Adsorbing low concentrations of Cr(VI) onto CeO$_2$@ZSM-5 and the adsorption kinetics, isotherms and thermodynamics

Jianrui Niu, Xiuxiu Jia, Yaqing Zhao, Yanfang Liu, Weizhang Zhong, Zengli Zhai and Zaixing Li

ABSTRACT

The CeO$_2$@ZSM-5 was prepared by the dipping method. We used ZSM-5 and CeO$_2$ as the carrier and load components, respectively. The aim was to reduce the low concentration of Cr(VI) in simulated wastewater (the concentration of Cr(VI) ranged from 0.2 to 1 mg/L). The characteristics of ZSM-5 and CeO$_2$@ZSM-5 samples were determined by X-ray powder diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and Brunauer–Emmett–Teller (BET). Characterization results showed that the particle size, BET surface area and pore volume for CeO$_2$@ZSM-5 was around 0.783 nm, 421.307 m$^2$/g and 0.313 m$^3$/g, respectively. In addition, the optimum conditions were obtained by the orthogonal test, and the details were as follows: optimal pH, adsorbent dose, initial concentration of Cr(VI) and equilibrium time were 3, 5 g/L, 0.6 mg/L and 70 min respectively. The removal of Cr(VI) was 99.56% in these conditions. The pseudo-second-order model best described the adsorption kinetics of Cr(VI) onto CeO$_2$@ZSM-5. Isotherm data were treated according to Langmuir, Freundlich and Temkin isotherm models. The results showed that the Freundlich adsorption isotherm model fitted best in the temperature range studied. Adsorption capacity increased with temperature, showing the endothermic nature of Cr(VI) adsorption. The desorption results showed the best recovery of Cr(VI) using 0.1 M HCl.

Key words | CeO$_2$@ZSM-5, Cr(VI) adsorption, kinetics, isotherms, thermodynamics

INTRODUCTION

Chromium is found in the sewage discharge of some enterprises, such as the production of leather, electroplating, printing, dyeing and the chemical industry. Chromium oxide is usually used as a paint and colorant. It can also produce chromium wastewater. Cr(III) and Cr(VI) are two common oxidation states of chromium found in the environment (Sharma et al. 2017), but Cr(VI) cannot be naturally degraded. It is highly carcinogenic and oxidative, and its toxicity is 100 times that of Cr(III). To sum up, if Cr(VI) cannot be processed in a timely and effective manner, it will cause serious harm to the human body and the environment.

There are many ways to remove Cr(VI), such as the adsorption method, chemical method, biological method, ion exchange method, electrolytic method, membrane separation method. The adsorption method is a relatively mature approach and is emerging as a potentially preferred alternative for the removal of heavy metals. Compared with other methods (Alothman et al. 2013), adsorption is the most efficient because of ease of operation, high-quality treated effluent and the fact that the adsorbent can be regenerated. There is much research on various chromium adsorption materials, the most commonly used being activated carbon (Alothman et al. 2013), graphite (Gopalakrishnan et al. 2015), carbon nanotubes (Mubarak et al. 2016) and zeolite (Choi et al. 2016), etc.

However, because of the presence of water and impurities in the channels, the adsorption capacity of natural adsorption materials is low (Hall et al. 1966). Choi et al. modified zeolite by replacing Si(IV) and Al(III) sites in the lattice with exchangeable cations such as sodium, magnesium, potassium, or calcium, resulting in a net negative charge (Choi et al. 2016). The Mg-modified adsorbent had a cadmium removal of more than 98% at an optimum pH
of 7. In addition, the adsorption capacity of Mg-zeolite was found to be 1.5–2.0 times higher than that of natural zeolite. Therefore, modified materials are mostly employed in practical applications. Since CeO₂ (ceria) has high oxidation and thermal stability, it tends to modify various catalysts to improve the activity of the catalyst (Salerno et al. 2017). The surface area and the number of bulk/sub-surface defects in the ceria seem to be the main properties determining the catalytic activity. Rivas et al. found that the introduction of CeO₂ on the zeolite HZSM-5 produced high catalytic activity and stability (Rivas et al. 2013). The zeolite ZSM-5 is a traditional molecular sieve developed by Mobil in the 1970s. Its high surface area and the fact that it is hydrophilic make it suitable for the sequestration of chromium. However, there have been few reports of applying CeO₂ to modifying a molecular sieve to remove heavy metal pollution in aqueous solutions. Therefore, this paper makes an attempt on it.

The present paper reports the results for the kinetic, equilibrium and thermodynamics studies of Cr(VI) adsorption onto CeO₂@ZSM-5. Since the effectiveness of adsorption relies strongly on operational conditions, parameters that may affect the adsorption including adsorbent dose, initial concentration, contact time and pH were evaluated. Both kinetic and equilibrium isotherm models were used to establish the process of adsorption. The results of this study showed that CeO₂@ZSM-5 was easy to prepare and efficient for treating low concentrations of chromium.

