Adsorption of crystal violet with diatomite earth&carbon by a modification of hydrothermal carbonization process

Zhang Yanzhuo, Li Jun, Chen Guanghui, Bian Wei, Lu Yun, Li Wenjing, Zheng Zhaoming and Cheng Xiaojie

ABSTRACT

The high colority and difficulty of decolorization are the most important tasks on printing and dyeing wastewater. This study investigates the ability of diatomite earth&carbon (DE&C) as an adsorbent to removal crystal violet (CV) from aqueous solutions. Fourier transform infrared spectroscopy results indicate the importance of functional groups during the adsorption of CV. The obtained N2 adsorption–desorption isotherm values accord with well IUPAC type II. Our calculations determined a surface area of 73.15 m² g⁻¹ for DE&C and an average pore diameter of 10.56 nm. Equilibrium data of the adsorption process fitted very well to the Langmuir model (R² > 0.99). The results of kinetics study showed that the pseudo-second-order model fitted to the experimental data well. The thermodynamic parameters were also evaluated. ΔH < 0, ΔS > 0 and ΔG < 0 demonstrated that the adsorption process was spontaneous and exothermic for dye. Furthermore the positive value of ΔS reflected good affinity of the CV dye.

Key words | adsorption, crystal violet, diatomite earth&carbon, hydrothermal carbonization

INTRODUCTION

Dyestuff is commonly used in a variety of industries, such as textiles, paper products, paints, and printing inks. Most of the dyes were used in textiles and the fixed degree of dyes were less than 100%. So there is more than 5 ~ 10% of the dye going into the environment through wastewater (Zheng et al. 2015). The difficulties of dyestuff wastewater treatment lie in the decolorization and dissociation under light (Ghaedi et al. 2012). Crystal violet (CV) is extensively used for the dyeing of cotton and silk printing, the manufacturer of paints and printing inks (Asok et al. 2006). CV is also known as methyl violet or gentian violet, as a kind of typical cationic dye, and it has many usages: biological stain, for the treatment of skin disease, as an additive to feed livestock and poultry to inhibit the breeding of mold, intestinal parasites and fungi (Saha et al. 2012a, 2012b). However, excessive amounts of CV is responsible for causing heart-beat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Ma et al. 2012). Therefore, the existence and potential risks of these dyestuffs should be controlled (Kozlowski et al. 2009).

There are a number of articles on removal of CV from aqueous solutions using different materials, such as Coir pith (Parab et al. 2009), NaOH-modified rice husk (Chakraborty et al. 2011), sawdust (Parab et al. 2009), sugarcane fiber (Parab et al. 2009), jute fiber carbon (Porkodi & Kumar 2007), grapefruit peel (Saeed et al. 2010), magnetic nanocomposite (Singh et al. 2011), palm kernel fiber (El-Sayed 2011), jackfruit leaf powder (Saha et al. 2012a, 2012b), pineapple leaf powder (Chakraborty et al. 2012), Nostoc linckia (Mona et al. 2011), manganese coated sepiolite (Eren & Afsin 2009) and raw zeolite (Eren et al. 2010).

As an ideal environmental mineral material, diatomite also possess microporous structure and larger specific surface area just like vermiculite, zeolite and montmorillonite (Slijivic et al. 2009). In addition, the adsorption performance of the modified diatomite can be improved prominently. Al-Ghoutia et al. (2007) studied the removal of methylene blue aqueous solutions by manganese oxidized diatomite. Physical and chemical modification methods were also investigated, Zhang et al. (2013) studied methylene blue adsorption on diatomite treated with sodium hydroxide. The above mentioned methods have been studied for many years. Nevertheless, there are some disadvantages in the present introduced adsorbents, such as waste of water, poisonous materials
and lower adsorption abilities. Recently, a kind of carbon-based nanomaterial has been introduced by the hydrothermal carbonization (HTC) process (Yu et al. 2004). HTC is an emerging, environmentally benign, and state-of-the-art technology for conversion of waste biomass to a coal-like, carbon-rich, and energy-dense solid hydrochar material (Unur et al. 2013; Sun et al. 2014). Compared with high-temperature modified technology, the modified diatomite with HTC method possessed tremendous oxygen-containing groups on their surfaces at lower temperature and hence could be used as adsorbents for water purification.

