Kinetic, isotherm, and thermodynamic studies of the adsorption of dyes from aqueous solution by cellulose-based adsorbents

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ABSTRACT

In this study, a highly efficient and eco-friendly porous cellulose-based aerogel was synthesized by grafting polyethyleneimine onto quaternized cellulose (PQC) to remove the anionic dye Congo Red (CR). The prepared aerogel had a good flexibility and formability. The adsorbents were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and elemental analysis. The results showed that there were many amino groups on CE/PQC aerogel and the structure was porous, which increased the adsorption capacity. The effects of initial concentration, adsorbent dose, contact time, temperature, and pH on the dye sorption were all investigated. The adsorption mechanism was also explored, including adsorption kinetics, adsorption isotherms and thermodynamic studies of adsorption. The results showed that the adsorption kinetics and isotherms fitted the pseudo-second-order kinetic model and Langmuir isotherm, respectively. The Langmuir isotherm revealed that the maximum theoretical adsorption capacity of the aerogels for CR was 518.403 mg g⁻¹. The thermodynamic parameters including Gibbs free energy change (ΔG⁰), enthalpy change (ΔH⁰) and entropy change (ΔS⁰), showed the adsorption process was exothermic and spontaneous. These results imply that this new absorbent can be universally and effectively used for the removal of dyes from industrial textile wastewater.

Key words | adsorption, aerogels, cellulose, Congo Red, polyethyleneimine, porous structure

INTRODUCTION

In recent years, the application of dyes in various industries, such as textile, paper, plastics, printing, rubber and food (Wang et al. 2014; Zhou et al. 2014), has caused severe environmental contamination and human health issues when not dealt with appropriately before disposal.

There are many methods to treat dye wastewater, including sorption (He et al. 2013; Zhou et al. 2014), flocculation (Cai et al. 2015), oxidation (Gomes et al. 2008), electrolysis (Wang 2009), liquid membrane separation (Dâas & Hamdaouï 2010) and other processes (Wu et al. 2011). Among them, the adsorption technique is regarded as a superior technique because of its low initial cost, simplicity of design, ease of operation, reusability and insensitivity to toxic pollutants (Mittal et al. 2010; Zhou et al. 2014; Liu et al. 2015b). Various types of adsorbents are used in treating dyes, for instance minerals (Anirudhan & Ramachandran...
carbon-based materials (Robati et al. 2016) and polymeric materials (Gupta et al. 2015). Recently, biological materials, based on natural or synthetic special functional materials, have been used widely as adsorbents because of their low cost, biodegradability, eco-friendly properties and high adsorption capacities; thus bioadsorbents have been selected as ideal adsorbents for the removal of dye (Zhu et al. 2011; Liu et al. 2015a).

As the most plentiful natural polysaccharide on the Earth, cellulose (CE) has numerous attractive properties: renewability, biodegradability, biocompatibility, good formability, eco-friendliness and low price (Liu et al. 2015a). In addition, cellulose also has good water-purification effects because it has abundant free –OH groups on the chain, enabling efficient removal of metal ions and dyes from water. However, owing to poor water solubility and relatively low chemical reactivity, the application of cellulose as an adsorbent is always limited. To improve the adsorption ability of cellulose, many investigators have tried to modify natural biopolymers with specific functional groups, such as amino (Mahmoud et al. 2013; Meder et al. 2013), carboxyl (Cai et al. 2013; Pitsari et al. 2013) and mercapto (Pan et al. 2012) groups. A promising strategy is to graft cationic groups on to cellulose to enhance the interactions between cellulose and anionic dyes. Aihua et al. (Pei et al. 2015) prepared surface quaternized cellulose nanofibrils with an adsorption capacity for anionic dyes. Liu et al. (Wang et al. 2016) found that quaternized cellulose modified with acrylamide increased its adsorption capacity for anionic dyes. Lin et al. (Liu et al. 2015a) reported that cellulose modified with acrylamide and acrylic acid can increase its adsorption sites for anionic and cationic dyes. Several reports have also demonstrated that a particular kind of cellulose-based material can remove dyes with different molecular structures. However, how to synthesize a new structure of cellulose-based adsorbent to remove dyes more effectively has become a hot topic all over the world.

