Removal of Hexavalent Chromium from Simulated Wastewater by Polyethylene Glycol–Modified D201 Resin-Supported Nanoscale Zero-Valent Iron

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Abstract In view of the increasingly prominent heavy metal pollution problem in water, D201 resin-supported polyethylene glycol–modified nanoscale zero-valent iron (PEG-nZVI/D201) was fabricated to remove Cr(VI) in wastewater. PEG-nZVI/D201 can overcome the agglomeration and oxidation drawbacks of nZVI effectively, and improve the removal efficiency of Cr(VI). Its Cr(VI) removal rate was 33.6% higher than that of bare nZVI when the dosage of PEG-nZVI/D201 was 1.0 g·L⁻¹, the Cr(VI) concentration was 50 mg·L⁻¹, and the initial pH was 5.0. The maximum adsorption capacity of Cr(VI) on PEG-nZVI/D201 reached 134.56 mg·g⁻¹ at 318 K. The Langmuir model better describes the adsorption of Cr(VI) on PEG-nZVI/D201. Thermodynamic parameters show that the adsorption process is spontaneous and endothermic. The mechanism of Cr(VI) removal by PEG-nZVI/D201 is as follows: firstly, protonated PEG-nZVI/D201 adsorbs Cr(VI) by electrostatic attraction, then nZVI reduces most of Cr(VI) to Cr(III) through its strong reducibility, and finally, Cr(III) can form CrₓFe₁₋ₓ(OH)₃ co-precipitation with Fe(III) produced by oxidation of nZVI.

Keywords Nanoscale zero-valent iron · D201 resin · Polyethylene glycol · Cr(VI) removal

1 Introduction

With the increase in the discharge of wastewater containing chromium in pharmaceutical, chemical, paint, leather, and other industries, the chromium pollution in water is becoming more and more serious (Owlad et al., 2009). Cr(III) and Cr(VI) are the two valence states of chromium (Wang et al., 2020). Cr(III) mainly exists in the environment in the form of Cr(H₂O)₆³⁺, Cr(H₂O)₃⁺, and CrO₂⁻, it is relatively stable and does little harm to the environment, and exists in human and animal bodies as essential trace elements. Cr(VI) mainly exists in the form of HCrO₄⁻ and H₂CrO₄ in an acidic environment, and in the form of CrO₄²⁻ in an alkaline environment (Vaiopoulou et al., 2012, Yoshinaga et al., 2018, Zhu et al., 2019a, Fu et al., 2013). Cr(VI) is thought to be more toxic to living cells than Cr(III) (Liu et al., 2021), it is generally not easy to be adsorbed by organic matter, and can be easily absorbed by plants and harm human health through the food chain (Costa et al., 2006). Many countries and organizations have set extremely strict emission standards for Cr(VI) wastewater. In China, Cr(VI) is considered to be a primary pollutant with
an allowable emission concentration of 0.5 mg·L$^{-1}$, while total chromium is limited to 1.5 mg·L$^{-1}$ (GB 8978–1996). Therefore, the reduction of Cr(VI) has attracted extensive attention of researchers. At present, many treatment methods of Cr(VI) have been gradually developed, such as chemical method, physicochemical method, and biological method (Enzo et al., 2019; Hedayatkhah et al., 2018; Xiong et al., 2019). Among them, the adsorption method of physicochemical is regarded as an effective measure in the treatment of chromium wastewater because of its high removal efficiency, wide application range, and simple operation (Elwakeel et al., 2020).

In recent years, due to its strong electron contribution and high reactivity, nZVI has been extensively employed as an excellent adsorption material in the treatment of various environmental pollutants and is one of the most promising remediation technologies for heavy metal wastewater (Lv et al., 2011; Madan et al., 2020; Theron et al., 2008). However, nZVI is prone to agglomeration deposition due to its high surface energy and magnetic characteristics, which leads to its poor reaction ability in wastewater treatment (O’Carroll et al., 2013). In addition, nZVI is also prone to passivation reaction with water to form a passivation layer, which reduces its reactivity and electron transport capacity (Sarathy et al., 2008). In order to overcome the shortcomings of nZVI, various methods have been used to solve these problems. For example, the problems of easy oxidation and agglomeration of nZVI are effectively solved by support and surface modification, which is beneficial to improve the electron utilization rate of nZVI (Tian et al., 2018; Wu et al., 2020). The commonly used support materials include biochar, resin, zeolite, bentonite, and so on. Among the above carriers, microporous styrene ion exchange resin (D201) has been widely used in the treatment of heavy metal wastewater due to its strong adsorption capacity, good regeneration performance, and high reusability (Gao et al., 2020). More importantly, D201-supported nZVI not only has the ability to adsorb heavy metals but also can prevent nZVI agglomeration. Some researchers have demonstrated that surfactants can enhance the physical stability of nZVI particles through steric hindrance (Stefaniuk et al., 2016). Common surfactants are carboxyl cellulose sodium, polyvinyl pyrrolidone, polyethylene glycol (PEG), lignin, and so on. Among them, PEG is suitable for modifying the D201/nZVI system due to its low cost, non-toxicity, and biodegradability. From the above analysis, it can be seen that D201-supported PEG-modified nZVI (PEG-nZVI/D201) composite can prevent the aggregation of nZVI, enhance its adsorption performance and physical stability. Up to now, PEG-nZVI/D201 composite has not been reported yet for the treatment of chromium-containing wastewater.

