Chromium removal with cross-linked chitosan adsorption and base-precipitation combination
Huixin Zhang, Feng Wang, Xiuhong Jin, Yuchao Zhu, Xiaona Li and Hongyong Zhou

ABSTRACT
A novel technique for a complete removal of both Cr(VI) and Cr(III) ions, namely cross-linked chitosan (CCTS) adsorption and base-precipitation combination, was studied in this work in great detail. The optimum conditions for Cr(VI) adsorption onto CCTS were determined as a function of pH, CCTS dosage and contact time, while Cr(III) precipitation was investigated as a function of pH value. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the Cr(VI) adsorption isotherm on CCTS. The Langmuir model agreed much better with experimental data than the Freundlich and D–R by a correlation coefficient ($R^2$) of 0.994. The capacity and Δ$G^\circ$ of CCTS for Cr(VI) were 70.4 mg/g and $-26.6$ kJ/mol respectively, indicating the feasible and spontaneous nature of the Cr(VI) sorption process. This combined technique was applied for real wastewater treatment from the electroplating industry and obtained a one-off retention in solution not more than 0.5 mg/L for both Cr(VI) and Cr total. These results meet the Chinese standards for effluent discharge.

INTRODUCTION
Environmental pollution caused by toxic heavy metals in industrial effluent has been an issue that has concerned the world for many years. Chromium ions are commonly considered hazardous to organisms and the environment (Tofighy & Mohammadi 2011). They mainly exist in the forms of Cr(III) and Cr(IV) in wastewater (Wan Ngah & Hanafiah 2008). Although Cr(III) is thought to be an essential nutrient required for sugar and fat metabolism, it is very toxic to aquatic organisms when its concentration exceeds 5.0 mg/L (Baroni et al. 2008; Gurgel & Gil 2009). Long-term contact causes skin allergies and cancers. Cr(VI) has been found to be carcinogenic and mutagenic to animals and humans (Yen et al. 2004). Therefore, the potential dangers of Cr(VI) and Cr(III) are quite obvious.

There are many techniques to treat wastewater containing chromium, such as ion-exchange, electrolytic reduction, chemical precipitation, adsorption and so on (Akhamd et al. 2011). However, all of the above techniques face problems in industrial practice, either because of difficulties in raising funds for complicated processing and high operational costs, or in handling large quantities of sludge, and are therefore not suitable for small-scale industries. Last but not least, any technique must completely meet the demands for effluent discharge standards issued by governments (Fujiwara et al. 2007). Thus, chitosan and other biomasses have been increasingly explored and used as adsorbents in recent years due to their low operation costs, stronger adsorption to metal-ions, short operation time and easy degradation (Sari et al. 2007), an advantage for a desirable and promising adsorbent, and can be applied to treat industrial effluent containing chromium ions (Sari et al. 2008; Uluozlu et al. 2008; Gazi & Shahmohammadi 2012). As far as the authors are aware, there has been no investigation reported in the literature that the technique of cross-linked chitosan (CCTS) adsorption and sodium hydroxide precipitation combination has been applied to treat wastewater containing chromium ions with different valences. In addition, the technique obtains high removal rates and can be easily used to treat industrial wastewater containing Cr(VI) and Cr(III). Furthermore, remnants of both Cr(VI) and Cr(III) in
solution met the requirements of the Chinese legislation for industrial emission.

The objective of the present work is to investigate the removal efficiencies of Cr(VI) and Cr(III) in wastewater by CCTS adsorption and sodium hydroxide precipitation combining technique. Optimum adsorption conditions were determined as functions of pH values, adsorbent dosage and contact time, while base-precipitation was also determined as a function of the pH values of solution. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were used to describe Cr(VI) adsorption onto CCTS.

**EXPERIMENTAL PROCEDURES**

**Reagents and equipment**

Chitosan from crustacean shells (Jinan Haidebei Marine Bio. Tech. Co., Jinan, China), with a molecular weight of 900,000 Da and not less than 95% degree of deacetylation was used. Other chemicals used in this work were of analytical reagent grade and were used without further purification. Double deionized water (Milli-Q Millipore 18.2 MΩ/cm conductivity) was used for all dilutions. A pH meter, pHS-3C model glass-electrode was employed for measuring pH values in the liquor. A thermo M6 flame atomic absorption spectrophotometer with deuterium background corrector was used for total Cr concentration measurement. All measurements were carried out in an air/acetylene flame. A 10-cm long slot-burner head, a hollow cathode lamp and air–acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer and optimized through experiments. A single beam Digital Spectra UV–vis spectrophotometer with glass cell (10 mm path length) was used for recording the absorbance of the produced complex Cr(VI) ions associated with diphenylcarbazide (DPC) at 540 nm in Cr(III) and Cr(VI) mixed ions solution. The concentrations of Cr(III) can be calculated from Cr total minus Cr(VI).