Therefore, it is necessary to develop a kind of non-pollution synthesis technology to modify diatomite. Herein, we introduced a green modified technology for preparing a diatomite earth&carbon (DE&C) by the HTC process using diatomite and glucose. In this article, DE&C was used as a potential material, and pretreated to be a dyestuff adsorbent to adsorb cationic CV from water. Some physical characteristics were also presented. Then removal capacity of DE&C was established by adsorption isotherms, kinetics and thermodynamic models.

**MATERIALS AND METHODS**

**Synthesis of the diatomite with carbon**

The raw diatomite was supplied by Tianfu Colloidal Co. Ltd (Jilin Province, China) and was grinded into about 80 mesh. Diatomite was used without further purification. The color of the diatomite was white (Figure 1(a)). In a classic process, 5 g of diatomite was dispersed in 80 ml of glucose solution (15 g glucose), then the solution was mixed using the magnetic stirrer at a speed of 500 r min⁻¹ for 30 min. Then the mixed solution was put into a Teflon lined stainless steel autoclave with a volume capacity of 100 mL. Finally, reaction kettle was sealed and placed in a muffle furnace at constant temperature of 180 °C for 12 h. The modified diatomite with carbon was obtained by washing and drying (Figure 1(b)).

**Reagents and solutions**

CV, molecular formula = C₂₅H₃₀N₃Cl, molecular number = 407.99, λ_max = 580 nm, is an alkaline dyestuff, and its pigment ions are positively charged. CV was prepared into a 1,000 mg L⁻¹ solution and used as the stock solution in the subsequent experiments. The pH was adjusted by adding a small amount of HCl or NaOH (1M).

**Instrumentation**

CV concentration was analyzed by measuring the absorbance values after and before each experiment with an ultraviolet-visible spectrophotometer (UV-765, Shanghai Precision and Scientific Instrument Co., Ltd) at a wavelength of 580 nm. The possible composition of the CV was investigated by Fourier transform infrared spectroscopy (FT-IR) meter (Alpha, Infrared Spectrometer Bruker, Germany). pH was measured by WTW MTQ/TC2020, meter (Germany). Temperature and oscillation velocity was controlled by constant-temperature shaking incubator (BS-1E, JinTan Medical Instrument). Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) were measured by specific surface analyzer (MICROMERTICS ASAP 2020, USA).

In this experiment, the maximum absorbance wavelength of CV was measured by an ultraviolet-visible spectrophotometer at a wavelength of 580 nm, and the concentration of dyestuff solution was calculated according to the standard curve. Before and after the adsorption of dyestuff to DE&C, the FT-IR spectrometry was recorded by an FT-IR meter with a wavelength range of 4,000 to 500 cm⁻¹ with a resolution of 4 cm⁻¹. The BET surface

![Figure 1](https://iwaponline.com/wst/article-pdf/73/6/1463/463077/wst073061463.pdf)
area of DE&C was measured in the relative pressure range from 0.05 to 0.4. Defined as the volume of liquid nitrogen corresponding to the adsorbed amount, the total pore volume was measured at a single point, where \( P/P_0 = 0.987 \). The pore size distributions were deduced from \( \text{N}_2 \) adsorption isotherms using the BJH method. Before measurements, DE&C was analyzed by adsorption/desorption test, using liquid nitrogen at 77 K and degassing for 15 h at 250 °C in the appropriate port of the adsorption analyzer.

**Adsorption studies**

Batch adsorption was put in a set of 1,000 mL flasks including 150 mL of CV solution with the concentration of 150 mg/L. The amount of 2.0 g of DE&C was added and controlled at different temperatures (20, 35 and 50 °C). The optimal pH value was 2.0 and it was used for the following experiments.

After adsorption equilibrium was achieved, the adsorbing capacity and removal rate \( (Y) \) of CV by DE&C was computed as follows:

\[
q_e = \frac{V(C_0 - C_e)}{M} \quad (1)
\]

\[
Y = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)
\]

where \( q_e \) is the amount of adsorbate adsorbed at the equilibrium, mg·g\(^{-1}\); \( C_0 \) is the initial concentration of CV in solution, mg·L\(^{-1}\); \( C_e \) is the liquid-phase dye concentration at equilibrium, mg·L\(^{-1}\); \( V \) is the volume of the solution, L; and \( M \) is the mass of the adsorbent used, g.