In this study, PEG-nZVI/D201 was prepared and applied to treat Cr(VI) in wastewater. The main purposes of this paper are to (1) explore the conditions for PEG-nZVI/D201 treatment of Cr(VI), (2) investigate the structure and properties of PEG-nZVI/D201, and (3) propose the adsorption mechanism of PEG-nZVI/D201 on Cr(VI) in wastewater.

2 Materials and Methods

2.1 Materials

The materials and reagents required for the experiment are shown in Table 1.

2.2 Synthesis of PEG-nZVI/D201

Synthesis of PEG-nZVI/D201 particles was performed by liquid phase reduction according to Eq. Specifically, 2.47 g FeSO$_4$·7H$_2$O and 0.50 g D201 resin were mixed with 100 mL aqueous ethanol solution in a three-necked flask to form a suspension, 1.00 g PEG was added to the above solution and dispersed by ultrasonic wave for 20 min. Continue stirring for 30 min under the condition of nitrogen to remove oxygen. 1.00 g NaBH$_4$ was added to the reaction mixture drop by drop and continued to stir for 30 min after the dripping to achieve a full reaction. Nitrogen continues to flow throughout the reaction; suspension containing PEG-nZVI/D201 particles was obtained. The black solid particles were washed rapidly for three times with anhydrous ethanol, then dried at 80°C for 8 h in a vacuum drying oven, and finally, PEG-nZVI/D201 was ground and collected. In order to compare the removal effect, nZVI, D201/nZVI, and PEG-nZVI were synthesized under similar conditions as reference.

\[
\text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow \text{Fe}^0 \downarrow + 2\text{B(OH)}_3 + 7\text{H}_2 \uparrow
\]
2.3 Characterization and Analytical Method

A transmission electron microscopy (TEM, Tecnai F20 model) was used to observe the morphology of PEG-nZVI/D201. The crystal structures of different materials were analyzed by X-ray powder diffractometer (XRD, XPert PRO MPD, Cu Kα radiation, 3 kW). The element valence states of PEG-nZVI/D201 before and after the reaction were analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi). The surface functional groups of PEG-nZVI/D201 were analyzed by an infrared spectrometer (FTIR, Nicolet iS50, KBr pellets). The concentration of Cr(VI) was determined with reference to dibenzoyl dihydrazine spectrophotometry (GB 7467–1987) with an ultraviolet–visible spectrophotometer (UV-6100S, MRTASH). The Cr(VI) removal efficiency and capacity were determined as Eqs. 2 and 3, respectively (Yao et al., 2013).

\[
RE\% = \frac{C_0 - C_t}{C_0} \times 100\%
\]  
\[
q_t = \frac{C_0 - C_t}{m} \times V
\]

where \(RE\) represents the removal rate at time \(t\) (min), \(C_0\) and \(C_t\) (mg·L\(^{-1}\)) stand for the initial and equilibrium concentrations of Cr(VI), respectively. \(q_t\) (mg·g\(^{-1}\)) stands for the removal capacity of Cr(VI) at \(t\) (min), \(V\) (L) denotes the solution volume, and \(m\) (mg) represents the quality of the adsorbent.

2.4 Adsorption and Desorption Experiments

The removal experiments were carried out in a conical flask (250 mL) containing 50 mL of 50 mg·L\(^{-1}\) Cr(VI) solution, its pH was adjusted to the preset value with 0.1 mol·L\(^{-1}\) H\(_2\)SO\(_4\) or NaOH, and preset dosage of PEG-nZVI/D201 was added into the Cr(VI) solution. The conical flask was shaken in a room temperature shaker at 150 r·min\(^{-1}\) for 60 min. At the preset time point, 1.0 mL reaction solution was taken from the conical flask, filtered with 0.22 μm single-use microporous membrane, and the absorbance of the filtrate was determined by a spectrophotometer. All experiments were undertaken in duplicate. The default reaction conditions were PEG-nZVI/D201 dosage 1.0 g·L\(^{-1}\), Cr(VI) concentration 50 mg·L\(^{-1}\), pH value 5.0 (peculiar circumstance exception). According to the influence of coexisting ions on Cr(VI) treatment in actual wastewater, the concentration of Mg\(^{2+}\) and Ca\(^{2+}\) were set as 200 mg·L\(^{-1}\), and the concentration of Cl\(^{-}\), CO\(_3\)^{2−} and PO\(_4\)^{3−} were set as 70 mg·L\(^{-1}\). For the reusability experiment, the used PEG-nZVI/D201 was collected by magnetic absorption, and the material was rinsed with deionized water and parsed with 30 mL of 1 mol·L\(^{-1}\) NaOH solution. Then, 10 mL of 1 mol·L\(^{-1}\) NaBH\(_4\) solution was used for reduction. The excess NaBH\(_4\) was washed three times with anhydrous ethanol, and the obtained PEG-nZVI/D201 was dried for the next cycle. For the stability experiment, the removal effect of Cr(VI) by nZVI and PEG-nZVI /D201 was measured after they were exposed to air for a specific time.
3 Results and Discussion