**Preparation of crossing-linked chitosan (CCTS)**

Twelve grams of chitosan were put in a 1,000 mL flask, immersed in 640 mL 1% (v/v) acetic acid solution, and dissolved by continual stirring. Then, 12 mL cross-linked agent was slowly added drop-wise with strong stirring, followed by 100 mL 5% (m/v) sodium hydroxide solution drop-wise. The reaction was in progress for 10 h under basic conditions. The resulting product was filtered, neutralized by washing with distilled water and acetone consequently, and finally dried in the oven. The dry product was ground into powder and sieved with an 80 mesh before application.

**Adsorption experiments**

Adsorption experiments were optimized at the desired pH value, contact time and sorption dosage using the necessary CCTS in 50 mL stoppered conical flasks containing 10.0 mL of test solution. Initial solutions with different concentrations of Cr(VI) or Cr(III) were prepared by proper dilution from stock 1,000 mg/L Cr(VI) or Cr(III) standards. Phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution resulting in a solution of pH 2.0. Acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 3.0–6.0. Mixed phosphate buffer (0.1 mol/L) was prepared by adding sodium hydroxide and potassium dihydrogen phosphate to result in pH 7.0.

The necessary amount of CCTS was then added and the contents in the flask were shaken for the desired contact time in an electrically thermostatic reciprocating shaker at 160 rpm. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time until there was no difference in the metal concentrations between two adjacent intervals. Then, CCTS in the flask was filtered through filter paper and the filtrate was analysed for metal concentrations with flame AAS. The adsorption ratio and adsorption capacity of Cr(VI) or Cr(III) were calculated as follows (Sahin et al. 2010; Kocak et al. 2011):

\[
\text{Adsorption ratio} \% = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \tag{1}
\]

\[
\text{Adsorption capacity (mg/g)} = \left( \frac{C_i - C_e}{V} \right) \times \frac{m}{1000} \tag{2}
\]

where \( C_i \) and \( C_e \) are the initial and equilibrium concentrations in g/L, respectively, \( V \) the aqueous solution volume in mL, \( m \) the adsorbent mass in grams. Sorption experiments for the effect of pH were conducted by using a solution with 50.0 mg/L of Cr(VI) or Cr(III) concentration with a CCTS dosage of 10.0 g/L. Throughout the study, the contact time was varied from 30 to 240 min, the pH from 2.0 to 7.0 and the sorbent dosage from 5.0 to 30.0 g/L.
Adsorption and precipitation of Cr(III)

The adsorption experiments of Cr(III) onto CCTS were conducted under the optimal conditions for Cr(VI) sorption obtained in the section above. Then, pH values were adjusted to sediment Cr(III) completely. The contents in the flask were filtrated through filter paper after the deposition was finished. The filtrate was analysed for Cr concentration by using flame atomic absorption spectrometry.

Adsorption isotherm models

The adsorption isotherms reveal the specific capacity on the adsorbents' surface at a constant temperature (Kong et al. 2011). Two isotherms, namely, the Langmuir and Freundlich models, were employed to describe them.

The Langmuir model assumes that adsorptions occur at specific homogeneous sites on the adsorbent without interaction between adsorbed molecules and transmigration of the adsorbate. This model was used successfully in many monolayer adsorption processes and can be written as follows (Langmuir 1918):

\[
\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}K_L} + \frac{C_e}{Q_{\text{max}}}
\]

where \(Q_e\) is the monolayer adsorption capacity of the adsorbent, \(C_e\) the equilibrium metal ion concentration in the solution in mg/L, \(Q_{\text{max}}\) the maximum monolayer adsorption capacity in mg/g and \(K_L\) the Langmuir adsorption constant related to the affinity of binding sites in m\(^3\)/g. \(Q_{\text{max}}\) and \(K_L\) are computed from the slopes and intercepts of the straight lines of the plot of \(C_e/Q_e\) vs \(C_e\).