MATERIALS AND METHODS

Raw material and reagents

ZSM-5 (Si/Al = 38) was purchased from Nankai University Catalyst Co., Ltd and was not processed before use. Cerium nitrate (Ce(NO₃)₃·6H₂O), sodium hydroxide (NaOH), anhydrous ethanol (CH₃CH₂OH) and potassium dichromate (K₂Cr₂O₇) were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. LH-Cr1 and LH-Cr2 were used as a standard reagents for determining chromium concentration and were undertaking the batch equilibrium technique. A solution with a known initial concentration of Cr(VI) was prepared and a certain mass of the ZSM-5 or CeO₂@ZSM-5 and 100 mL of the Cr(VI) solution was added to the batch adsorbent. Influencing factors: adsorption doses, initial concentrations of Cr(VI), pH and contact time were varied from 0.1 to 0.9 g, 0.1 to 1 mg/L, 2 to 11 and 20 to 100 min, respectively. The reaction was placed in a constant temperature oscillator which was set at a temperature of 25 °C and a speed of 150 rpm for 60 min. The concentration of Cr(VI) was established after suction filtration. We also did the orthogonal experiment to optimize the conditions. The residual chromium concentration was determined by heavy metal multi-parameter tester.

Preparation of CeO₂@ZSM-5

CeO₂@ZSM-5 were prepared by impregnation of the ZSM-5 (3 g) with an aqueous solution (200 mL) of cerium nitrate for 12 hours at room temperature. Simple ZSM-5 modified by CeO₂ loading (11 wt%) was obtained. A rotating evaporator was used to remove the moisture. The sample was then dried at 110 °C for 2 hours followed by calcination at 550 °C for 3 hours. The resulting CeO₂@ZSM-5 was characterised using several analytical techniques.

Characterization techniques

X-ray powder diffraction (XRD) patterns were recorded with a D/Max-2500 diffractometer using CuKα (0.154 nm) radiation in the region between 5 and 55° (2θ) at a speed of 2° per min. Brunauer–Emmett–Teller (BET) surface area, pore volume, micropore surface area and average pore diameter were determined by nitrogen adsorption at 77 K, using 3Flex analyzer (Micromeritics, ASIQM000100-6), surface area and pore scale analyzer. The surfaces of the natural zeolite and CeO₂@ZSM-5 were imaged using a scanning electron microscope (SEM), JEOL 6300F. Elemental analysis was done by an energy dispersive X-ray (EDX) spectroscopy instrument equipped with SEM. The Fourier transform infrared spectroscopy (FTIR) spectra of the adsorbent were recorded with the KBr pellet method using a Nicolet 6700 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed using an X-ray photoelectron spectrometer (EscaLab 250xi).

Adsorption analysis

A stock solution of Cr(VI) (100 mg/L) was prepared using potassium dichromate dissolved in double-distilled water. All working solutions of varying concentrations were obtained by successive dilution. The pH of the solution was adjusted to the required value using 0.1 M HCl and 0.1 M NaOH. Adsorption experiments for ZSM-5 and CeO₂@ZSM-5 were undertaken by the batch equilibrium technique. A solution with a known initial concentration of Cr(VI) was prepared and a certain amount of the ZSM-5 or CeO₂@ZSM-5 and 100 mL of the Cr(VI) solution was added to the batch adsorbent. Influencing factors: adsorption doses, initial concentrations of Cr(VI), pH and contact time were varied from 0.1 to 0.9 g, 0.1 to 1 mg/L, 2 to 11 and 20 to 100 min, respectively. The reaction was placed in a constant temperature oscillator which was set at a temperature of 25 °C and a speed of 150 rpm for 60 min. The concentration of Cr(VI) was established after suction filtration. We also did the orthogonal experiment to optimize the conditions. The residual chromium concentration was determined by heavy metal multi-parameter tester.
The adsorption capacities were calculated based on the differences in the concentrations of solutes before and after the experiment according to Equations (1) and (2):

\[ \begin{align*}
\text{Equation (1)} & : \quad q_e = \frac{(C_0 - C_e) \cdot v}{m} \\
\text{Equation (2)} & : \quad E = \frac{(C_0 - C_e)}{C_0} \times 100\% 
\end{align*} \]

where \( q_e \) is the concentration of the adsorbed solute (mg/g); \( E \) is the removal rate (%); \( C_0 \) and \( C_e \) are the initial and final (equilibrium) concentrations of Cr(VI) (mg/L); \( v \) (ml) is the volume of the solution and \( m \) (g) is the mass of adsorbent.