3.1 Characterization of PEG-nZVI/D201

The TEM images of PEG-nZVI/D201 and nZVI/D201 are presented in Fig. 1. The modified nZVI particles have spherical or chain structures, which is different from the reports in the literature that nZVI easily aggregates into dendrites (Fig. 1a) (Li et al., 2008). Compared with nZVI in nZVI/D201 (Fig. 1c), nZVI in PEG-nZVI/D201 has a more regular spherical morphology (Fig. 1b).

Figure 2 demonstrates the XRD patterns of different materials. The apparent peak of nZVI at 44.5° belongs to the (110) crystal plane, indicating that iron ions are reduced to nZVI by NaBH₄ (Fu et al., 2015). The diffraction peak of nZVI in the modified material has an obvious contraction, which is caused by the poor crystallinity and small particle size of the modified material (Gao et al., 2020). D201 resin has no significant diffraction peak due to its amorphous nature. In addition, the diffraction peak at 34.9° indicates that Fe₂O₃ exists on the surface of PEG-nZVI/D201, that is, part of the prepared nZVI particles has been oxidized (Zhang et al., 2013).

The FTIR spectra of PEG-nZVI/D201 and PEG are presented in Fig. 3. The photoelectron peak at 679 cm⁻¹ represents Fe–O stretching, indicating that Fe₂O₃ and Fe₃O₄ exist in PEG-nZVI/D201 (Son et al., 2018). The absorption peak at approximate
1633 cm\(^{-1}\) is assigned to the C–C tensile vibration peak on D201 styrene-based ion exchange resin, indicating that nZVI is successfully loaded by D201 (Wang et al., 2017a, b). PEG-nZVI/D201 has photoelectron peaks at 3454, 2872, and 1077 cm\(^{-1}\), corresponding to the –OH stretching vibration peak, –CH\(_2\) stretching vibration peak and CH\(_2\)–O–CH\(_2\) group, which can also be identified on the PEG spectrum (Hamdy et al., 2020; Singh et al., 2014). All these results confirm that PEG-nZVI/D201 has been successfully prepared.

The surface element composition of PEG-nZVI/D201 is determined by XPS. Figure 4a shows the whole region scan XPS spectra of PEG-nZVI/D201 before and after the reaction. The characteristic peaks of PEG-nZVI/D201 before the reaction near 285, 529, and 711 eV are related to the binding energies of C 1s, O 1s, and Fe 2p (Kera et al., 2016). Figure 4c shows the Fe 2p XPS spectra of PEG-nZVI/D201 before the reaction, there are characteristic peaks of nZVI at 706.1 eV, Fe(II) at 709.3 and 722.6 eV, Fe(III) at 710.8 and 724.3 eV, and their contents in total iron are 18%, 44%, and 38%, respectively (Li et al., 2016). Only a small amount of nZVI has been detected possibly because the surface of nZVI is oxidized or surrounded by Fe\(_3\)O\(_4\) particles.

Fig. 4 XPS spectra of PEG-nZVI/D201. a full spectrum, b Cr 2p, c, d Fe 2p, and e, f O 1s.
The existence of Fe(II) and Fe(III) on the PEG-nZVI/D201 surface further suggests that nZVI may be partially oxidized to Fe₂O₃ and Fe₃O₄ during the preparation process, which is conform with the result observed in the XRD patterns. Figure 4e illustrates the O 1s XPS spectra of PEG-nZVI/D201 after the reaction. The characteristic peak at 529.6 eV corresponds to the –O²⁻ functional group, which represents the oxygen-containing compound in PEG-nZVI/D201. The characteristic peak at 530.1 eV corresponds to the –OH functional group of PEG. The characteristic peak at 531.8 eV corresponds to H₂O, indicating the presence of bound water on the PEG-nZVI/D201 surface (Zhou et al., 2019).