The Freundlich model (Wang et al. 2003) can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich model in linear form is:

\[
\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

where \(Q_e\) is the amount of metal ion adsorbed by per unit mass of CCTS in mg/g, \(C_e\) the equilibrium concentration of metal in mg/L, \(K_f\) a Freundlich constant related to adsorption capacity, \(n\) an empirical parameter related to adsorption intensity and varies depending upon the heterogeneity of the adsorbate materials.

The change in free energy (\(\Delta G^\circ\)) can be calculated from the following equation:

\[
\Delta G^\circ = -RT \ln K_D
\]

where \(R\) is the gas constant of value 8.314 J/(mol K), \(T\) the temperature in Kelvin and \(K_D\) \((Q_e/C_e)\) the distribution coefficient.

The Dubinin–Radushkevich isotherm equation (Anayurt et al. 2009) is expressed by:

\[
\ln Q_e = \ln Q_m - \beta \varepsilon^2
\]

where \(Q_e\) is the mass amount of metal ions adsorbed per unit weight of biomass in mg/g, \(Q_m\) is the maximum sorption capacity in mg/g, \(\beta\) is the activity coefficient related to the mean sorption free energy in mol\(^2\)/J\(^2\) and \(\varepsilon\) is the Polanyi potential \((\varepsilon = RT \ln (1 + 1/C_e))\). The mean sorption free energy \((E; \text{kJ/mol})\) is as follows:

\[
E = \frac{1}{\sqrt{-2\beta}}
\]

The \(E\) (kJ/mol) value implies sorption mechanism as chemical ion-exchange or physical adsorption. If it lies between 8 and 16 kJ/mol, the sorption process takes place chemically, while if \(E < 8\) kJ/mol, the sorption process proceeds physically.

RESULTS AND DISCUSSION

Effect of pH

One of the important factors affecting adsorption of metal ions is the acidity of the solution. This parameter directly relates to the competitive ability of hydrogen ions or protonated functional groups with metal ions to active sites on the adsorbent surface (Sari et al. 2008). The effect of pH on the adsorption of Cr(VI) or Cr(III) on CCTS was studied at pH 2.0–7.0 for Cr(VI) and Cr(III), respectively. The results are presented in Figure 1.

The higher adsorption ratio of Cr(VI) could be found when the acidity is at the stronger end. For example, when the pH value varies from 2.0 to 4.0, the adsorption ratio is around 99.0%. Once the pH value surpasses 5.0, the adsorption ratio decreases drastically. The pH dependency of Cr(VI) sorption ratio could be attributed to protonization...
of amino groups in CCTS chains receiving a proton and carrying a positive charge, which provides a favourable condition for adsorption of Cr$_{2}$O$_{7}^{2-}$ and CrO$_{4}^{2-}$ anions when pH < 5.0. The reaction equations are as follows:

\[ \text{CCTS} - \text{NH}_2^+ + \text{H}^+ \rightarrow \text{CCTS} - \text{NH}_3^+ \]
\[ 2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \]
\[ 2\text{CCTS} - \text{NH}_3^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{CCTS} - \text{NH}_3^+ \cdot \text{Cr}_2\text{O}_7^{2-} + \text{H}_3\text{N} - \text{CCTS} \] (8)

The CCTS surface was more negatively charged as the pH of the solution increased from 2.0 to 7.0. The sorption of Cr(VI) anions became difficult due to electric repulsion and presented a significant decreasing tendency in retention. There might be some risk for CCTS oxidation by Cr$_{2}$O$_{7}^{2-}$ at a strong acidic pH range, or Cr$_{2}$O$_{7}^{2-}$ and CrO$_{4}^{2-}$ reduction by organic pollutants in acidic wastewater, especially in the presence of sulfonate:

\[ 2\text{Cr}_2\text{O}_7^{2-} + 3\text{C} + 16\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 3\text{CO}_2 + 8\text{H}_2\text{O} \] (9)

Therefore, the pH for good and smooth sorption of CCTS is never controlled below pH 3.0.

