Chitosan resins synthesised by improved drop-sphere-forming method for Cr(VI) removal from aqueous solutions
Shunyi Li, Zhenjun Wu, Bin Li, Rencheng Zhu and Yan Wang

ABSTRACT
An improved drop-sphere-forming (IDSF) method was applied to synthesise chitosan resin. Chitosan resin was synthesised by the self-made device and cross-linked with epichlorohydrin. The influences of concentration of chitosan-acetic acid solution, air flow, reaction time and the dosage of epichlorohydrin were investigated during synthesising. The satisfactory chitosan particles were prepared by chitosan-acetic acid solution (3%) under a controlled air flow of 0.6 m³ h⁻¹. After 6 h of reaction at 80 °C with an epichlorohydrin dosage of 2 mL per 5 mL wet resin, the chitosan cross-linked resin has the best adsorption capacity. After 2 h of adsorption at pH = 3.0 and 25 °C with an adsorbent dosage of 2 g L⁻¹, the maximum adsorption capacity (112 mg g⁻¹) was reached for an initial Cr(VI) concentration of 146 mg L⁻¹. Compared with other adsorbents, this synthesis method was simple and economic; moreover, the cross-linked chitosan resin can remove Cr(VI) efficiently.

Key words | adsorption, characterisation, chitosan, synthesis

INTRODUCTION
Chitosan, as a derivative from deacetylation of chitin (Lasko & Hurst 1999), is an important natural polymer possessing several favourable characters, including good biodegradability, biocompatibility, antibacterial property and low toxicity (Yu et al. 2010). Due to the biodegradability and biocompatibility, chitosan is regarded as an attractive material in various fields of applications ranging from agriculture and wastewater treatment to pharmaceuticals, food and personal care (Gorochovceva et al. 2005). Chitosan is widely considered as an efficient biosorbent for chromium; this is because the amino groups of chitosan serve as the coordination sites (Wu et al. 2010).

Chitosan resin can be synthesised through various chemical methods. The traditional method of preparing chitosan resin is reverse suspension crosslinking (Li et al. 2008); however, this method needs plenty of reagents and has complicated procedures (Yang et al. 2009). In this study, a novel device for synthesising chitosan resin was made and an improved drop-sphere-forming (IDSF) method (He et al. 2001) was applied to synthesise chitosan resin. Compared with the traditional process, this method consumes few reagents and less energy. In addition, this device has low cost, a simple structure and a convenient operation. The cross-linked resin, prepared by the IDSF method, has good chemical stability and mechanical strength.

METHOD
Synthesising chitosan resin
Optimisation of synthesis conditions
A certain amount of chitosan (2, 3 and 4 g) was dissolved in 100 mL of 2% (v/v) acetic acid (Hena 2010), making the chitosan-acetic acid solution with concentrations of 2, 3 and 4%. After standing at room temperature for 12 h, the viscous solution was added into the syringe of the improved chitosan resin synthesis device (Figure 1). Under a controlled air flow (0.16, 0.24, 0.32, 0.40, 0.48, 0.56 and 0.64 m³ h⁻¹) around the syringe needle, the solution was added dropwise into the sodium hydroxide solution (2.5 M). Through the experiment, the optimal synthesis conditions were found. The reaction mixture was filtered, and the obtained white precipitates were washed several times with distilled water until the wash water became neutral (Elwakeel 2010).
Optimisation of cross-linking conditions

Epichlorohydrin was used as the cross-linking reagent (Chen et al. 2008). Five millilitres of wet chitosan resin obtained as above was added to 20 mL of distilled water followed by different doses of epichlorohydrin (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 mL). This mixture was stirred for an additional different reaction time (2, 4, 6, 8, 12, 18 and 24 h) at 80°C (He et al. 2000). After that, the precipitate was filtered off, washed thoroughly with distilled water, and then dried under vacuum to constant weight. Finally, the obtained resin was immersed in HCl (0.1 M) for 24 h, and then washed several times with distilled water and dried. By measuring the adsorption capacity, the optimal cross-linking conditions were determined.