3.2 Remediation of Cr(VI)-Contaminated Water

3.2.1 Effect of Different Adsorbents

Considering the influence of PEG-nZVI/D201 composition on Cr(VI) treatment, the removal performance of different adsorbents was studied. The results (Fig. 5a) show that the removal rates of nZVI, D201, PEG-nZVI, D201/nZVI, and PEG-nZVI/D201 are 54.99%, 57.35%, 64.28%, 70.33%, and 88.54%, respectively. PEG-nZVI/D201 has the best removal effect on Cr(VI), while pure nZVI has the worst removal effect. After D201 or PEG modification of nZVI, the Cr(VI) removal rate of D201/nZVI or PEG-nZVI/D201 is higher than that of pure nZVI, because D201 and PEG can prevent nZVI from agglomeration and make it more stable. The results show that D201 and PEG-modified nZVI is beneficial to increase the removal rate of Cr(VI).

3.2.2 Effect of PEG-nZVI/D201 Dosage

The removal efficiency of Cr(VI) with different dosages was experimentally studied (Fig. 5b). This is a 50% increase in the removal rate of Cr(VI) when the dosage of PEG-nZVI/D201 increases from 0.5 to 1.0 g·L⁻¹. This is because the removal of Cr(VI) mainly takes place on the PEG-nZVI/D201 surface, and the specific surface area of PEG-nZVI/D201 increases with the increase of dosage, which increases the active sites required for the reaction and boosts the removal efficiency of Cr(VI). However, the removal rate of Cr(VI) increases slightly when the dosage increases from 1.0 to 1.5 g·L⁻¹. Considering the economy of actual production, the dosage of PEG-nZVI/D201 is set at 1.0 g·L⁻¹.

3.2.3 Effect of Initial Cr(VI) Concentration

In order to explore the effect of the Cr(VI) initial concentration on its removal, a series of adsorption experiments of initial Cr(VI) concentration were carried out. The results are shown in Fig. 5c. When the Cr(VI) concentration increases from 20 to 150 mg·L⁻¹, the removal rate of Cr(VI) by PEG-nZVI/D201 decreases from 98.7 to 59.5%. When the initial Cr(VI) concentration decreases, the PEG-nZVI/D201 surface active sites are greater than the number of Cr(VI), PEG-nZVI/D201 can completely remove Cr(VI) from aqueous solution. The number of Cr(VI) increases with the increase of initial Cr(VI) concentration, while the number of active sites on the surface of PEG-nZVI/D201 remains unchanged, and the removal rate will inevitably decrease. The initial concentration of Cr(VI) is set at 50 mg·L⁻¹.

3.2.4 Effect of pH Value

Figure 5d illustrates the pH dependence of the Cr(VI) removal. More specifically, with the increase in pH value, the removal rate of Cr(VI) decreases. Under acidic conditions, a high concentration of H⁺ will increase the protonation and positive charge of the PEG-nZVI/D201 surface, while Cr(VI) generally exists in the soluble form of HCrO₄⁻ and has a negative charge, which facilitates the electrostatic adsorption between PEG-nZVI/D201 and Cr(VI) (Peng et al., 2017). In addition, H⁺ in the solution can accelerate the corrosion rate of nZVI and make it be oxidized to produce more Fe(II), which has a strong ability and can reduce Cr(VI) to Cr(III), thus improving the removal of Cr(VI) (Ji et al., 2018). Under alkaline conditions, a low concentration of H⁺ will weaken the protonation and positive charge of the PEG-nZVI/D201 surface, while Cr(VI) mainly exists in the form of CrO₄²⁻ (Shi et al., 2011). Thus, the electrostatic adsorption between PEG-nZVI/D201 and Cr(VI) will be weakened, resulting in poor PEG-nZVI/D201 removal performance. In addition, Cr(III) and Fe(III) readily form a hydroxyl passivation layer with OH⁻, which is adsorbed on the PEG-nZVI/D201 surface to inhibit the reaction (Zhou et al., 2008). In
Fig. 5 Effect of a different adsorbents, b PEG-nZVI/D201 dosage, c initial Cr(VI) concentration, d pH value, and e coexisting ions on Cr(VI) removal. (Experimental conditions: PEG-nZVI/D201 dosage 1.0 g·L⁻¹, initial Cr(VI) concentration 50 mg·L⁻¹, initial pH 5.0, and contact time 60 min.
this study, PEG-nZVI/D201 still shows good removal performance when pH is higher than 10.0, which may be due to the high dispersity and reactivity of PEG-nZVI/D201. Environmental and economic considerations are required in practical applications, the optimal pH value is set to 5.0.