Moreover, the removal ratios of Cr(III) fluctuated in the range of 50~60%, which is much lower than those for Cr(VI) when the pH value varies from 2.0 to 5.0. The maximum adsorption ratio for Cr(III) was found to be a little more than 60%, at pH 6.0 without any sediment formation, as shown in Figure 1. However, when pH was beyond 7.0, precipitation of Cr(OH)$_3$ was generated. That is why removal of Cr(III) presents a steep rising pattern once the pH increased to 7.0. The increase contributes to both adsorption of CCTS and deposition of hydroxide. It seems hardly possible to achieve a satisfactory removal ratio only by CCTS sorption.

Effect of adsorbent dosage

The adsorbent dosage is an important parameter because this determines the capability for a given initial Cr(VI) concentration. The adsorbent efficiency for Cr(VI) as a function of the adsorbent dosage was investigated and the results are shown in Figure 2. The adsorption ratio steeply increases with the dosage of CCTS; adsorbent rose from 2.0 to 10.0 g/L. The maximum sorption ratio reached 98.7% for Cr(VI) at the adsorbent dosage of 10.0 g/L and the increase in sorption ratio was insignificant with a further increase in adsorbent dosage over 10.0 g/L. This result can be interpreted by the fact that for better adsorption, more functional groups or active sites must be available for sorption interaction. The total of available active sites increases with an increasing dosage of adsorbent. This increase was slowed down if the sites were continuously occupied. Finally, no significant improvement occurred in the retention of Cr(VI) after the surface of CCTS was saturated with the metal ions.

Effect of contact time

Contact time is one of the important parameters for the successful use of the CCTS adsorbent for rapid sorption and practical application. The effect of contact time on the sorption for Cr(VI) onto CCTS is shown in Figure 3. It can be
seen that the effect of adsorption time on the adsorption ratio was considerably increased within a period of 1 h and then it was nearly constant without any enhancement, whereas the adsorbing reached adsorption equilibrium and the kinetic curve became flat consequently. The adsorption ratio was a maximum of about 99.0%. Therefore, the optimum contact time was selected as about 1 h for further experiments.

### Adsorption and precipitation of Cr(III)

The adsorption of Cr(III) by CCTS was carried out under the optimal conditions as the Cr(VI) adsorption determined above. It was found that the adsorption ratio was only 57.0% at pH = 3.0. Then the base-precipitation was employed to remove Cr(III) ion remnants. The results are shown in Figure 4. It can be seen that Cr(III) ion removal is not satisfied when the pH value is below 7.0 or beyond 10.0, which suggests chromium hydroxide is an amphiprotic compound. Cr(III) could not be precipitated thoroughly when pH was lower than 7.0 and the precipitation would be partly redissolved after the pH value was beyond 10.0. Therefore, it must be carried out within the pH range of 8.0 and 9.0 to remove Cr(III) thoroughly.

**Cr(VI) and Cr total removal from the mixed solution of both Cr(VI) and Cr(III) ions**

In this section, the water sample was prepared against electroplating wastewater composition in Table 1. The molar ratio of Cr(VI) and Cr(III) was maintained at 1:1, and the total Cr remained at 100.0 mg/L. The optimal conditions for sorption were conducted as obtained in the section Adsorption experiments. The results for the combined treatment of CCTS sorption and base-precipitation are shown in Table 2. The data suggest that it is in favour of CCTS to adsorb Cr(VI) from the solution bearing both Cr(VI) and Cr(III). Cr(VI) and total Cr that remain in the solution are 0.32 and 0.97 mg/L, respectively, which are below the maximum allowable limits in Chinese effluent discharge standards.

Moreover, the combined technique was applied to deal with real chromium electroplating wastewater from the banknote printing industry, in which the ratio of Cr(VI) to

Table 1 | Average composition of electroplating bath solution

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Cl⁻</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>Mg</td>
</tr>
</tbody>
</table>

Table 2 | Combined CCTS adsorption and base-precipitation for mixed valent solution of chromium (sorption pH: 3.0–4.0; deposition pH: 8.0; CCTS dosage: 10.0 g/L; temperature: 25°C)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Initial (mg/L)</th>
<th>After sorption (mg/L)</th>
<th>After settlement (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Cr</td>
<td>100.0</td>
<td>43.33</td>
<td>0.97</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>50.0</td>
<td>0.65</td>
<td>0.32</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>50.0</td>
<td>42.68</td>
<td>0.65</td>
</tr>
</tbody>
</table>
Cr(III) is about 1:3. Table 1 shows the average composition of real electroplating bath solution. Typical values of total Cr in the said effluent vary from 37 to 88 mg/L through the year, although they may sometimes rise to 300–480 mg/L due to technical blow-down or cleansing of the electroplating pool, or drop down to 8–10 mg/L due to introduction of process water and rinsing of the workshop. The treatment was carried out on a solution composed of an extra addition of real bath solution into the real wastewater to adjust Cr to 500 mg/L, while the ratio of different valent Cr ions was maintained at 1:3. The treatment results were well-satisfied. The concentration of Cr(VI) is left at about 0.30 ~ 0.42 mg/L and the total Cr drops to about 0.90 ~ 0.99 mg/L; these concentrations are obviously lower than those required by Chinese discharge standards for industrial effluent.