In this research, we designed porous cellulose-based aerogels by mixing CE and polyethyleneimine grafted onto quaternized cellulose (PQC) together and the polyethyleneimine with abundant amino groups was grafted onto quaternized cellulose to increase the adsorption performance of cellulose. In the aerogel bioadsorbents system, the cellulose is a carrier, with its strong backbone or skeleton structure, and the PQC is an effective adsorbent, with abundant amino groups to remove anionic dye under neutral or mildly acidic conditions. Congo Red (CR) was selected as the model pollutant to investigate the adsorption performance of CE/PQC aerogels.

MATERIALS AND METHODS

Materials

Medical absorbent cotton was purchased from HeNan Piaoan Group. NaOH, urea, sodium borohydride, sodium hydrogen sulfite and CR were obtained from Sinopharm Chemical. (3-Chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC), epichlorohydrin (ECH) and polyethyleneimine were obtained from Aladdin Reagent. Distilled water was used for the whole experiment, and all reagents were used in the experiments without any further purification.

Preparation of quaternized cellulose

Water-soluble quaternized cellulose (QC) derivatives were prepared in accordance with previous work (Song et al. 2008). In brief, a certain amount of CHPTAC solution was added dropwise to 100 g of cellulose solution (2 wt %, in NaOH/urea aqueous solution), and left to react for 24 hours at 25 °C. The reaction product was neutralized with HCl aqueous solution. Finally, the solution was freeze-dried with lyophilizer to obtain the purified products.

Preparation of polyethyleneimine grafted quaternized cellulose

The grafted copolymer of CE and polyethyleneimine was synthesized by a facile crosslinking method. The whole synthetic strategy is shown in Figure S1 (available with the online version of this paper). In brief, 2 g of QC was dissolved to 100 mL of distilled water with 0.25% NaOH, and it was kept in an oil bath at 60°C with continuous stirring at 400 rpm. Then, a certain quality of polyethyleneimine was added to the flask. After 10 min, ECH was added slowly to the reaction system. The reaction was continued for 3 hours at the same stirring speed and temperature. After that, the resulting product was washed five times in ethanol. The obtained PQC copolymer was dried overnight at 60°C.

For the preparation of a series of PQC samples with different grafting efficiencies, different qualities of polyethyleneimine for each reaction were carried out; all samples and other details are listed in Table S1 (available online). The eventual corresponding products were named PQC1, PQC2, and PQC3, respectively. The grafting efficiency (GE) was monitored by
the weighting method as shown Equation (1) (Cai et al. 2013):

\[ GE = \frac{W_g - W_0}{W_0} \times 100\% \]  

where \( W_0 \) (g) and \( W_g \) (g) are the qualities of QC and PQC, respectively.

**Preparation of CE/PQC aerogels**

Cellulose solution was obtained according to the appropriate method. Cellulose was dissolved in a water solution with 7% NaOH and 12% urea at a low temperature (−20 °C) to obtain 2 wt % solution. The cellulose solution was centrifuged at 5,000 rpm for 10 min to remove residual impurities. Subsequently, the desired amount of PQC and ECH were added to the cellulose solution to crosslink the cellulose into hydrogel. In order to shape the aerogel, we used a beaker as a mold. The mixed solution was poured into a beaker to control the specimen thickness at 0.5 cm and diameter at 6.0 cm. After the solution had gelled, it was immersed in ethanol for coagulation. After coagulation, the hydrogel was washed with deionized water until neutral. Finally, the resulting products were freeze-dried (Martin Christ, Germany) for 24 hours at −50 °C.