3.2.5 Effect of Coexisting Ions

The actual wastewater may contain several coexisting ions, which may compete with Cr(VI) for suitable active sites on PEG-nZVI/D201, so it is necessary to study the influence of co-existing anions on Cr(VI) removal rate by PEG-nZVI/D201. Figure 5e shows that the coexistence of most cations and anions has a slight negative effect on the removal of Cr(VI). For co-existing anions, because their charge are the same as that of Cr(VI) ion, they may compete with each other for adsorption, which will theoretically have a negative effect on the adsorption of Cr(VI). Moreover, PO$_4^{3-}$ has a strong affinity for iron hydroxide (Zeng et al., 2004). CO$_3^{2-}$ can be adsorbed on the PEG-nZVI/D201 surface, and react with Fe(II) to form FeCO$_3$ or Fe$_2$(OH)$_2$CO$_3$, which consumes iron ions and occupies the active sites. Therefore, the existence of PO$_4^{3-}$ and CO$_3^{2-}$ is not conducive to the removal of Cr(VI). However, the negative effects of the three anions (Cl$^-$, PO$_4^{3-}$, and CO$_3^{2-}$) are very small and almost negligible. This may be due to the low concentration (70 mg·L$^{-1}$) of coexisting anions.

For coexisting cations, Ca$^{2+}$ and Mg$^{2+}$ have negative effects on Cr(VI) removal because both of them can react with OH$^-$ to form hydroxy-oxygen precipitation (Lo et al., 2006). The inhibition effect of Ca$^{2+}$ is smaller due to the dissolution rate of Ca(OH)$_2$ is obviously higher than that of Mg(OH)$_2$, and the amount of Ca(OH)$_2$ precipitate formed on the PEG-nZVI/D201 surface is less than that of Mg(OH)$_2$ (Zhu et al., 2019b).

3.3 Reusability and Stability of PEG-nZVI/D201

Regeneration capacity is an important performance to evaluate the sustainability of adsorbents in wastewater treatment. Figure 6a shows the removal efficiency of PEG-nZVI/D201 is higher than 90% after seven cycles, but the removal rate of PEG-nZVI and nZVI decreases significantly. These results indicate that PEG-nZVI/D201 has a high recycling capacity under the set experimental conditions.

When nZVI and PEG-nZVI/D201 are exposed to air, the removal rate of Cr(VI) declined with the increase in exposure time (Fig. 6b). The removal performance of PEG-nZVI/D201 and nZVI after exposed to air for 24 h decreases by 7.1% and 14.5%, respectively. The oxidation resistance of PEG-nZVI/D201 is better than that of nZVI, which may be because D201 resin supported with nZVI reduces the chance of nZVI contacting with oxygen. The above
results show that PEG-nZVI/D201 has better stability than pure nZVI.

3.4 Adsorption Performance

In the adsorption experiment, it is necessary to explore the adsorption kinetics to describe the adsorption process and determine the main control steps. The pseudo-first-order (Eq. 4) and pseudo-second-order (Eq. 5) kinetic equations were used to analyze the adsorption process (Rivero-Huguet et al., 2009).

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(4)

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

(5)

where \(k_1\) (min\(^{-1}\)) and \(k_2\) (g·mg\(^{-1}\)·min\(^{-1}\)) are respectively the kinetic rate constants of pseudo-first order and pseudo-second order kinetic equations. \(q_t\) and \(q_e\) (mg·g\(^{-1}\)) stand for the adsorption amount of Cr(VI) on PEG-nZVI/D201 at time \(t\) and at equilibrium.

According to the experimental data, the fitting results of the two kinetic models are shown in Figs. 7a, b, and the related kinetic parameters calculated by Eqs. 4 and 5 are shown in Table 2. The correlation coefficient of pseudo-first-order (\(R_1^2\)) and pseudo-second-order (\(R_2^2\)) kinetic models are 0.9601 and 0.9960, and the equilibrium adsorption capacity is 72.40 and 76.22 mg·g\(^{-1}\), respectively. The value of \(R_2^2\) of the pseudo-second-order kinetic model is greater than that of the pseudo-first-order kinetic model and is greater than 0.99. These results indicate that the pseudo-second-order kinetic model is more suitable to describe the adsorption of Cr(VI) on PEG-nZVI/D201, and the adsorption process is chemisorption including valence force produced by electron sharing or exchange between adsorbent and adsorbate (Lv et al., 2012).

The effect of temperature on the performance of the adsorbent is distinguished by the adsorption isothermal model parameters at different temperatures (Chen et al., 2012). The Cr(VI) concentration was set at 50–400 mg·L\(^{-1}\); the reaction temperature was set at 288–318 K and Langmuir and Freundlich adsorption isotherms (Eqs. 6 and 7) were used to analyze the adsorption properties of Cr(VI) by different adsorbents and discuss the adsorption mechanism of adsorbents (Lalley et al., 2016; Wang et al., 2017a, b).

| Parameters | Pseudo-first-order | Pseudo-second-order |
|------------|-------------------|---------------------|
| \(q_e\) (mg·g\(^{-1}\)) | 72.40 | 76.22 |
| \(k\) (min\(^{-1}\)) | 0.02913 | 0.00192 |
| \(R_2^2\) | 0.9601 | 0.9960 |

Fig. 7 The fitting result of a pseudo-first-order kinetic model and b pseudo-second-order kinetic model. (Adsorption conditions: Cr(VI) concentration 50 mg·L\(^{-1}\), PEG-nZVI/D201 dosage 1.0 g·L\(^{-1}\), pH 5.0, and contact time 100 min)
\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}
\]  \hspace{1cm} (6)

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]  \hspace{1cm} (7)

where \(q_m\) stands for the maximum adsorption capacity (mg·g\(^{-1}\)). \(K_L\) (L·mg\(^{-1}\)) and \(K_F\) (L·mg\(^{-1}\)) refer to the adsorption equilibrium constants of Langmuir and Freundlich models, respectively. \(n\) is the adsorption constant of the Freundlich model.