RESULT AND DISCUSSION

Structure and morphology analysis

As shown in Table 1, the surface area and pore volume of ZSM-5 decreased when it was modified with CeO₂. This was caused by the active sites obstructing some of the main channels of ZSM-5, which impeded the diffusion of N₂ through these channels. The average pore diameter of ZSM-5 increased when it was modified with CeO₂. A probable explanation is that the CeO₂ blocked a large proportion of the smallest pore diameters, therefore the average pore diameter increased. Another explanation is that the high temperature of calcination caused some of the small holes to collapse (Wu et al. 2015). After absorbing Cr(VI), the surface area and pore volume of CeO₂@ZSM-5 all have a little decrease compared to before. The nitrogen sorption isotherms of the ZSM-5 (Figure 1(a)) and CeO₂@ZSM-5 (Figure 1(b)) show a lag ring is formed when \( P/P_0 \) is between 0.4 and 0.9.

Figure 2(a) shows that the relative intensity of the quartz peak, 2\( \theta \) around 28.55, 33.07 and 47.48, increased when ZSM-5 was modified with CeO₂. These three 2\( \theta \) angles can be indexed to the crystal plane diffraction peaks to (111), (200) and (220), respectively. Those typical peaks of CeO₂ indicated that Ce had been successfully loaded onto ZSM-5. The same set of characteristic peaks was also observed for CeO₂@ZSM-5, indicating that ZSM-5 maintained its original structure. This conclusion matches well with some previous studies (Liu et al. 2017).

Figure 2(b) shows the FTIR spectra of CeO₂@ZSM-5 before and after the Cr(VI) adsorption. The peaks at 796 cm\(^{-1}\), 1,099 cm\(^{-1}\) and 3,448 cm\(^{-1}\) were assigned to the Al-O stretching, Si-O stretching and -OH stretching vibrations. The peak observed at about 452 cm\(^{-1}\) was ascribed to the occurrence of Ce-O stretching (Liu et al. 2017; Sharma et al. 2017). The occurrence of the above-mentioned peaks revealed the cross-linking of Ce and ZSM-5. But after the adsorption of Cr(VI), the intensities

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**Table 1** | Textural parameters of the ZSM-5 and CeO₂@ZSM-5 employed in this study

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( A_{\text{BET}} ) m(^2)/g</th>
<th>Pore volume m(^3)/g</th>
<th>D spacing nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>421.307</td>
<td>0.371</td>
<td>0.744</td>
</tr>
<tr>
<td>ZSM-5(Cr(VI))</td>
<td>416.245</td>
<td>0.302</td>
<td>0.647</td>
</tr>
<tr>
<td>CeO₂@ZSM-5</td>
<td>558.532</td>
<td>0.313</td>
<td>0.783</td>
</tr>
<tr>
<td>CeO₂@ZSM-5(Cr(VI))</td>
<td>550.458</td>
<td>0.279</td>
<td>0.745</td>
</tr>
</tbody>
</table>

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**Figure 1** | (a) Adsorption/desorption isotherms of nitrogen at 77 K for ZSM-5 and CeO₂@ZSM-5; (b) BET pore-size distribution.
and position of some peaks (Ce-O, Al-O, and Si-O) changed, which indicated that those groups were responsible for the adsorption of Cr(VI) onto CeO$_2$@ZSM-5.

The surface elemental composition of CeO$_2$@ZSM-5 was determined using XPS analysis, as shown in Figure 2(c), which revealed the presence of Ce and O elements in the CeO$_2$@ZSM-5. The high-resolution spectrum of Ce 3d is shown in Figure 2(d); two types of Ce atoms are present: Ce$^{3+}$ (888.02 eV) and Ce$^{4+}$ (882.25 eV). As shown in Figure 2(e), the O 1s spectrum of CeO$_2$@ZSM-5 could be fitted and de-convoluted into three different peaks, corresponding to C-O (532.75), -OH (531.18 eV) and Ce-O (530.02 eV) (Naushad et al. 2017). The adsorption of Cr(VI) onto CeO$_2$@ZSM-5 was also supported using XPS.
As shown in Figure 2(f), the appearance of the Cr2p1/2 and Cr2p3/2 spectrum after the adsorption demonstrated that Cr(VI) was adsorbed onto CeO2@ZSM-5.

To further study the material, SEM-EDX elemental mapping was performed to show the difference between Cr(VI) distribution inside and outside the pores. The SEM images revealed information about the details of the surface and morphology of the particles. Figure 3(a) displays partially developed crystalline laminar habits and conglomerates of compact crystals. There were many tiny pores between particles. Some of them showed a reunion phenomenon, which suggested a large surface polarity and specific surface area of ZSM-5 (Al-Othman et al. 2012). Figure 3(c) shows that there was no obvious change in crystalline structure, maintaining the basic skeleton structure and larger specific surface area of CeO2@ZSM-5, which indicated that there was no obvious damage to the basic skeleton of ZSM-5 after the modification. The comparison of Figure 3(b) and 3(d) shows that some fine particles adhered to the surface of ZSM-5 after the modification, indicating that CeO2 had been successfully loaded onto the surface of ZSM-5, which matched well with the BET and XRD results.