**Characterization of materials**

The Fourier transform infrared (FTIR) spectra of CE, QC, PQC1, PQC2 and PQC3 samples were measured in KBr pellets using an AVATAR 360 FTIR spectrophotometer (Nicolet, USA) to record the spectra in the range of 4,000–400 cm\(^{-1}\). The elemental analysis of samples was performed using a Carlo Erba 1,108 Elemental Analyzer. The morphology of the adsorbents and its pore structure were characterized by scanning electron microscopy (SEM) (SU8010, Hitachi, Japan).

**Adsorption of dyes experiments**

For the adsorption experiments, the anionic dye CR was used in this study. Batch adsorption experiments were carried out by using a shaking bath THZ-82B (Jiangsu, China) with a shaking speed of 150 rpm until the system achieved equilibrium. Typically, 0.025 g of adsorbent and 25 mL of dye solution were added to a 100 mL glass flask and then shaken at 150 rpm and at 30 °C. The UV-vis spectra (UV-1100D, Shanghai) measured the concentration of residual dye in the solution, and the dye concentration was calculated by the absorbance at the maximum absorption (500 nm). The adsorption capacity and dye removal efficiency of CR on were obtained according to Equations (2) and (3):

\[ q = \frac{V(C_0 - C_t)}{m} \]  

Dye removal (%) = \( \frac{C_0 - C_t}{C_0} \times 100\% \)

where \( q \) is the adsorption capacity (mg g\(^{-1}\)), \( V \) is the solution volume (L), \( C_0 \) is the initial dye concentration (mg L\(^{-1}\)), \( C_t \) (mg L\(^{-1}\)) is the dye concentration in the solution at time \( t \) (min) and \( m \) is the adsorbent mass (g).

**RESULTS AND DISCUSSION**

**Materials characterization**

The FTIR spectra of CE, QC, and a series of PQC copolymers are shown in Figure 1. The biggest difference in the FTIR spectra of QC and PQC are the absorption peaks at 1,060, 1,610 and 3,200 cm\(^{-1}\) compared with the pure CE sample. In Figure 1(a), the characteristic peaks at 2,983 cm\(^{-1}\) and 3,400 cm\(^{-1}\) could be ascribed to C-H and -OH stretching vibrations, respectively. As shown in Figure 1(b), the unique characteristic peaks at 1,060 and 1,185 cm\(^{-1}\) are ascribed to the stretching vibrations of the C-N group, indicating that quaternary ammonium had been grafted on CE. According to Figure 1(c)–1(e), the broad absorption band at 3,200 cm\(^{-1}\) and 1,610 cm\(^{-1}\) for the copolymers is ascribed to the stretching vibrations of the −NH\(_2\) groups, and the two absorption peaks become stronger and stronger, which shows that the −NH\(_2\) group contents increased. The absorption peak at 1,410 cm\(^{-1}\) could be ascribed to N-H stretching. These characteristic absorption peaks are correspond to polyethyleneimine, which indicate that polyethyleneimine modified QC successfully.

In the aerogel system, cellulose acts as a frame with its strong backbone or skeleton structure, which keeps a good formability and strong mechanical performance. From Figure 1(f), we can see the aerogel has a heterogeneous porous structure. This result reveals that during the process of CE/PQC aerogel formation, the crosslinking between cellulose and PQC generated the support structure of the aerogel, and the evaporation of water during the freeze-drying process led to the heterogeneous pore structure (Wang et al. 2016). The typical well-defined porous and
interconnected three-dimensional framework structure can provide more adsorption space to remove dye effectively.

**Elemental analysis and the choice of optimum adsorbent**

The results of the elemental analysis of CE, QC and a series of PQC copolymers are shown in Table S1. Only three elements, that is, carbon, hydrogen and nitrogen, were analyzed. The results show that there was 0.01% nitrogen content in CE, which could be due to trace quantities of unisolated proteins. Compared to CE, the nitrogen content of QC increased to 1.79%, proving that the quaternary ammonium groups had been successfully grafted onto CE. In the series of PQC copolymers, when the quality of polyethyleneimine increased from 1.5 g to 3.0 g, PQC2 showed significant variation in nitrogen content. However, the change in the nitrogen content of PQC3 was not obvious in the case of increasing the quality of polyethyleneimine from 3.0 g to 4.5 g.

