td>
<td>20.5</td>
<td>Ardejani et al. (2008)</td>
</tr>
<tr>
<td>Congo Red</td>
<td>Raw clinoptilolite</td>
<td>16.90</td>
<td>Akgul (2014)</td>
</tr>
<tr>
<td>Congo Red</td>
<td>Iron-grafted clinoptilolite</td>
<td>36.70</td>
<td>Akgul (2014)</td>
</tr>
</tbody>
</table>

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**Figure 4** | The Freundlich and Langmuir adsorption isotherm fitting curves at 25, 35 and 45 °C.

**Figure 5** | Adsorption kinetics of DR23 adsorption on SBA at different concentrations.
DR23 adsorbed was initially high but slowed as time increased until equilibrium was reached after 4 h. The three stages such as initial stage, fast external gradual, and final equilibrium stage, which are key steps for the DR23, were observed. In the initial stages of adsorption, DR23 was mainly rapidly adsorbed on the external surface of SBA. In the second stage, the adsorption was slower as DR23 needed to diffuse inside the SBA, and the final step is the slow step in which the adsorption of DR23 attained equilibrium. In addition, the DR23 concentration in the contaminated liquid decreased as time progressed, which also slowed down the rate of adsorption (Nautiyal et al. 2016).

The kinetic fitting data are presented in Table 5, and the model constants were obtained from the linear q_t vs t1/2 plot (Figure 6). A theoretical maximum adsorption amount (q_m) calculated using the PSO equation showed good agreement with the experimental values (Table 5). According to the linear correlation (R^2), the PSO model was better fitting. Therefore, the adsorption of DR23 by SBA is better described by the PSO reaction kinetics model. This result was consistent with previously published studies (Ren et al. 2016), which suggested that the adsorption rate was proportional to the square of the number of vacant active adsorption sites on the biochar surface. It also suggested

<table>
<thead>
<tr>
<th>C_0 (mg/L)</th>
<th>q_e,exp (mg/g)</th>
<th>k_1 (min^-1)</th>
<th>q_e,cal (mg/g)</th>
<th>R^2</th>
<th>k_2 (g/(mg·min))</th>
<th>q_e,cal (mg/g)</th>
<th>R^2</th>
<th>K_d (mg/(g·min^{1/2}))</th>
<th>θ (mg/g)</th>
<th>R^2</th>
<th>α (mg/(g·min))</th>
<th>β (g/mg)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>39.20</td>
<td>0.02</td>
<td>1.33</td>
<td>0.3529×10^{-2}</td>
<td>39.22</td>
<td>1.0000</td>
<td>1.30</td>
<td>25.84</td>
<td>0.3529×10^{16}</td>
<td>1.06</td>
<td>0.6151</td>
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<tr>
<td>40</td>
<td>73.48</td>
<td>0.02</td>
<td>25.42</td>
<td>0.7815×10^{-3}</td>
<td>74.68</td>
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<td>3.71</td>
<td>31.25</td>
<td>0.6625×10^{2}</td>
<td>0.10</td>
<td>0.8917</td>
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</tr>
<tr>
<td>60</td>
<td>93.93</td>
<td>0.02</td>
<td>30.86</td>
<td>0.8401×10^{-3}</td>
<td>94.61</td>
<td>0.9993</td>
<td>4.20</td>
<td>45.09</td>
<td>0.7697×10^{3}</td>
<td>0.11</td>
<td>0.9492</td>
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<tr>
<td>80</td>
<td>97.79</td>
<td>0.02</td>
<td>27.87</td>
<td>0.7888×10^{-3}</td>
<td>98.04</td>
<td>0.9992</td>
<td>4.09</td>
<td>50.41</td>
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<td>0.13</td>
<td>0.9372</td>
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<tr>
<td>100</td>
<td>99.79</td>
<td>0.02</td>
<td>19.91</td>
<td>0.6046×10^{-3}</td>
<td>100.00</td>
<td>0.9997</td>
<td>3.92</td>
<td>55.77</td>
<td>0.7267×10^{5}</td>
<td>0.16</td>
<td>0.8998</td>
<td></td>
<td></td>
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<tr>
<td>120</td>
<td>110.98</td>
<td>0.03</td>
<td>28.22</td>
<td>0.9079×10^{-3}</td>
<td>111.86</td>
<td>0.9999</td>
<td>4.44</td>
<td>63.05</td>
<td>0.6511×10^{5}</td>
<td>0.14</td>
<td>0.8893</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: q_e,exp: experimental values; q_e,cal: calculated values.