Sorption experiment

The adsorption capacity of chitosan cross-linked resin was obtained by soaking 0.05 g of dry resin in a flask. Potassium dichromate was dissolved in water to simulate chromium wastewater. Fifty millilitres of various initial concentrations of potassium dichromate solution was added to the flask, and the initial concentrations of Cr(VI) were from 20 to 160 mg L⁻¹. The initial pH of solution was adjusted to 3.0. The flask was shaken while keeping the temperature at 25°C for 2 h (Ng et al. 2003). The residual concentration of Cr(VI) was measured spectrophotometrically at 540 nm using the Diphenylcarbazide method. The adsorbed capacity of the cross-linked chitosan resin for Cr(VI) was calculated as follows (Zou et al. 2011):

\[ q_e = V \times \left( C_0 - C \right)/m \]

where \( C_0 \) (mg L⁻¹) is the initial concentration of the Cr(VI) solution, \( C \) (mg L⁻¹) is the concentration of the solution, which was taken at each time interval, \( V \) (L) is the volume of the solution in the flask, and \( m \) (g) is the weight of the resin added into the flask.

RESULTS AND DISCUSSION

Preparation of chitosan cross-linked resin

Effect of the concentration of chitosan solution

Chitosan was dissolved in acetic acid and formed a viscous solution (Geng et al. 2005). The viscosity of the chitosan-acetic acid solution has a direct impact on the pelletised property of chitosan. The chitosan resin, which was synthesised by high-viscosity chitosan–acetic acid solution, was almost not spherical and with a tail. In contrast, the chitosan resin synthesised by low-viscosity chitosan solution had an irregular shape and diverse diameters. Through experiment, the optimal concentration of chitosan–acetic acid solution was 3%. Under such conditions, the chitosan resin can be synthesised with a spherical shape and uniform diameter.

Effect of the air flow

Through experiment, the air flow was the other determinant for synthesising chitosan resin. Air flow determined the residence time of the viscous chitosan solution around the syringe needle. The correct air flow is beneficial to the addition of the chitosan solution. High air flow can break the chitosan bead whereas the low air flow cannot blow the chitosan bead into the sodium hydroxide solution. In this study, the chitosan solution was added dropwise to sodium hydroxide solution under an air flow of 0.56 m³ h⁻¹.

Effect of the cross-linking time

In the cross-linking stage, the reaction time was the key factor for synthesising chitosan cross-linked resin (Xue et al. 2011). To study the effects of the reaction time of cross-linking on the synthesis of chitosan cross-linked resin, the resin was studied at various cross-linking times while keeping the epichlorohydrin dosage of 0.5 mL per 5 mL wet chitosan resin. In this study, the Cr(VI) adsorption capacity was used as the value to judge the effect of reaction time. The results are shown in Figure 2(a).

Figure 2(a) shows the adsorption of Cr(VI) by cross-linked chitosan resin at different reaction times and at the...
epichlorohydrin dosage of 0.5 mL per 5 mL wet chitosan resin. In the experiments, the uptake of Cr(VI) was at a maximum at the reaction time of 6 h. When the cross-linking time was below 6 h, the adsorption capacity and cross-linking degree of the chitosan cross-linked resin were increased steadily with increasing time, peaking at 6 h. After that, both of them declined gradually with increased time. The main reason for the drop of value was that the chitosan cross-linked resin swelled and was destroyed in solution. Based on experimental results, the optimal reaction time of the process was suggested as 6 h.

Effect of the dosage of epichlorohydrin

To study the effects of the amount of cross-linking reagent on the Cr(VI) absorption capacity of chitosan cross-linked resin, the dosage of epichlorohydrin was studied at various ratios while keeping other reaction conditions constant (Hu et al. 2014). When the amount of the cross-linking reagent was relatively low, the Cr(VI) absorption capacity of the chitosan cross-linked resin was slightly low. That is because Cr(VI) was absorbed primarily through the amino of chitosan and chloride which was provided by epichlorohydrin. The Cr(VI) absorbency of the resin was gradually enhanced when increasing the amount of epichlorohydrin. When the dosage was around 2.0 mL per 5 mL wet resin, the absorption capacity reached its maximum value (Figure 2(b)). When the amount of the cross-linking reagent was increased further, the Cr(VI) absorption capacity began to decrease. It is considered that all the hydroxyl functional groups of chitosan may participate in the cross-linking process and part of the amino groups may start to react with epichlorohydrin. Therefore, the number of amino groups reacting with Cr(VI) reduced; meanwhile, the Cr(VI) absorption capacity of the chitosan cross-linked resin declined. Through experiment, the optimum dosage of epichlorohydrin was 2.0 mL per 5 mL wet resin.