In these PQC copolymers, with the change of nitrogen content, the dye removal efficiency also changed. And PQC2 showed the best dye removal efficiency, so PQC2 was chosen as the adsorbent. The initial dye concentration, adsorbent dosage, time and pH were investigated to evaluate the adsorption characteristics of CE/PQC2 aerogels.

**Adsorption of CR**

**Effect of initial dye concentration**

The effects of initial dye concentration on adsorption capacity were investigated in a range from 100 to 1,000 mg L\(^{-1}\) at pH 7.0 at 303 K for 300 min; 1.4 g/L adsorbent dosage was selected. As can be seen from Figure 2(a), the dye adsorption capacities onto the adsorbent increased with the increase of the initial dye concentration. The maximum adsorption capacity for CR reached 441.34 mg g\(^{-1}\) at the initial dye concentration of 1,000 mg L\(^{-1}\). The removal efficiency of CR decreased gradually with the increase in concentration of dye solutions, which might be due to a lower initial concentration offering more vacant active sites for adsorption, and then saturated sites were not able to capture the dye molecules (Wu et al. 2015).

**Effect of adsorbents dosage on adsorption performance**

Figure 2(b) shows the effect of adsorbent dosage on the dye removal efficiency by adding 25 mL of dye solution to an initial concentration of 500 mg L\(^{-1}\) at pH 7.0 at 303 K for 300 min. The dye removal efficiency increased with increasing adsorbent dosage. This result could be explained by the active sites on the surface of CE/PQC increasing with the increase in adsorbent dosage, and thus surface area was available for adsorption, making it easier for the dye molecules to penetrate into the adsorption sites.

**Effect of contact time**

The extent of dye removal versus time in different concentration is plotted in Figure 2(c). It can be seen that the system achieved adsorption equilibrium after 300 minutes for all concentrations ranging from 100 to 1,000 mg L\(^{-1}\) at pH 7.0 at 303 K; 1.4 g/L adsorbent dosage was selected, and the color of the dye gradually levels off. In the adsorption process, the dye molecules migrated from the aqueous
solution onto the surface of the bioadsorbent, and first formed van der Waals force between. Subsequently, electrostatic interactions occurred when the anionic dye CR was close enough to the adsorption sites (−NH₂) on the surface of cellulose-based bioadsorbent (Zhou et al. 2013). More dye particles accumulated on the active sites of the adsorbent with increasing adsorption time, finally reaching a plateau (Zhou et al. 2014), which might be due to the active sites of the adsorbents being occupied, so that more dye could not be accommodated. Besides, with the adsorption time increase, the solution became diluted, the contact probability between dye molecules and adsorbents reduced, which led to the adsorption equilibrium.

Effect of pH value on adsorption performance

In the CE/PQC2 aerogels, polyethyleneimine with abundant amino groups was grafted onto QC. To investigate the influence of pH on the dye removal efficiency, the pH of the dye solution was selected in the range of 3.0 to 11.0, and the temperature was selected at 303 K for 300 min. The pH value of the aqueous solution was adjusted using hydrochloric acid (0.05 mol L⁻¹) or sodium hydroxide (0.05 mol L⁻¹). Figure 2(d) shows that the removal efficiency of the CE/PQC2 aerogels continuously decreased with increasing pH values. As is known, CR is a typical anionic dye and has abundant negative charges in aqueous solution. At lower pH values (pH < 7), the −NH₂ groups in PQC2 were protonated to −NH₃⁺ groups. As a result, the electrostatic attractions between the positively charged adsorbent and the negatively charged dye were strong. By contrast, under alkaline conditions, it became more difficult for −NH₂ to be protonated and the −NH₃⁺ concentration decreased, which did not favour electrostatic attractions between adsorbent and anionic dye, leading to the dye removal efficiency decreasing (Liu et al. 2015a).