Figure 3 | (a), (b) SEM photographs of ZSM-5; (c), (d) SEM photographs of CeO2@ZSM-5; (e) EDX spectrum of CeO2@ZSM-5 and (f) spectrum of CeO2@ZSM-5 with Cr(VI) adsorption.
Figure 3(e) and 3(f) show the EDX spectra of the two samples (CeO₂@ZSM-5 before and after the absorption of Cr(VI)). Because the pore area occupied a small percentage in the images, elemental mapping would not work. Here, only EDX spectrum was used to identify if there was any Cr(VI) on the surfaces inside the pores (Dai et al. 2016). Comparing Figure 3(e) with 3(f), it can be seen that there were some peaks inside the pores of CeO₂@ZSM-5 attributed to Cr(VI) in the EDX spectrum. This suggested that Cr(VI) had been successfully adsorbed onto CeO₂@ZSM-5.

**Effect of pH and adsorption mechanism**

The solution pH is one of the most important parameters affecting the adsorption process (Alothman et al. 2013). The pH determines the surface charge of the adsorbent, the degree of ionization and adsorbent characteristics. In order to evaluate the effect of pH on the uptake of hexavalent chromium, 0.5 g of adsorbent was mixed with 100 mL of the chromium solution with initial concentration of 0.6 mg/L and different pH values (from 3 to 11) and shaken at room temperature for 60 min.

As shown in Figure 4(a), the percentage removal of Cr(VI) was 99% and 89% after adsorption onto CeO₂@ZSM-5 and ZSM-5, respectively, indicating that the adsorption capacity of CeO₂@ZSM-5 was greater than ZSM-5. Within the range of pH values from 3 to 11, the adsorption capacity decreased drastically with increasing pH. This suggests that the adsorption of the adsorbent is clearly pH dependent. The CeO₂@ZSM-5 sample could remove 99% of Cr(VI) in acidic conditions (pH = 3) while only 40% in alkaline conditions (pH = 11). Hence, the removal of Cr(VI) was relatively higher in the lower pH ranges. The adsorption processes are hindered at high pH because of the competitive adsorption between OH⁻ and Cr₂O₇²⁻ (Kumar et al. 2016). Analogous results have been achieved by other authors (Awual et al. 2016; Kenawy et al. 2017).

As per Figure 5(a), there was a large number of H⁺ ions at lower pH, which neutralized the negatively charged adsorbent surface and thereby increased the diffusion of chromate ions into the bulk of the adsorbent (Rao et al. 2002). It has been reported by other researchers that at pH 3–4, the dominant form of Cr(VI) is HCrO₄⁻ (Alothman et al. 2013). So, Cr(VI) was adsorbed on the surface of
CeO$_2$@ZSM-5 mostly in the form of HCrO$_4$. Beyond that, it can be inferred that surface adsorption is not the only mechanism involved in the adsorption process. At lower pH, protons (H$^+$) adsorbed on the surfaces of CeO$_2$@ZSM-5 bring about more positive charges and thereby enhance the electrostatic attraction between the surfaces and negatively charged Cr(VI) anions. Also, higher acid concentrations restrain hydrolysis of the chromium ions (Zhou et al. 2013). The entire cycle process of this study is shown in Figure 5(b).

**Effect of contact time and adsorption kinetics**

In order to evaluate the effect of contact time, 0.5 g of adsorbent was mixed with 100 ml of the chromium solution with an initial concentration of 0.6 mg/L at pH 3 and shaken at room temperature for 20–100 min. Figure 4(b) shows the effect of contact time on the uptake of chromium. As can be seen in this figure, the uptake of chromium ions increases with increasing contact time and reaches equilibrium after 70 min. Actually, the adsorption rate was expected to be very rapid initially and then slowly decrease until it reached equilibrium in 70 min, caused by adsorbent saturation. With increasing contact time, the uptake of chromium remained almost constant and the removal rate was 99.24%, which is close to 100%.

To investigate the mechanism of adsorption processes, kinetic models were used to analyse the experimental data. Several kinetic models such as pseudo-first-order and pseudo-second-order have been applied to find the adsorption mechanism. The equation of the two kinetic models is expressed as follows:

The pseudo-first-order equation is given as Equation (3):

$$\lg(Q_e - Q_t) = \lg Q_e - \frac{k_1}{2.303} \cdot t$$  \hspace{1cm} (3)

The pseudo-second-order equation is given as Equation (4):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \cdot t$$  \hspace{1cm} (4)

where $Q_e$ and $Q_t$ are the amounts of adsorbed Cr(VI) on the adsorbent at equilibrium and at time $t$, respectively (mg/g), and $k_1$ is the first-order adsorption rate constant (min$^{-1}$), $k_2$ is the second-order adsorption rate constant (g/(mg·min)), and $Q_e$ is the adsorption capacity calculated by the pseudo-second-order kinetic model (mg/g).