**RESULTS AND DISCUSSION**

**Characterization of diatomite**

**FT-IR analysis**

DE&C possesses significantly greater adsorption capacity over untreated diatomite. In order to investigate why, we explored the surface functional groups of diatomite by FT-IR analysis. Figure 2 shows the FT-IR spectra for raw diatomite, DE&C and DE&C after adsorption. In spectra of Figure 2(a), the main peak of functional groups were described at 3,442, 1,634, 1,401, 1,096, 796 and 619 cm\(^{-1}\). The peak at 3,442 cm\(^{-1}\) may be attributed to the hydrogen atom that is attached to Si-H. The peak at 1,634 cm\(^{-1}\) was probably caused by flexural vibration of H-OH in water molecule. The peak at 1,401 cm\(^{-1}\) is due to stretching vibration of C-O and flexural vibration of H-OH. The peak at 1,096 cm\(^{-1}\) was attributed to Si-O-H. The peaks at 796 and 618 cm\(^{-1}\) were caused by the flexural vibration of Si-O-Si or Si-O.

There are some differences of the major keys in the spectra between raw diatomite and DE&C. Compared with raw diatomite, some new peaks occurred in the spectra of DE&C (Figure 2(b)). The peaks at 2,346 and 2,300 cm\(^{-1}\) reflected the group of amines (-NH\(_2\)). After diatomite was modified with carbonaceous components, the new bands, including the 1,724 cm\(^{-1}\) bands of carbonyl groups and the 1,619 cm\(^{-1}\) band of C=C (Demir-Cakan et al. 2009), appear in the FT-IR spectrum of the DE&C. These results demonstrate that the natural diatomite earth has been successfully modified by the functional carbonaceous components.

**Figure 2** | FT-IR spectra of adsorbents: (a) raw diatomite and (b) DE&C.
**BET analysis**

Figure 3(a) shows the N₂ adsorption–desorption isotherm values for DE&C. The obtained adsorption isotherm matches well the Type IV isotherm as classified by the IUPAC (Sing 1985), which refers to a multi-layer reversible adsorption process, in this case, interaction between DE&C and CV. There is a clear H3-type hysteresis loop from $P/P_0 = 0.04$ to 0.987. The attribute of the Type H3 loop, which does not exhibit any limiting adsorption at high $P/P_0$, is observed with aggregates of plate-like particles giving rise to slit-shaped pores.

Figure 3(b) shows distribution of DE&C pore size on the basis of the BJH model. Using the BET equation, we obtained a calculated surface area for DE&C of 73.15 m² g⁻¹. Respective total pore volume and average pore diameters were 0.4758 cm³ g⁻¹ and 10.56 nm. There are many kinds of diatomite in the world, and many factors affect the surface area. Although DE&C possesses decreased surface area compared with raw diatomite, the determined surface area value was greater than that of calcined diatomite (52.56 m² g⁻¹), as reported by Lin (Lin et al. 2007). Therefore, BET surface area and total pore volume of DE&C suggest that it is a superior porous adsorbent.

**Adsorption isotherm**

An adsorption isotherm indicates how adsorption molecules reach the equilibrium state during the adsorbing process of both liquid and solid phases. The time needed to reach the equilibrium state is called the adsorption equilibrium time. The balance between adsorbing time and dye adsorption capacity reflects the saturated adsorption capacity of the adsorbent under the operating conditions. It is a very significant step to fit different isothermal adsorption models by data analysis, and finally to work out a model best fit for the adsorbing process. Two adsorption isotherms, Langmuir model and Freundlich model, were used to fit the experimental data. The applicability of these two isotherm equations was evaluated by correlation coefficients ($R^2$).

**Freundlich adsorption isotherm**

The Freundlich adsorption isotherm was applied to reveal uneven multilayer adsorption by the adsorbent. The assumed prerequisite is that with increase in adsorbing temperature, the number of adsorption sites increases exponentially (Daraei et al. 2015).

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where $K_F$ is the Freundlich constant, (mg·g)⁻¹·(L·mg⁻¹)¹/n, which represents the adsorption capacity; $n$⁻¹ represents adsorption heterogeneity degree, if $0 < n^{-1} < 1$, the adsorption process is available and works well. Figure 4(a) shows that the Freundlich model linearly fitted to the experimental data, which described the adsorption of CV by DE&C at 20, 35, and 50°C. The results of $K_F$, $n$⁻¹ and $R^2$ are listed in Table 2. With the concentration of 50–250 mg L⁻¹, $n$⁻¹ of Freundlich model was all less than 1. When $n$⁻¹ ranges from 0 and 1, which measure the adsorption intensity or surface heterogeneity (Zhang et al. 2015), surface adsorption can be carried out easily. The $R^2$ were 0.9208, 0.9854 and 0.9751 under the three temperatures. The experimental data lie within the concentration range, but the Freundlich adsorption isotherm deviated from the trend line. The experimental results showed that Freundlich adsorption isotherm, which was used to describe the polymolecular layer, did not fit these data.
The Freundlich adsorption isotherm showed that the activation energies carried by surface groups towards various adsorption reactions were different, and that the adsorption reaction happened on different adsorption sites.