Adsorption kinetics of CR

The adsorption kinetics include the pseudo-first-order kinetic model, pseudo-second-order kinetic model and...
intraparticle diffusion model (Metin et al. 2015; Ghorai et al. 2014). The formulas of pseudo-first-order kinetic and pseudo-second-order kinetic models are shown in Equations (4) and (5):

\[
\ln \left( \frac{q_e}{q_t} \right) = \ln \frac{q_e}{C_0} - k_1 t
\]

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

where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the amounts of dye adsorbed at equilibrium and at time \( t \), respectively. \( k_1 \) (min\(^{-1}\)) is the pseudo-first-order rate constant and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second-order rate constant.

The intraparticle diffusion model (Zhang et al. 2012) is also employed to study the kinetic model. The intraparticle diffusion equation is expressed in the following form:

\[
q_t = k_p (t^{1/2}) + C
\]

where \( k_p \) (mg g\(^{-1}\) min\(^{-1/2}\)) is the rate constant of intraparticle diffusion. \( C \) is the constant related to the thickness of the boundary layer, which is in direct ratio to the effect of the boundary layer. The values of \( k_p, C \) and \( R^2 \) are also listed in Table 1.

In the Table, the values of \( R^2 \) for CR obtained from the pseudo-second-order kinetic model were higher than the pseudo-first-order kinetic model with different initial concentrations. Combined with the experimental values, \( q_e \) did not well fitted to those calculated from the linear plots (Figure S2(a)) (Figure S2 is available with the online version of this paper). This demonstrated that the adsorption process did not comply with the pseudo-first-order model. In Figure S2(b), the linear plots of \( t/q_t \) versus \( t \) showed that the experimental values are in good agreement with calculated values at different initial concentrations. The correlation coefficient (\( R^2 \)) for the pseudo-second-order model had higher values (>99%, Table 1) than the pseudo-first-order model. This demonstrated that the pseudo-second-order adsorption mechanism was predominant, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, providing the best correlation with the data.

From the Figure S2(c), we can see that the adsorption of the CR dyes by porous cellulose-based adsorbents is essentially relevant to three continuous steps. The three stages are shown in Figure S2(c). The first stage was external surface adsorption or instantaneous adsorption. The second stage was gradual adsorption, where intraparticle diffusion was rate-controlled. The third stage was the final equilibrium adsorption process, where the intraparticle diffusion rate slowed down owing to the extremely low dye concentration in solution (Zhang et al. 2012).

### Adsorption isotherms

It is important to investigate adsorption isotherms, including Langmuir isotherm, Freundlich isotherm and Temkin isotherm (Lin et al. 2017), so as to analyze the adsorption data of CR on the bioadsorbents. The Langmuir isotherm and Freundlich isotherm mathematical expressions are shown in Equations (7)–(9):

\[
\frac{C_e}{q_e} = \frac{1}{bq_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

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

\[
\ln q_e = \frac{RT}{d} \ln (AC_e)
\]

#### Table 1 | Kinetic parameters of pseudo-first-order and pseudo-second-order models for the adsorption of CR onto CE/PQC2 aerogel