The simulation results of adsorption isotherms plot are shown in Fig. 8 and Table 3. The adsorption capacity of PEG-nZVI/D201 rises with the increase in temperature, suggesting that the adsorption process is endothermic. The maximum adsorption capacities of PEG-nZVI, D201/nZVI, and PEG-nZVI/D201 for Cr(VI) at 298 K are 86.78, 95.45, and 123.96 mg·g\(^{-1}\), respectively. The \(R^2\) of the Langmuir isothermal adsorption model is larger than that of Freundlich at all temperatures, suggesting that the adsorption of Cr(VI) by the three adsorbents is more consistent with Langmuir equations, the adsorption sites are uniformly distributed on the adsorbent surface, this adsorption process was monolayer adsorption.

![Langmuir and Freundlich models for Cr(VI) removal by PEG-nZVI (a), D201/nZVI (b), and PEG-nZVI/D201 (c). (Adsorption conditions: PEG-nZVI/D201 dosage 1.0 g·L\(^{-1}\), pH 5.0, and contact time 180 min)](image_url)
The comparison between the results of this study and other similar materials is shown in Table 4. By comparing the contact time, temperature, initial pH, and maximum adsorption capacity, the results demonstrate that PEG-nZVI/D201 prepared in this work has superior performance for Cr(VI) adsorption.

In order to infer the main force, the adsorption heat of Cr(VI) removal by PEG-nZVI/D201 is calculated, which is also conducive to reveal the reaction mechanism of the adsorption process. The thermodynamic parameters are obtained by Eqs. 8–10 and listed in Table 5 (Zhang et al., 2015).

\[ K_c = q_m \cdot K_L \]  

\[ \Delta G^0 = -RT \cdot \ln K_c \]  

\[ \ln K_c = \frac{-\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R} \]  

where \( R \) represents the molar gas constant (8.314 J·K\(^{-1}\)·mol\(^{-1}\)). \( \Delta G^0 \) and \( \Delta H^0 \) stand for the standard Gibbs free energy change and adsorption enthalpy (kJ·mol\(^{-1}\)), respectively. \( \Delta S^0 \) (J·mol\(^{-1}\)·K\(^{-1}\)) stands for the standard enthalpy change. The meanings of \( q_m \) and \( K_L \) can be referred to Eq. 6. \( T \) refers to the thermodynamic absolute temperature.

From the \( \Delta G^0 \) value of the three adsorbents less than 0, it can be found that the adsorption is

### Table 3 The adsorption isotherm parameters of Cr(VI) removal by different adsorbents

| Adsorbent          | Temperature (K) | Langmuir \( q_m \) (mg·g\(^{-1}\)) | Freundlich \( K_L \) (L·mg\(^{-1}\)) | \( R^2 \) | \( K_F \) (L·mg\(^{-1}\)) | \( n \) | \( R^2 \) |
|--------------------|-----------------|-----------------------------------|-------------------------------------|----------|-----------------------|-------|----------|
| PEG-nZVI           | 288             | 82.94                             | 0.0129                              | 0.9937   | 5.384                 | 0.4285| 0.9929   |
|                    | 298             | 86.78                             | 0.0156                              | 0.9957   | 10.07                 | 0.3485| 0.9728   |
|                    | 308             | 92.3                              | 0.0206                              | 0.9856   | 13.22                 | 0.3217| 0.9795   |
|                    | 318             | 98.03                             | 0.0313                              | 0.9905   | 19.07                 | 0.279 | 0.9726   |
| D201/nZVI          | 288             | 85.37                             | 0.0128                              | 0.9969   | 7.873                 | 0.3823| 0.9809   |
|                    | 298             | 95.45                             | 0.0135                              | 0.9904   | 9.171                 | 0.3776| 0.9875   |
|                    | 308             | 101.71                            | 0.0184                              | 0.9909   | 13.14                 | 0.3363| 0.9767   |
|                    | 318             | 108.58                            | 0.027                               | 0.9861   | 18.81                 | 0.2965| 0.9653   |
| PEG-nZVI/D201      | 288             | 119.23                            | 0.0287                              | 0.9869   | 20.01                 | 0.3055| 0.9699   |
|                    | 298             | 123.96                            | 0.0377                              | 0.9878   | 25.23                 | 0.2779| 0.9634   |
|                    | 308             | 126.01                            | 0.0589                              | 0.9718   | 32.3                  | 0.2458| 0.9666   |
|                    | 318             | 134.56                            | 0.0869                              | 0.9806   | 41.55                 | 0.2182| 0.9417   |