**Langmuir adsorption isotherm**

The assumed prerequisite of the Langmuir adsorption isotherm is that the surfaces of the adsorbent are even, contain a monomolecular layer, and no interaction force exists between the adsorbed molecules (Manshouri et al. 2012).

\[
\frac{C_x}{q_e} = \frac{C_x}{q_m} + \frac{1}{b \times q_m}
\]

where \(q_m\) is the maximum adsorbing capacity, mg·g\(^{-1}\); and \(b\) refers to Langmuir constant;

Figure 4(b) shows the equilibrium data in Langmuir isotherm expressions at 20, 35, and 50 °C. In Table 1, the maximum adsorbing capacities were 100.00 mg L\(^{-1}\), 192.31 mg L\(^{-1}\), and 109.89 mg L\(^{-1}\) at 20 °C, 35 °C, and 50 °C respectively, among which the \(q_m\) at 35 °C was the highest. Compared with other adsorbents, this result indicated that the adsorption capacity (192.31 mg L\(^{-1}\)) was at top level. Then the \(R^2\) were 0.9915, 0.9900 and 0.9980, respectively. Langmuir adsorption isotherm was qualified to describe the experimental data. Table 2 shows a comparison of adsorption capacity and compared with others.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (q_m) (mg·g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coir pith</td>
<td>65.53</td>
<td>Parab et al. (2009)</td>
</tr>
<tr>
<td>NaOH-modified rice husk</td>
<td>44.87</td>
<td>Chakraborty et al. (2011)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>37.83</td>
<td>Parab et al. (2009)</td>
</tr>
<tr>
<td>Sugarcane fiber</td>
<td>10.44</td>
<td>Parab et al. (2009)</td>
</tr>
<tr>
<td>Jute fiber carbon</td>
<td>27.99</td>
<td>Porkodi &amp; Kumar (2007)</td>
</tr>
<tr>
<td>Grapefruit peel</td>
<td>254.16</td>
<td>Saeed et al. (2010)</td>
</tr>
<tr>
<td>Magnetic nanocomposite</td>
<td>81.70</td>
<td>Singh et al. (2011)</td>
</tr>
<tr>
<td>Palm kernel fiber</td>
<td>78.90</td>
<td>El-Sayed (2011)</td>
</tr>
<tr>
<td>Jackfruit leaf powder</td>
<td>43.39</td>
<td>Saha et al. (2012a, 2012b)</td>
</tr>
<tr>
<td>Pineapple leaf powder</td>
<td>78.22</td>
<td>Chakraborty et al. (2012)</td>
</tr>
<tr>
<td>Nostoc linckia</td>
<td>72.11</td>
<td>Mona et al. (2011)</td>
</tr>
<tr>
<td>Raw sepiolite</td>
<td>131</td>
<td>Eren &amp; Afsin (2009)</td>
</tr>
<tr>
<td>Raw zeolite</td>
<td>77</td>
<td>Eren et al. (2010)</td>
</tr>
<tr>
<td>Manganese coated sepiolite</td>
<td>319</td>
<td>Eren &amp; Afsin (2009)</td>
</tr>
</tbody>
</table>

**Figure 4** | Adsorption isotherms for CV adsorption by DE&C at different temperatures: (a) Freundlich isotherm and (b) Langmuir isotherm.