Characterisation of chitosan cross-linked resin

To identify possible interactions between chitosan resin and epichlorohydrin, Fourier transform infrared (FTIR) spectra were obtained for the chitosan resin before and after cross-linking. The results are presented in Figure 3. The appearance of peaks at 1,381 and 3,438 cm\(^{-1}\) for chitosan are due to stretching vibrations of hydroxyl groups, and the appearance of peaks at 1,640 and 3,438 cm\(^{-1}\) for chitosan are a result of deformation vibration and stretching vibration of amide groups, respectively, which indicates the existence of hydroxyl groups and amide groups in chitosan. After cross-linking, the FTIR spectrum of the resin in Figure 3(b) depicted a shift of the peak at 3,438–3,434 cm\(^{-1}\) and at 1,381–1,350 cm\(^{-1}\) (Cestari et al. 2010); moreover, these peaks decreased. The information indicated that the amide and hydroxyl groups in chitosan may participate in the cross-linking process.

The surface morphology of the cross-linked chitosan resin was examined by scanning electron microscopy (SEM). As shown in Figure 3(c), The SEM images show that cross-linked chitosan resin is nearly spherical in shape and uniform in size, with an average diameter of 0.2 mm. The diameters of the pore of the resin mainly range between 20 and 40 nm. This means that the cross-linked chitosan resin can be regarded as a kind of mesoporous material.

Sorption properties of chitosan cross-linked resin

Based on experimental analysis, the pH of the solution was found to be the main factor determining adsorption capacity. In the experiments, the high adsorption is observed in the pH
range of 3.0–5.0 (Babel & Kurniawan 2004). Consequently, the equilibrium uptake of Cr(VI) was at a maximum at pH 3.0 for the concentration range studied. That is because Cr (VI) exists in several anionic forms such as Cr_2O_7^{2-}, HCr_2O_7^- , CrO_4^{2-} , and CrO_4^{2-} depending on the concentration of the chromium ion and the pH of the solution (Udaybhaskar et al. 1990). At lower pH (pH = 3–5), because of the existing protonation of amino groups, the chitosan is positively charged, whereas the dichromate ion exists mainly as an anion. As a result, the electrostatic attraction can proceed between chitosan and Cr(VI) (Boddu et al. 2003). However, at a pH > 5.0, the chitosan undergoes deprotonation and exists in a neutral form, so little interaction occurs between Cr(VI) and cross-linked chitosan resin; thus the adsorption capacity decreases. Below pH 5.0, the decrease in the amount of Cr(VI) adsorbed on cross-linked chitosan resin is due to a change in the form of Cr(VI). Below pH 2.0, Cr(VI) exists primarily as H_2CrO_4 and therefore cannot interact with protonated chitosan through an ion exchange mechanism. In view of this, all experimental data were collected at pH 3.0 (Sengupta et al. 1986).

Figure 4(a) shows the adsorption of isotherms of Cr(VI) by cross-linked chitosan resin at different temperatures and at a pH of 3.0. It can be clearly seen that the adsorption capacity increases along with the increasing of temperature. Experiments show that the adsorption process is endothermic in nature, and the temperature raising is beneficial for the intraparticle diffusion of Cr(VI) ions into the pores of the adsorbent.

The adsorption data in Figure 4(a) were treated according to the following Langmuir equation (Donia et al. 2008):

$$
\frac{C_e}{q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{K_L Q_{\text{max}}}
$$

where $C_e$ is the equilibrium concentration of chromate anions in solution (mg L$^{-1}$), $q_e$ is the adsorbed value of chromate anions at equilibrium concentration (mg g$^{-1}$), $Q_{\text{max}}$ is the maximum adsorption capacity (mg g$^{-1}$) and $K_L$ is the Langmuir binding constant, which is related to the energy of adsorption (L mg$^{-1}$). Plotting $C_e/q_e$ against $C_e$ gives a straight line with a slope and intercept equal to $1/Q_{\text{max}}$ and $1/K_L Q_{\text{max}}$, respectively. The Langmuir adsorption isotherm of Cr(VI) ion on cross-linked resin is shown in Figure 4(b). At all temperatures of the experiment, the Langmuir adsorption isotherm exhibits an approximately linear relationship. The correlation coefficients of the Langmuir