The regression correlation coefficients and constants of the pseudo-first-order and pseudo-second-order kinetic models are shown in Table 2. As can be seen in this table,

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$Q_e$ (mg/g)</th>
<th>$k_2$ (g/(mg·min))</th>
<th>$R^2$</th>
<th>$Q_e$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.0252</td>
<td>0.9770</td>
<td>0.0156</td>
<td>0.0939</td>
<td>0.9917</td>
<td>0.1755</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0308</td>
<td>0.9572</td>
<td>0.2099</td>
<td>0.0293</td>
<td>0.9991</td>
<td>0.2976</td>
</tr>
<tr>
<td>0.7</td>
<td>0.0271</td>
<td>0.9739</td>
<td>0.3958</td>
<td>0.0160</td>
<td>0.9903</td>
<td>0.4135</td>
</tr>
</tbody>
</table>
the theoretical adsorption of hexavalent chromium obtained by the pseudo-second-order kinetic model were 0.1755 mg/g, 0.2976 mg/g, 0.4135 mg/g at the initial concentration of 0.5 mg/L, 0.6 mg/L and 0.7 mg/L, respectively, which was very close to the actual measurement of hexavalent chromium equilibrium adsorption 0.1738 mg/g, 0.2885 mg/g, 0.4069 mg/g. However, they are very different from those of the pseudo-first-order kinetic model. In addition to this, the fitting degree of the pseudo-second-order kinetic model was 0.99 in the three concentrations, so the kinetic adsorption can be very well described by the pseudo-second-order equation, which indicates that the adsorption rate of CeO₂@ZSM-5 for Cr(VI) is directly proportional to the square of the unoccupied adsorption site of the adsorbent. Other researchers (Naushad et al. 2016, 2017) have also been reported similar results for the adsorption of Cr(VI) (Figure 6).

**Effect of adsorbent dose**

The effect of adsorbent dose on the uptake of chromium is shown in Figure 4(c). The experiments were done using different amounts of adsorbent (0.1–0.9 g) at the optimum pH and contact time. With the increase in adsorbent from 0.1 to 0.5 g, the uptake of Cr(VI) increases because the number of available adsorption sites increases. This phenomenon is consistent with the kinetic studies, which indicate that the adsorption rate is directly proportional to the square of the unoccupied adsorption sites of the adsorbent. However, for higher doses (>0.5 g), the uptake efficiency is almost constant because all of the adsorbate had already sorbed to the active sites of adsorbent. The removal rate of ZSM-5 and CeO₂@ZSM-5 is 93% and 99% respectively when the adsorbent dose is 9 g/L, while it is 91% and 99% when the amount is 5 g/L. It can be seen that the removal rates are almost indistinguishable in both cases. Maximum uptake of chromium occurred when using 0.5 g adsorbent. Therefore it was chosen as the adsorbent optimum amount for further experiments. This result was expected because for a fixed initial solute concentration, increasing amount of adsorbent provides greater surface area (or adsorption sites) (Alothman et al. 2013).

**Effect of the initial concentration of Cr(VI)**

The uptake of Cr(VI) by ZSM-5 and CeO₂@ZSM-5 was studied in the range of 0.2–1 mg/L, while the other conditions such as adsorbent dose, pH, and contact time were constant. The results are presented in Figure 4(d). The removal efficiency is decreased with the increasing concentration of Cr(VI) in solution. The active sites of the adsorbent were saturated over time. CeO₂@ZSM-5 showed an excellent removal efficiency in the treatment of low concentration wastewater, and the removal rate was 97.52%. In the initial concentration of 0.6 mg/L, the removal rate of Cr(VI) reached 91.67% when using ZSM-5 as the adsorbent. As the concentration went up, the removal rate decreased, so 0.6 mg/L was chosen as the optimal initial concentration.

**Conditions optimization**

In view of the effect of various factors on the percentage removal, four major factors were mentioned as follows (Table 3): initial concentration of Cr(VI) (A), pH value (B), CeO₂@ZSM-5 dosage (C) and reaction time (min) (D). In this experiment, an L₉(3)⁴ orthogonal experiment was designed, and the optimal treatment conditions were obtained by using the removal rate of Cr(VI) as the objective.