**Table 1** | Constants of adsorption isotherms of crystal violate on DE&C at different temperatures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>20</th>
<th>35</th>
<th>50</th>
</tr>
</thead>
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<tr>
<td>Langmuir, the whole concentration range (50–250 mg L(^{-1}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(q_m) (mg·g(^{-1}))</td>
<td>100.00</td>
<td>192.31</td>
<td>109.89</td>
</tr>
<tr>
<td>(b) (L·mg(^{-1}))</td>
<td>0.9902</td>
<td>0.0137</td>
<td>0.0185</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9915</td>
<td>0.9900</td>
<td>0.9980</td>
</tr>
<tr>
<td>Freundlich, the whole concentration range (50–250 mg L(^{-1}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_F) (mg·L(^{-1})) (L·mg(^{-1}))(^{1/n})</td>
<td>9.86</td>
<td>3.76</td>
<td>3.23</td>
</tr>
<tr>
<td>(n) (^{-1})</td>
<td>0.663</td>
<td>0.837</td>
<td>0.806</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.9208</td>
<td>0.9854</td>
<td>0.9751</td>
</tr>
</tbody>
</table>

Table 2 | Comparison of CV adsorption capacity of DE&C with other reported adsorbents
reported in literature for different adsorbents to adsorb CV from aqueous solutions. DE&C has a larger adsorption capacity compared with other adsorbents.

**Adsorption kinetics**

In order to better describe the adsorption process, explain the reaction process and determine the control principles from the perspective of kinetics, various kinetic models would be built. The major models include models of pseudo-first-order kinetics and pseudo-second-order kinetics and were used to study the reaction pathway and rate-controlling step during the adsorption of CV by DE&C.

**Pseudo-first-order kinetic model**

Pseudo-first-order kinetic model was presented by Lagergren, and was used to study the adsorbing process of liquid-phase to solid-phase system (Lagergren 1898).

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

(5)

where \( q_t \) is the adsorption capacity during period \( t \), mg·g\(^{-1}\); \( q_{e,cal} \) is the theoretical equilibrium adsorption capacity, mg·g\(^{-1}\); \( k_1 \) is the pseudo-first-order kinetic model constant, min\(^{-1}\).

By plotting of \( \log(q_e - q_t) \) and \( t \) for different initial dye concentrations, linear lines were obtained and constant \( k_1 \) can be calculated from the isothermal straight slope and intercept (Figure 5(a)). As showed in Table 3, \( q_{e,cal} \) was much smaller than \( q_{e,exp} \), and \( R^2 \) lied between 0.8918–0.9815, which indicated that the experimental data did not fit to this pseudo-first-order kinetic model. Therefore, this model cannot well describe the whole adsorbing process, but is widely used in the primary stage of the adsorption process.

**Pseudo-second-order kinetic model**

Pseudo-second-order kinetic model was proposed by Ho and McKay, and can be used into deep analysis of kinetic data (Ho & McKay 1999). The model is expressed as:

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

(6)

where \( k_2 \) is the pseudo-second-order kinetic model constant, g·(mg·min\(^{-1}\))\(^{-1}\).

By plotting of \( t/q_t \) and \( t \) for different initial dye concentrations, linear lines were obtained and constant \( k_2 \) can be calculated from the isothermal straight slope and intercept (Figure 5(b)). According to Table 3, the calculated \( q_{e,cal} \) values also agree very well with the \( q_{e,exp} \). \( R^2 \) ranges from 0.9928 to 0.9998, which indicates high correlation.
Therefore, the pseudo-second-order kinetic model was much more suitable for fitting the experimental data than pseudo-first-order kinetic model. These results indicated that the adsorption process experiment belongs to the pseudo-second-order kinetic model.

### Intraparticle diffusion model

Adsorption kinetics involves various adsorbing mechanisms, where one major restriction is the diffusion mechanism. The diffusion mechanism cannot be determined by pseudo-first-order or pseudo-second-order kinetic models, but was analyzed by internal granular diffusion kinetic model. The equation is expressed as follows:

\[ q_t = k_3 t^{0.5} + C \]  \hspace{1cm} (7)