Figure 3 | The FTIR spectra for the chitosan resin before (a) and after (b) cross-linking. (c) SEM images of cross-linked chitosan resins.
isotherm model were 0.9964, 0.9976 and 0.9984 at 30, 40, 50 °C, respectively. Besides that, the values of $Q_{\text{max}}$ obtained from the Langmuir plots (84.19, 95.99 and 112.57 mg g$^{-1}$) are approximately equal to the experimental ones (86.81, 96.34 and 112.74 mg g$^{-1}$). The results suggest that the adsorption reaction occurs mainly at the monolayer at all temperatures. Moreover, the value of $K$ is large, indicating that the cross-linked chitosan resin employed has a high adsorptive capability (Minamisawa et al. 2004).

The removal mechanism of Cr(VI) may include both physical adsorption of Cr(VI) on the surface or inside of the resin and ion exchange between Cr(VI) and the chitosan resin (Ramnani & Sabharwal 2006). As shown in Figure 4(a), the Cr(VI) absorption capacity of the chitosan cross-linked resin increases with increasing initial concentration of Cr(VI). The results show that the concentration difference may serve to drive the Cr(VI) diffusion, and high initial concentration may accelerate the external diffusion. After the external diffusion, the Cr(VI) may diffuse through the pores of resin and interact with the active site of chitosan. The results showed that the maximum adsorption capacity (112 mg g$^{-1}$) was reached for an initial Cr(VI) concentration of about 146 mg L$^{-1}$.

Comparison of cross-linked chitosan resin with other adsorbents

The adsorption capacity of Cr(VI) onto cross-linked chitosan resin was compared with other adsorbents reported in the literature and is shown in Table 1. Cross-linked chitosan resin synthesised by IDSF method has a higher adsorption capacity than chitosan, non-cross-linked chitosan and the chitosan-Fe$^0$ nanoparticles. Chitosan coated with poly 3-methylthiophene and chemically modified magnetic chitosan resins are found to have relatively large adsorption capacities of 127.62 and 145.60 mg g$^{-1}$, respectively. However, these types of chitosan resins need more reagents and a complicated synthetic procedure. Compared with the chitosan coated with these resins, during the cross-linking procedure of this paper, epichlorohydrin is the only reagent used to enhance the rigidity of resin. Not only is the synthetic procedure simple, but the absorption efficiency remains relatively high. Because of the need for less chemical reagent and energy, this method would be a simply and economic choice in practice.

### Table 1 | Comparison of adsorption capacities of Cr(VI) with other adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg g$^{-1}$)</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>22.09</td>
<td>3</td>
<td>Aydin &amp; Aksoy (2009)</td>
</tr>
<tr>
<td>Non-cross-linked chitosan</td>
<td>78.00</td>
<td>5</td>
<td>Schmuhl et al. (2001)</td>
</tr>
<tr>
<td>Cross-linked chitosan (IDSF method)</td>
<td>112.57</td>
<td>3</td>
<td>This paper</td>
</tr>
<tr>
<td>Chitosan–Fe$^0$ nanoparticles</td>
<td>60.20</td>
<td>6</td>
<td>Geng et al. (2009)</td>
</tr>
<tr>
<td>Chitosan coated with poly 3-methylthiophene</td>
<td>127.62</td>
<td>2</td>
<td>Hena (2010)</td>
</tr>
<tr>
<td>Chemically modified magnetic chitosan resins</td>
<td>145.60</td>
<td>3</td>
<td>Elwakeel (2010)</td>
</tr>
</tbody>
</table>

CONCLUSION

Chitosan cross-linked resin was prepared with an IDSF method. The Cr(VI) absorption capacity of the chitosan cross-linked resin was studied at different conditions. The
optimal conditions to synthesise the resin showing the highest absorption capacity was identified; moreover, the absorption capacity of the prepared resin in potassium dichromate solution can be as high as 112 mg g⁻¹. In addition, the absorption capacity of the prepared resin was found to be influenced by time, pH, temperature and the initial concentration of Cr(VI). Finally, the removal mechanism may include both physical adsorption and chemical adsorption. To be specific, not only is Cr(VI) adsorbed on the surface and inside the resin but it also interacted with the active site of chitosan resin. Moreover, compared with the other adsorbents, this kind of cross-linked chitosan resin can be considered as a promising material for the removal of Cr(VI) from wastewater.

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