### Table 4 Comparison of the maximum adsorption capacity of Cr(VI) by PEG-nZVI/D201 with those of other materials

| Adsorbent           | Contact time (min) | Temperature (°C) | Initial pH | \( q_m \) (mg·g\(^{-1}\)) | Reference                  |
|---------------------|--------------------|------------------|------------|--------------------------|----------------------------|
| nZVI@LDH-1          | 120                | 25               | 7.0        | 5.59                     | (Zhao et al., 2020)        |
| nZVI/GNS            | 180                | 25               | 5.5        | 27.72                    | (Li et al., 2016)          |
| nZVI@PACB-700       | 360                | 25               | 4.0        | 22.24                    | (Song et al., 2020)        |
| nZVI-Fe\(_3\)O\(_4\) | 240                | 25               | 8.0        | 29.43                    | (Lv et al., 2012)          |
| nZVI/AC/CA          | 480                | 25               | 2.0        | 35.25                    | (Wen et al., 2019)         |
| Humus-supported nZVI| 90                 | 25               | 6.5        | 40.40                    | (Fu et al., 2017)          |
| Sepiolite-supported nZVI | 60            | 28               | 6.0        | 43.86                    | (Fu et al., 2015)          |
| nZVI@MG            | 120                | 30               | 8.0        | 66.20                    | (Lv et al., 2014)          |
| nZVI@K-GCN         | 480                | 35               | 3.0        | 68.60                    | (Guo et al., 2020)         |
| CS-nZVI-R          | 720                | 25               | 4.0        | 101.84                   | (Fan et al., 2020)         |
| PEG-nZVI/D201      | 180                | 25               | 5.5        | 123.96                   | This work                  |
spontaneous in nature. The absolute value increases with increasing temperature, indicating that more effective uptake at higher temperature (Zhao et al., 2010). The positive value of $\Delta H^0$ indicates that the adsorption of Cr(VI) is endothermic, which is in agreement with the previous finding (Wang et al., 2021). In general, the absolute value of $\Delta H^0$ less than 20 kJ·mol$^{-1}$ belongs to physical adsorption, in 80–200 kJ·mol$^{-1}$ belongs to chemical adsorption (Li et al., 2010). The $\Delta H^0$ values of three adsorbents are found to range between 25.22 and 31.50 kJ·mol$^{-1}$ in the temperature range from 288 to 308 K, suggesting that the adsorption is a combination of chemical adsorption and physical adsorption. The value of $\Delta S^0$ is positive, meaning that the chaos degree of the reaction system increases after the adsorption reaction (Wang et al., 2019).

| Adsorbent         | Temperature (K) | $\Delta G^0$ (kJ·mol$^{-1}$) | $\Delta H^0$ (kJ·mol$^{-1}$) | $\Delta S^0$ (J·mol$^{-1}$·K$^{-1}$) |
|-------------------|----------------|-------------------------------|-------------------------------|--------------------------------------|
| PEG-nZVI          | 288            | $-0.28$                       | 26.51                         | 93.03                                |
|                   | 298            | $-1.21$                       |                               |                                      |
|                   | 308            | $-2.14$                       |                               |                                      |
|                   | 318            | $-3.07$                       |                               |                                      |
| D201/nZVI         | 288            | $-0.11$                       | 25.22                         | 89.54                                |
|                   | 298            | $-0.99$                       |                               |                                      |
|                   | 308            | $-1.87$                       |                               |                                      |
|                   | 318            | $-2.75$                       |                               |                                      |
| PEG-nZVI/D201     | 288            | $-2.81$                       | 31.50                         | 119.13                               |
|                   | 298            | $-4.00$                       |                               |                                      |
|                   | 308            | $-5.19$                       |                               |                                      |
|                   | 318            | $-6.38$                       |                               |                                      |

3.5 Cr(VI) Removal Mechanism

In order to further elucidate the adsorption mechanism of Cr(VI) on PEG-nZVI/D201, the XPS spectrum of used PEG-nZVI/D201 was analyzed. A new characteristic peak belonging to Cr 2p appears near 577 eV (Fig. 4a), indicating that the high absorbability of PEG-nZVI/D201 makes Cr adsorbed to its surface. The characteristic peaks at 576.8 and 586.5 eV attribute to Cr(III), while the characteristic peaks at 579.5 and 589.7 eV attribute to Cr(VI) (Fig. 4b), which account for 76% and 24% of the total Cr, respectively (Wang et al., 2019). The above results show that most of Cr(VI) is adsorbed on PEG-nZVI/D201 surface, and then rapidly reduced to Cr(III) by nZVI with high reducibility, while a small part of Cr(VI) exists on PEG-nZVI/D201 surface. As it can be seen from the XPS spectra of Fe 2p after the reaction, the characteristic peak of nZVI is not found, which may be related to the change of the valence state of nZVI in the reduction reaction. The characteristic peaks at 710.3 and 723.5 eV belong to Fe(II), and 711.3 and 725.0 eV belong to Fe(III) (Zhu et al., 2021). The area ratio of Fe(III)/Fe(II) increases from 0.86 to 1.75 after the reaction, which confirms that nZVI involves the reduction of Cr(VI) and is oxidized to Fe(II) or Fe(III). Besides, Fe(II) can serve as a reductant for Cr(VI) and is oxidized to Fe(III). The peak area of $O_{2-}^-$ in the O1s binding energy increases (Fig. 4f), which further indicates that the oxidation products increased obviously after the reaction.