where \( k_3 \) (mg·g\(^{-1}\)·min\(^{-0.5}\)) is the internal granule diffusion speed constant; \( C \) is the intercept; the values of \( q_t \) and \( t^{0.5} \) can be calculated from \( k_3 \), \( C \) and \( R^2 \). By data fitting, Figure 5(c) shows the intraparticle diffusion model of dyestuff CV under different initial concentrations. This multi linear curve showed that several steps occurred during the whole adsorbing process. The curve can be divided into three parts: a straight-up part, a slowly-rising part and a smooth-steady part. During the first part, CV diffuses rapidly around the superficial thin layer of DE&C (membrane diffusion); during the second part, CV is diffused inside the adsorbent granule (in-granule diffusion); and during the third part, the adsorption is equilibrium. \( k_3 \) and \( C \) can be indicated from the data of the second part. The fitting performance of the figure lines was high. \( R^2 \) was between 0.8631 and 0.9868, which showed that these experimental data can be well described by the intraparticle diffusion model. The adsorption equilibrium time is less than 60 min at all the concentration ranges. As the second part does not pass the original point, the inside-adsorbent diffusion of DE&C was the controlling step during the adsorbing process. However, membrane diffusion was also another controlling step. The constant \( k_3 \) and the intercept \( C \) were analyzed. Table 3 shows that \( k_3 \) and \( C \) both increased as the initial concentration was improved, which indicated that the internal diffusion rate increased with the rise of initial concentration. The increase of initial concentration will lead to higher concentration gradient, and finally to faster diffusion and quicker adsorption. When \( C \) increases, \( k_3 \) was higher, which indicates that the increase on boundary layer thickness and the boundary layer will affect the adsorption as follows: a larger intercept indicates greater effect of boundary layer.

### Adsorption thermodynamic

Thermodynamic parameters were important indicators of the application of adsorbing process, including \( \Delta G^0 \), \( \Delta H^0 \) and \( \Delta S^0 \).

\[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  \hspace{1cm} (8)

\[ K_d = \frac{q_e}{C_e} \]  \hspace{1cm} (9)

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  \hspace{1cm} (10)

where \( \Delta G^0 \) is the Gibbs free energy, kJ·mol\(^{-1}\); \( R \) is gas constant, 8.314 J·(mol·K\(^{-1}\)); \( T \) is the temperature, K; \( \Delta H^0 \) is the enthalpy change, kJ·mol\(^{-1}\); and \( \Delta S^0 \) is the entropy change, J·K\(^{-1}\).

According to Table 4, at 293, 308, and 323 K, the values of \( \Delta G^0 \) and \( \Delta H^0 \) were all negative, which indicated that the adsorption may be a spontaneous exothermic process.

Therefore, this means that with the temperature increases, energy is not available to improve the adsorption. If \( \Delta S^0 \) was positive during the adsorbing process, the degree
of confusion was raised on the interface between solid and liquid phases; the positive value of $\Delta S^0$ reflects that dyestuff showed high affinity towards DE&C (Auta & Hameed 2014). In this experiment, under 50–250 mg/L, the values of $\Delta S^0$ were positive, which indicated that in the whole concentration range, DE&C showed high adsorption affinity to CV. In summary, the adsorption of CV by DE&C is a spontaneous exothermic process.

**CONCLUSION**

This novel modification method demonstrates that DE&C, a green adsorbent, exhibits excellent adsorption capacity for CV. FT-IR results indicate that functional groups play a crucial role during the adsorption of CV. The BET and BJH results showed that DE&C also owned a larger specific surface area (73.15 m²·g⁻¹). Regarding the adsorption of CV onto DE&C, Comparing $R^2$ values, the Langmuir isotherm fit experimental data better than the Freundlich isotherm. The adsorbing process of DE&C acting on CV fits the pseudo-second-order kinetic model (average $R^2 > 0.99$). During the adsorbing process the measured values of $\Delta G^0$ were all negative, which indicates the process was spontaneous. The values of $\Delta H^0$ were all negative, which additionally indicates that the adsorbing process was exothermal. Values of $\Delta S^0$ in the entire concentration were positive, which indicates the affinity of CV toward DE&C. The modified diatomite prepared in this work has a promising application in wastewater treatment for alkaline dyes removal.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


**Table 4** | Thermodynamic parameters of CV adsorption by aerobic granular sludge

<table>
<thead>
<tr>
<th>$C_0$ (mg·L⁻¹)</th>
<th>$\Delta G^0$ (kJ·mol⁻¹)</th>
<th>$\Delta H^0$ (kJ·mol⁻¹)</th>
<th>$\Delta S^0$ (J·mol⁻¹·K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293 K</td>
<td>308 K</td>
<td>323 K</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>–0.37</td>
<td>–1.28</td>
<td>–2.57</td>
</tr>
<tr>
<td>100</td>
<td>–1.59</td>
<td>–1.12</td>
<td>–0.28</td>
</tr>
<tr>
<td>150</td>
<td>–2.19</td>
<td>–1.64</td>
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<tr>
<td>200</td>
<td>–2.03</td>
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<td>–0.50</td>
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<tr>
<td>250</td>
<td>–2.69</td>
<td>–0.97</td>
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