Figure 6 | Linear fits of the kinetics models for DR23 adsorption on SBA.
that the adsorption process was controlled by a chemisorption mechanism that involved electron sharing or electron transfer between the SBA and DR23 (Sun et al. 2014). According to the $R^2$ in Table 5, the adsorption process of DR23 was not controlled by PFO, IPD and EM models.

The adsorption of DR23 onto SBA was a complex process that was controlled by reaction rate and diffusion, which more resembled the PSO kinetics model. That the PSO model incorporated and explained the external liquid film diffusion, surface adsorption, and intra-particle diffusion processes (Vadivelan & Kumar 2005) meant that the PSO model was more comprehensive, and accurately described the adsorption mechanisms of DR23 on SBA. We concluded that the rate-limiting step was chemisorption, as confirmed by the PSO model (Sun et al. 2014).

**Thermodynamic study on DR23 removal efficiency**

The adsorption isotherms of DR23 on SBA were evaluated with the aforementioned initial concentration at different temperatures including 25, 35, and 45 °C (Figure S4). The maximum amount of DR23 adsorbed by SBA increased from 102.14 to 106.55 to 110.46 mg/g as the temperature increased from 25 to 35 to 45 °C, respectively. This confirmed that the adsorption performance of SBA was enhanced by an increased operating temperature.

The positive value of $\Delta H^0$ (Table 6) shows the endothermic nature of the adsorption process of DR23 on SBA. The magnitude of $\Delta H^0$ can infer the type of adsorption. The heat generated during physical adsorption locates in the range of 2.1–20.9 kJ/mol and the range of 80–200 kJ/mol for chemisorption (Chowdhury et al. 2011). Gibbs free energy of adsorption ($\Delta G^0$) is determined by the van’t Hoff equation (Fan et al. 2013). The negative values of $\Delta G^0$ (Table 6) indicate that the adsorption reaction is spontaneous. The adsorption increased with the increasing temperature and DR23 is conductively adsorbed on the surface of SBA.

### Table 6 | Thermodynamic study

<table>
<thead>
<tr>
<th>C0 (mg/L)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (J/(mol·K))</th>
<th>$\Delta G^0$(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>298 K</td>
<td>308 K</td>
</tr>
<tr>
<td>20</td>
<td>51.33</td>
<td>198.77</td>
<td>–7.41</td>
</tr>
<tr>
<td>40</td>
<td>55.50</td>
<td>210.98</td>
<td>–6.66</td>
</tr>
<tr>
<td>60</td>
<td>37.53</td>
<td>142.76</td>
<td>–4.89</td>
</tr>
<tr>
<td>80</td>
<td>22.36</td>
<td>84.38</td>
<td>–2.69</td>
</tr>
<tr>
<td>100</td>
<td>10.48</td>
<td>40.86</td>
<td>–1.61</td>
</tr>
<tr>
<td>120</td>
<td>2.70</td>
<td>13.00</td>
<td>–1.20</td>
</tr>
</tbody>
</table>

**Regeneration**

The regenerative capacity of an adsorbent indicates how reusable and economical the adsorbent is. The pyrolysis method was used to desorb and regenerate spent SBA. The reusability was tested in three cycles of DR23 dye adsorption studies, after which the $\eta(\%)$ was still greater than 97% (Figure S5). This suggested that $\text{SBA}_{re}$ maintained a good capacity for removing DR23 and show the potential to be a reusable adsorbent. These results indicate that SBA can efficiently adsorb low-concentration DR23 continuously in the wastewater treatment.