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Figure 6  | (a) Pseudo-first-order, (b) pseudo-second-order sorption kinetics of Cr(VI) onto CeO₂@ZSM-5.
As can be seen from Table 4, the four influencing factors were ranked according to their influence: pH > initial concentration > reaction time > adsorbent dose. The pH value was the main factor affecting the adsorption and the optimum technological conditions for the reaction were A3B2C2D3 through the above experiments. To be specific, the initial concentration, pH, adsorbent dose and reaction time were 0.6 mg/L, 3, 0.5 g/L, and 70 min, respectively, and the removal rate of hexavalent chromium was 99.56% under these conditions.

### Adsorption isotherms

Adsorption isotherm studies are important for identifying the efficacy of adsorption. Some well-known ones are Freundlich, Langmuir, Temkin and Redlich–Peterson (Sharma et al. 2011). In this study, Langmuir, Freundlich and Temkin isotherm models were used to establish the adsorption equilibrium between the adsorbent and metal ions. For this purpose, 100 ml of the chromium solution with concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 mg/L were prepared at room temperature and the adsorption of hexavalent chromium was calculated by Equation (5) at pH 3, using 0.5 g adsorbent and a contact time of 70 min.

The Langmuir model assumes that a monomolecular layer is formed when adsorption takes place without any interaction between the adsorbed molecules. The Langmuir model can be represented as:

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]  

(5)

The linearized form of the Langmuir equation is Equation (6):

\[
\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m} \cdot \frac{1}{C_e}
\]  

(6)

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, \( R_L \), which is defined by Hall et al. (1966) as Equation (7):

\[
R_L = \frac{1}{1 + K_L C_0}
\]  

(7)

where \( C_e \) is the equilibrium concentration (mg/L), \( q_e \) the amount of metal ion sorbed (mg/g), \( q_m \) is \( q_e \) for a complete monolayer (mg/g), \( K_L \) is a constant related to the affinity of the binding sites (L/mg). When \( 0 < R_L < 1 \), the adsorption is in a favorable direction, while it is negative when \( R_L > 1 \).

The experimental data were plotted as \( C_e/q_e \) versus \( C_e \) and shown in Figure 7(a). Values of the Langmuir constants \( q_m \) and \( K_L \) were obtained by linear regression and shown in Table 5.

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of Cr(VI) at equilibrium. This equation can be written in the linear form given as below (8) and (9):

\[
q_e = K_F C_e^{1/n}
\]  

(8)

\[
\lg Q_e = \lg k + \frac{1}{n} \lg C_e
\]  

(9)

where \( q_e \) and \( C_e \) are the equilibrium concentrations of Cr(VI) in the adsorbed (mg/g) and liquid phases (mg/L),

### Table 3 | The factors of orthogonal experiment

<table>
<thead>
<tr>
<th>Factors</th>
<th>A Initial concentration (mg/L)</th>
<th>B pH</th>
<th>C Adsorbent dose (g/L)</th>
<th>D Contact time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>2</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>3</td>
<td>4</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>4</td>
<td>5</td>
<td>70</td>
</tr>
</tbody>
</table>

### Table 4 | The results and analysis of orthogonal experiments

<table>
<thead>
<tr>
<th>Influencing factor</th>
<th>Removal rate(%)</th>
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</thead>
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<tr>
<td>K1</td>
<td>92.261 90.050 94.450 94.783</td>
</tr>
<tr>
<td>K2</td>
<td>95.867 97.700 96.300 93.033</td>
</tr>
<tr>
<td>K3</td>
<td>96.657 96.450 93.450 96.383</td>
</tr>
<tr>
<td>R2</td>
<td>6.200 7.650 2.850 3.350</td>
</tr>
</tbody>
</table>

As can be seen from Table 4, the four influencing factors were ranked according to their influence: pH > initial concentration > reaction time > adsorbent dose. The pH value was the main factor affecting the adsorption and the optimum technological conditions for the reaction were A3B2C2D3 through the above experiments. To be specific, the initial concentration, pH, adsorbent dose and reaction time were 0.6 mg/L, 3, 0.5 g/L, and 70 min, respectively, and the removal rate of hexavalent chromium was 99.56% under these conditions.
respectively, $K_F$ and $n$ are the Freundlich constants which are related to adsorption capacity and intensity, respectively. The experimental data were plotted as $\ln q_e$ versus $\ln C_e$ and shown in Figure 7(b). To determine the maximum sorption capacity, it is necessary to operate with constant initial concentration $C_0$ and variable weight of sorbent, thus $\ln q_e$ is the extrapolated value of $\ln q$ for $C = C_0$ (Djeribi & Hamdaoui 2008).

The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions. The linear form of the Temkin isotherm model is described as follows:

$$q_e = B_t \ln(K_T) + B_t \ln(C_e)$$  \hspace{1cm} (10)

where $B_t$ (heat of sorption) is $RT/b$ and $K_T$ is the equilibrium binding constant (L/mg). The Temkin parameters $B_t$ and $K_T$ were determined from the plot of $q_e$ versus $\ln C_e$.