| \( C_0 \) | Pseudo-first-order model | | Pseudo-second-order model | | Intraparticle diffusion | |
|---|---|---|---|---|---|
| \( k_1 \) | \( q_e \) | \( R^2 \) | \( k_2 \) | \( q_e \) | \( R^2 \) | \( k_p \) | \( C \) | \( R^2 \) |
| 200 | 0.0145 | 125.286 | 0.9021 | 3.012 \( \times \) 10\(^{-6} \) | 185.185 | 0.9921 | 7.971 | 57.551 | 0.8687 |
| 400 | 0.0134 | 226.060 | 0.8306 | 6.564 \( \times \) 10\(^{-7} \) | 322.581 | 0.9946 | 14.24 | 86.684 | 0.8897 |
| 600 | 0.0166 | 263.534 | 0.9009 | 2.525 \( \times \) 10\(^{-7} \) | 400.000 | 0.9983 | 17.568 | 134.490 | 0.8313 |
| 800 | 0.0186 | 275.807 | 0.9735 | 1.809 \( \times \) 10\(^{-7} \) | 434.783 | 0.9990 | 18.328 | 157.080 | 0.8609 |
| 1,000 | 0.0196 | 243.180 | 0.9865 | 1.268 \( \times \) 10\(^{-7} \) | 454.545 | 0.9992 | 18.221 | 187.340 | 0.8052 |
where $q_e$ is the adsorption capacity at the equilibrium (mg·g$^{-1}$), $q_{\text{max}}$ is the theoretical maximum adsorption capacity (mg·g$^{-1}$), $C_e$ is the equilibrium concentration of dye solution (mg·L$^{-1}$), and $b$ is a Langmuir isotherm constant related to the energy of adsorption. $K_f$ (L·mg$^{-1}$) and $n$ are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbents, respectively. $A$ (L·mg$^{-1}$) and $d$ (J·mol$^{-1}$) are the Temkin constants. $R$ is the universal gas constant 8.314 J·mol$^{-1}$·K$^{-1}$, and $T$ is the absolute temperature (303 K, 313 K and 323 K for CR).

The isotherm parameters were summarized from Figure S3 (available online) and tabulated in Table 2. As shown in Figure S3, it is evident that the Langmuir isotherm model reveals a better fit to the experimental data than the other two models studied here. According to the Table 2, the data fit best with the Langmuir model, which illustrates that adsorption took place on the homogeneous surface of adsorbents. The Langmuir model shows that $q_{\text{max}}$ is 518.403 mg·g$^{-1}$ in 323 K which is similar to the value 498.754 mg·g$^{-1}$, obtained by experiment. The values of $b$ are found to be within the range of 0 to 1, indicating that the adsorbents were favorable for adsorption of CR. For the Freundlich model, the values of $K_f$ verified that adsorption process is easy and adsorption capacities increased with the increases in initial dye concentration. By calculating from the Freundlich model, $n > 1$ confirmed favourable adsorption processes. For the Temkin model, the higher values of $d$ indicated a strong bonding force between dyes and adsorbents. Combined with the comparison of these results from the three isotherm models, the Langmuir model had higher $R^2$ (>0.99) values than other two isotherm models, verifying that the adsorption process was a monolayer adsorption.

### Thermodynamic studies of adsorption

Figure 3 shows the influence of temperature on adsorption at different dye initial concentrations. The dye removal efficiency for CR increases with the increase in temperature in the range from 303 K to 323 K. The effect of temperature on the dye adsorption capacity by CE/PQC2 bioadsorbent is shown in Figure 3(b). The experiments were also carried out at 303, 313, and 323 K. As shown in Figure 3(b), the adsorption capacity increases with increasing temperature in different dye initial concentrations. It could be explained by the fact that the adsorption of dyes on the bioadsorbent is an endothermic process.

### Table 2 | Isotherm parameters for the adsorption of CR on CE/PQC2 aerogel

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>Temkin isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b$ (L·mg$^{-1}$)</td>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>303</td>
<td>0.027</td>
<td>465.116</td>
<td>0.9990</td>
</tr>
<tr>
<td>313</td>
<td>0.034</td>
<td>481.696</td>
<td>0.9989</td>
</tr>
<tr>
<td>323</td>
<td>0.036</td>
<td>518.403</td>
<td>0.9990</td>
</tr>
</tbody>
</table>

![Figure 3](https://iwaponline.com/wst/article-pdf/77/11/2699/244602/wst077112699.pdf)