**Adsorption isotherms**

The capacity of an adsorbent can be described by equilibrium sorption isotherms, which indicates the surface nature of the adsorbent and its affinity. The Langmuir isotherm is based on monolayer adsorption on the active sites of the adsorbent while the Freundlich isotherm explains the adsorption on a heterogeneous (multiple layer) surface with uniform energy (Neto et al. 2005; Sahin et al. 2010). The adsorption data in the experiment were fitted by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models, as shown in Figures 5–7.

**Figure 5** shows the linear Langmuir isotherm obtained by plotting the $C_e/Q_e$ versus equilibrium concentration values. The correlation coefficient ($R^2$) was found to be 0.994 for the adsorption of Cr(VI), indicating that the equilibrium data fitted the Langmuir model well. The maximum adsorption capacity ($Q_m$) was found to be 70.4 mg/g-CCTS for Cr(VI). The $K_L$ value was found to be 44.5 L/mg for Cr(VI). The Gibbs free energy change ($\Delta G^\circ$) was calculated to be $-26.6$ kJ/mol for Cr(VI). The negative $\Delta G^\circ$ value indicates the thermodynamically feasible and spontaneous nature of the sorption process.

**Figure 6** shows the Freundlich isotherms obtained by plotting ln $Q_e$ vs ln $C_e$. The value of maximum adsorption capacity ($Q_m$) can be deduced to be 9.48 mg/L for Cr(VI). The $K_f$ and $n$ values were found to be 9.48 L/mg and 2.66 individually. The correlation coefficient ($R^2$) was found to be 0.886 for the adsorption of Cr(VI) ions. This indicated that the equilibrium data are of a worse fit by the Freundlich model than by the Langmuir model and
Table 3 | Maximum sorption capacity comparison with the literature

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>pH</th>
<th>T/°C</th>
<th>Model used to calculate adsorption capacities</th>
<th>Adsorption capacity (mg/g) Cr(VI)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan cross-linked</td>
<td>3.0</td>
<td>30</td>
<td>Langmuir</td>
<td>84.31</td>
<td>Qian et al. (1999)</td>
</tr>
<tr>
<td>Chitosan-coated fly ash</td>
<td>5.0</td>
<td>25</td>
<td>Langmuir</td>
<td>33.27</td>
<td>Yue et al. (2011)</td>
</tr>
<tr>
<td>Protonated chitosan</td>
<td>7.0</td>
<td>30</td>
<td>Langmuir</td>
<td>7.5</td>
<td>Kousalya et al. (2010)</td>
</tr>
<tr>
<td>Carboxylated chitosan</td>
<td>7.0</td>
<td>30</td>
<td>Langmuir</td>
<td>8.3</td>
<td>Kousalya et al. (2010)</td>
</tr>
<tr>
<td>Grafted chitosan</td>
<td>7.0</td>
<td>30</td>
<td>Langmuir</td>
<td>9.3</td>
<td>Kousalya et al. (2010)</td>
</tr>
<tr>
<td>Moss biomass</td>
<td>5.0</td>
<td>25</td>
<td>D–R</td>
<td>42.1</td>
<td>Sari et al. (2008)</td>
</tr>
<tr>
<td>Chitosan cross-linked</td>
<td>3.0</td>
<td>25</td>
<td>Langmuir</td>
<td>70.4</td>
<td>In this study</td>
</tr>
</tbody>
</table>

Thus, a pseudo method was employed to interpret the sorption process. The combined technique was applied in real electroplating wastewater treatment from the banknote printing industry. The results meet the Chinese standards for effluent discharge.

**REFERENCES**


First received 10 October 2012; accepted in revised form 25 January 2013