Linear plots for the Temkin adsorption isotherm are shown in Figure 7(c) for Cr(VI) adsorption on CeO$_2$@ZSM-5. The Temkin constants were determined from the slope and intercept of a linear plot of $q_e$ versus $\ln C_e$ and are given in Table 5.

As shown in Table 5, the fitting parameters of the Langmuir model, Freundlich model and Temkin model were 0.9401, 0.9941 and 0.9726, respectively. This implies that the Freundlich model had a higher correlation coefficient value as compared to the Langmuir and Temkin isotherms. Other researchers (Naushad et al. 2016) have also reported

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Isotherm parameters for the adsorption of Cr(VI) metal ion onto CeO$_2$@ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir model</td>
<td>Freundlich model</td>
</tr>
<tr>
<td>$q_m$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>0.2392</td>
<td>58.1489</td>
</tr>
</tbody>
</table>
similar results for the adsorption of Cr(VI). Figure 7(d) shows that the \( R_L < 1 \), which indicate that the adsorption process is in a favorable direction. The parameter \( n \) in the Freundlich model is 1.2046 (>1), indicating that the adsorption process is spontaneous, which is consistent with the conclusion that the adsorption is in the favorable direction when \( R_L < 1 \).

**Effect of temperature and thermodynamics**

Temperature has a distinct effect on the adsorption capacity of an adsorbent. The adsorption of Cr(VI) onto CeO\(_2@\)ZSM-5 was analyzed at different temperatures (288, 298, 308 and 318 K). The thermodynamic parameters, such as \( \Delta H^° \) (enthalpy change), \( \Delta G^° \) (standard free energy), and \( \Delta S^° \) (entropy change) were calculated. The values of \( \Delta H^° \) and \( \Delta S^° \) were obtained from the slopes and intercepts of the plots of \( \ln K_c \) versus \( 1/T \) (as shown in Figure 8) by the following equation:

\[
\ln K_c = -\frac{\Delta H^°}{RT} + \frac{\Delta S^°}{R}
\]  

(11)

The values of \( \Delta G^° \) was calculated using the following equation:

\[
\Delta G^° = \Delta H^° - T \Delta S^°
\]  

(12)

where \( R \) (8.314 kJ/molK) is the gas constant, \( T \) (degrees Kelvin), absolute temperature, and \( K_c \) (L/mg), the standard thermodynamic equilibrium constant defined by \( C_0 \cdot C_c \cdot C_e \). It may be observed from Table 6 that the value of \( \Delta G^° \) was negative, indicating the spontaneous nature of the adsorption process. The values of \( \Delta G^° \) were more negative at higher temperatures, showing that higher temperature favored the adsorption of Cr(VI) onto CeO\(_2@\)ZSM-5. The positive value of \( \Delta S^° \) revealed an increase in the randomness at the solid/solution interface during the adsorption process. Value of \( \Delta H^° \) was positive, indicating the endothermic nature of the adsorption. Other researchers (Al-Othman et al. 2012; Alqadami et al. 2017) have also reported similar results for the adsorption of Cr(VI).

**Effect of coexisting ions**

Industrial discharges may contain a large number of other ions that may have a competitive effect on Cr(VI) adsorption, such as Mg\(_2^+\), Ca\(_2^+\), Na\(^+\), K\(^+\), Cu\(_{2}^+\) and Fe\(_{3}^+\). Thus the adsorption of Cr(VI) onto CeO\(_2@\)ZSM-5 was studied in the presence of these ions. The experiment was carried out in a batch mode where 0.5 g of the adsorbent was in 100 mL of aqueous solution containing Cr(VI) ions and known quantities of those coexisting ions. The adsorption of Cr(VI) onto CeO\(_2@\)ZSM-5 was 99.56% before addition of any ions. On addition of those ions, the adsorption of Cr(VI) onto CeO\(_2@\)ZSM-5 was slightly decreased in the order Na\(^+\) (97.15%) > K\(^+\) (95.21%) > Mg\(_{2}^+\) (93.31%) > Ca\(_{2}^+\) (92.43%) > Fe\(_{3}^+\) (86.68%) > Cu\(_{2}^+\) (86.49%) (Figure 9(a)). Thus, CeO\(_2@\)ZSM-5 could be very well used for Cr(VI) removal in the presence of these competing ions. This result was in accordance with the hydrated ion radius. The ions with smaller hydrated radius easily enter the pores of the adsorbent, resulted in higher adsorption (Sharma et al. 2017).