**Possible adsorption mechanisms of SBA on DR23**

The adsorption mechanisms of DR23 by SBA rely on the physico-chemical properties of the adsorbate solution and adsorbent; the general adsorption mechanisms are presented in Figure 8. This was confirmed by SEM, XRD, FTIR characterization of SBA, $\text{SBA}_{ad}$, and $\text{SBA}_{re}$ (Figure 7). As presented in Figure 7(a)–7(c), SBA is a porous material, the pore distribution shows the presence of macroporous and mesoporous structure on the SBA surface. The macropores facilitate the mass transfer of DR23 solution from bulk solution and penetrate the inner surface of SBA and are adsorbed on the mesopores of SBA. The nature of the solution, such as the pH, is the key factor that could determine the adsorption mechanisms; at low pH value, the attractive electrostatic interaction controls the adsorption mechanisms whereas, at high pH value, the repulsion electrostatic interaction between anionic DR23 and anionic SBA negatively affect the adsorption of DR23. The XRD spectra of SBA, $\text{SBA}_{ad}$, and $\text{SBA}_{re}$ were evaluated and are shown in Figure 7(d). There was almost no change in detected diffraction peaks in the three samples, while the order of peak intensity is $\text{SBA} > \text{SBA}_{re} > \text{SBA}_{ad}$. The functional groups of SBA are evidence of the chemical bonding between the SBA and DR23 during the adsorption. This is the evidence that the adsorbed DR25 covered the surface of the SBA, causing the diffraction peak intensity to decrease slightly, and the intensity was restored after regeneration. FTIR spectroscopy of SBA, $\text{SBA}_{ad}$, and $\text{SBA}_{re}$ (Figure 7(e)) was obtained to identify which functional groups and moieties were involved in the adsorption of DR23. The presence of the peak at 1,589.1 cm$^{-1}$ was related to N-H vibration coupled with C-N stretching mode or the vibration of C= C and C = O (Yao et al. 2017). The peaks centered at 1,384.6 and 1,085.7 cm$^{-1}$ were attributed to C-C and C-OH vibrations, respectively.
In addition, the peak at 574.7 cm$^{-1}$ was related to the Fe-O vibrational mode of SBA (Weng et al. 2013; Luo et al. 2016) and peaks at 464 cm$^{-1}$ were attributed to Si-O-Si (Song et al. 2014; Gong et al. 2015). The peaks corresponding to each functional group on the surface of SBA$_{ad}$ were slightly lower than those of SBA, and they were restored after regeneration, which indicated that each functional group participated in the adsorption of DR23 on the surface of SBA through different mechanisms.

The π-π interactions could determine the adsorption mechanisms; it was reported by Khraisheh et al. (2005) that Si-O-Si may act as an active site for dye adsorption through π-π interactions. Nitrogen-containing functional groups and Si-O-Si groups may be involved in the adsorption process of DR23 onto SBA. The bonding interactions are evidence of the adsorption mechanisms; for example, the hydrogen bond was formed between the nitrogen in DR23 and SBA (Vargas et al. 2011). Furthermore, C = C (or C = C) and C = O bonds will interact with O and -NH in DR23 through C-O bond interaction and hydrogen bond interaction, respectively. C-OH, as a Bronsted acid site, will provide an electron-accepting site for DR23. Thus, the possible mechanisms that occur during DR23 adsorption, which include physical interaction, π-π interaction, C-O bond
interaction, hydrogen bond interaction, and electrostatic adsorption, are summarized in Figure 8.

CONCLUSIONS

We reported an environmental valorization platform of sludge to prepare a valuable sludge biochar-based adsorbent by pyrolysis with hydrothermal treatment and applied it in the adsorption of Direct Red 23. The SBA of 0.5 g/L was found as the optimum amount to remove DR23 at a concentration of 20 mg/L, reaching a removal efficiency of 98.64%. Factors such as pH of solution showed a negative effect on DR23 removal at high pH values; however, increased temperatures were shown to favor adsorption. The adsorption process of DR23 onto SBA was described well by the Langmuir isotherm and PSO kinetics model. The possible mechanisms of DR23 adsorption onto SBA include physical interaction, π-π interaction, C-O bond, hydrogen bond interaction, and electrostatic adsorption. We indicated also a high recovery possibility and potential reuse of the adsorbent after three cycles, therefore, it is a promising and valuable adsorbent for decontaminating wastewater sourced from the printing and dyeing industry.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


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