The effect of temperature on different concentrations, (a) dye removal efficiencies, and (b) dye adsorption capacities on the adsorbent.
To study whether the adsorption process is feasible and endothermic, Gibbs free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$), and entropy change ($\Delta S^0$) were employed and calculated according to the following Equations (11) and (12) (Zhu et al. 2011; Lakouraj et al. 2015):

$$K_c = \frac{q_e}{C_e}$$

$$\ln K_c \left( \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \right)$$

$$\Delta G^0 = -RT \ln K_c$$

where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $q_e$ is the adsorption capacity at equilibrium (mg g$^{-1}$), $C_e$ is the equilibrium concentration of dye (mg L$^{-1}$), $T$ is the absolute temperature (K), and $K_c$ is the equilibrium constant of adsorption (L mol$^{-1}$).

In Table 3, the negative values of $\Delta G^0$ at various temperatures (303, 313 and 323 K) show the spontaneous and feasibility nature of adsorption onto the aerogel bioadsorbent. The negative value increases at higher temperatures, which confirms that the adsorption amounts at equilibrium must increase with increases in temperature. The positive value of $\Delta H^0$ in the temperature range of 303 to 323 K indicates again that the adsorption process is endothermic and that chemisorption is taking place. The positive value of $\Delta S^0$ show a good affinity between CR and bioadsorbent, which confirms the adsorption process is random, occurring at the solid–solution interface (Sancha et al. 2010; Ai et al. 2011; Yu et al. 2013).

**Adsorption mechanism**

The adsorption capacity of the adsorbent is determined by various factors such as the structure and functional behavior of the adsorbate molecules, the surface of the adsorbent and the interactions between the adsorbent and the adsorbate all influence the dye adsorption mechanism. As shown in Figure 4, CR is a planar molecule, and can be easily adsorbed on the cellulose-based bioadsorbents by van der Waals forces and hydrogen bonding (Gong et al. 2015). Especially, the effect studies of pH demonstrated that the electrostatic interactions between dyes and the adsorption sites of the bioadsorbent were the main interaction forces, because the removal efficiency of the bioadsorbent had a higher value under neutral or mildly acidic conditions, shown in Figure 2(d). Moreover, adsorption capacity and efficiency commonly depend on the number of available active sites and the microstructure of the bioadsorbent. Thus, it was decided that the possible interactions involved in CR major adsorption process is electrostatic interaction and hydrogen bonding. These possible interactions between the dye molecules and the cellulose-based bioadsorbent are shown in Figure 4.

| Thermodynamic parameters at different temperatures |
|---|---|---|---|
| $T$ (K) | $\Delta G^0$ (kJ mol$^{-1}$) | $\Delta H^0$ (kJ mol$^{-1}$) | $\Delta S^0$ (J mol K$^{-1}$) |
| 303 | -2.035 | 20.009 | 72.752 |
| 313 | -2.762 | - | - |
| 323 | -3.490 | - | - |

**CONCLUSIONS**

In this research, CE/PQC aerogels were synthesized and evaluated as a novel bioadsorbent for the removal of an anionic dye. The experimental results showed that dye sorption on CE/PQC aerogels had a higher removal efficiency than CE and QC. The study of the influence of pH revealed that the bioadsorbent possessed an excellent adsorption performance under acid and neutral conditions. The adsorbents
was shown to have a porous and three-dimensional framework structure by SEM. From the adsorption kinetics study, the pseudo-second-order adsorption model was a better fit than the pseudo-first-order model. The Langmuir isotherm model fitted with experimental data better than the Freundlich and Temkin isotherm models, and the maximum theoretical adsorption capacity of the aerogel bioadsorbent was 518.403 mg g\(^{-1}\) at 323 K. The thermodynamic studies provided evidence for the feasibility and spontaneous nature of the adsorption process. Above all, CE/PQC aerogels could be promising adsorbents for the treatment of dye wastewater.

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