The influence of pH (Fig. 5d) and coexisting ions (Fig. 5e) demonstrate that Cr(VI) is adsorbed on the PEG-nZVI/D201 surface through electrostatic adsorption. TEM images (Fig. 1) show that PEG is applied to the surface of nZVI to disperse nZVI particles. FTIR spectra (Fig. 3) prove that PEG and D201 successfully modify nZVI and reduce the oxidation rate of nZVI particles.

To sum up, the reaction mechanism can be divided into three steps (Fig. 9). At first, PEG-nZVI/D201 adsorbs Cr(VI) on its surface by electrostatic interaction. In detail, PEG-nZVI/D201 is easy to protonate under acidic conditions, this makes its surface be positively charged, which contributes to the electrostatic adsorption of $Cr_{2}O_{7}^{2-}$ and $HCrO_{4}^{-}$ (Sun et al., 2014).
Secondly, most of $\text{Cr}_2\text{O}_7^{2-}$ and $\text{HCrO}_4^{-}$ are converted to Cr(III) by nZVI and Fe(II), nZVI and Fe(II) further are oxidized to Fe(II) and Fe(III) (Eqs. 11–14) (Singh et al., 2012). Finally, Cr(III) and Fe(III) are apt to form $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ and $\text{Cr}_x\text{Fe}_{1-x}\text{OOH}$ co-precipitation (Eqs. 15 and 16) (Fan et al., 2019). With the consumption of $\text{H}^+$, the increasing amount of $\text{OH}^-$ in solution promotes the generation of Cr(III) hydroxides (Eqs. 17 and 18) (Zhang et al., 2019), meanwhile the coagulation of $\text{Fe(OH)}_3$ causes precipitation of Cr(III).

$$\text{Cr}_2\text{O}_7^{2-} + 3\text{Fe}^0 + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{Fe}^{2+} + 7\text{H}_2\text{O} \quad (11)$$

$$\text{HCrO}_4^{-} + \text{Fe}^0 + 7\text{H}^+ \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} + 4\text{H}_2\text{O} \quad (12)$$

$$\text{HCrO}_4^{-} + 3\text{Fe}^{2+} + 7\text{H}^+ \rightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+} + 4\text{H}_2\text{O} \quad (13)$$

$$\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{FeCr}_2\text{O}_4 \quad (14)$$

$$(1-x)\text{Fe}^{3+} + x\text{Cr}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3 + 3\text{H}^+ \quad (15)$$

$$(1 - x)\text{Fe}^{3+} + x\text{Cr}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Cr}_x\text{Fe}_{1-x}\text{OOH} + 3\text{H}^+ \quad (16)$$

$$2\text{Fe}^{3+} + 6\text{OH}^- \leftrightarrow 2\text{Fe(OH)}_3 \leftrightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (17)$$

$$2\text{Cr}^{3+} + 6\text{OH}^- \leftrightarrow 2\text{Cr(OH)}_3 \leftrightarrow \text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (18)$$

### 4 Conclusion

PEG-nZVI/D201 was successfully prepared by co-modifying nZVI with D201 resin and PEG. PEG-nZVI/D201 can effectively remove Cr(VI) because D201 resin as a carrier and PEG as a stabilizer can inhibit the agglomeration and oxidation of nZVI. The removal of Cr(VI) by PEG-nZVI/D201 takes place in a wide pH range. The maximum adsorption capacity of PEG-nZVI/D201 for Cr(VI) is 134.56 mg·g$^{-1}$ at 318 K. Based on experiment data and characterization results, the reaction mechanism for Cr(VI) removal may be described as follows: Cr(VI) is first adsorbed on the PEG-nZVI/D201 surface by electrostatic attraction. Secondly, Cr(VI) is reduced to Cr(III) by nZVI as electron donors, and nZVI is oxidized to Fe(II) and Fe(III). Thirdly, Cr(VI) is removed in a way of $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ coprecipitation formed between Cr(III) and Fe(III) on the surface of PEG-nZVI/D201.

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**Data Availability** All data generated or analyzed during this study are included in this published article.
Declarations

Conflict of Interest  The authors declare no competing interests.

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