**Desorption studies**

To assess the material feasibility for potential application, it must be assessed not only on adsorptive ability, but also on regeneration and reusability. Previous studies have reported various regeneration methods, such as using HCl (Awual et al. 2016), NaCl (Zhou et al. 2010) and NaOH (Liu et al. 2017).
In this study, the regeneration of CeO$_2$@ZSM-5 was tested using NaOH (0.1 M), NaCl (0.1 M) and HCl (0.1 M), all stirred for 1 hour at 25 °C. As shown in Figure 9(b), the initial efficiency was 99.56%, and then 89.2%, 65.2%, 52.7% after five regeneration cycles when using HCl, NaOH, NaCl as the eluent, respectively. The result showed that CeO$_2$@ZSM-5 could be easily regenerated and had a high recyclability over multiple cycles, with the best eluent being HCl (0.1 M).

Comparison studies

In order to justify the validity of CeO$_2$@ZSM-5 as a good adsorbent for the removal of Cr(VI), we carried out a comparison with previously published similar studies. As shown in Table 7, we compared various items such as initial concentration, contact time, adsorption capacity, percentage removal and number of reuses. In this study, for the purpose of reducing low concentration of Cr(VI) in aqueous solution, the initial concentration of metal ions was only 0.6 mg/L, which caused a lower adsorption capacity when compared with other works, which had an initial concentration greater than 50 mg/L. Even so, the percentage removal of CeO$_2$@ZSM-5 in our work was the highest. It can be seen that the percentage removal of Cr(VI) onto CeO$_2$@ZSM-5 was 89.2% after five regeneration cycles, a better regenerative effect than other adsorbents. What is more, it provided the shortest reaction time. Beyond those, other advantages such as easy preparation and lower cost made CeO$_2$@ZSM-5 a better prospect.

CONCLUSIONS

In this study, CeO$_2$ was loaded onto ZSM-5 by impregnation and used for the removal of Cr(VI) in low concentrations in aqueous solution (the concentration of Cr(VI) ranged from 0.2 to 1 mg/L). The structural order and textural properties of ZSM-5 and CeO$_2$@ZSM-5 were examined by XRD, BET, SEM-EDX, FTIR and XPS. The effects of important parameters such as pH, adsorbent dose, initial concentration and contact time of Cr(VI) were studied and the

Table 7  Comparison of adsorption capacities of different adsorbents towards Cr(VI)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial concentration (mg/L)</th>
<th>Contact time (min)</th>
<th>$q_e$ (mg/g)</th>
<th>Percentage removal</th>
<th>Number of reuses</th>
<th>Percentage removal after reuse</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized activated carbon</td>
<td>50</td>
<td>$24 \times 60$</td>
<td>5.59</td>
<td>41.56%</td>
<td>–</td>
<td>–</td>
<td>Al-Othman et al. (2012)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>80</td>
<td>120</td>
<td>27.64</td>
<td>69.10%</td>
<td>–</td>
<td>–</td>
<td>Alothman et al. (2013)</td>
</tr>
<tr>
<td>ZrO$_2$/Fe$_3$O$_4$/chitosan</td>
<td>70</td>
<td>120</td>
<td>–</td>
<td>84.70%</td>
<td>6</td>
<td>–</td>
<td>Kumar et al. (2016)</td>
</tr>
<tr>
<td>CN-cl-PL(AA)NHG</td>
<td>60</td>
<td>180</td>
<td>19.80</td>
<td>72.50%</td>
<td>–</td>
<td>–</td>
<td>Sharma et al. (2017)</td>
</tr>
<tr>
<td>CeO$_2$@ZSM-5</td>
<td>0.6</td>
<td>70</td>
<td>0.24</td>
<td>99.56%</td>
<td>5</td>
<td>89.2%</td>
<td>This work</td>
</tr>
</tbody>
</table>

![Figure 9](https://iwaponline.com/wst/article-pdf/77/9/2327/2327.pdf)
optimal conditions were set at 3, 5 g/L, 0.6 mg/L and 70 min, respectively, resulting in a removal rate of Cr(VI) was 99.56%. The Freundlich isotherm showed better agreement with the experimental data ($R^2 = 0.9941$) and the maximum adsorption capacity obtained from the Langmuir isotherm was 0.2392 mg/g. Kinetic studies indicate that adsorption equilibrium data fitted well with the pseudo-second-order model and the thermodynamic parameters showed the endothermic and spontaneous nature of the adsorption process. The competitive ions had only a small adverse effect of the adsorption of Cr(VI) onto CeO$_2$@ZSM-5. This adsorbent was easily recovered by desorption in 0.1 M HCl. Recycling experiments showed that the CeO$_2$@ZSM-5 still possessed high Cr(VI) adsorption efficiency and good stability after five cycles, which would enhance the economics of practical applications for the removal of Cr(VI) from wastewater.

**ACKNOWLEDGEMENTS**

This work was supported by the Natural Science Foundation of Hebei Province (E2016208116), the Science and Technology Plan of Hebei Province (15272408D) and the PhD startup fund.

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First received 10 January 2018; accepted in revised form 23 March 2018. Available online 9 April 2018.