Removal of Cr(VI) by modified diatomite supported NZVI from aqueous solution: evaluating the effects of removal factors by RSM and understanding the effects of pH
Yongxiang Zhang, Zhenjun Tian, Qi Jing, Yuanyuan Chen and Xuezheng Huang

ABSTRACT
In this study, a novel composite of modified diatomite supported nanoscale zero-valent iron (mD-NZVI) was synthesized and characterized. The effects of four factors (mD-NZVI dose, temperature, contact time and initial pH) on the removal of Cr(VI) by mD-NZVI were studied by experimental work and analyzed by response surface methodology (RSM). A second-order polynomial equation fitted by Box-Behnken design was used as a statistical model and proved to be precise in describing the significance of four factors. The analysis results show that the effects of four factors on the removal efficiency of Cr(VI) were significant (F value is 19.83), initial pH was found to be the key factor. In addition, the effect of initial pH was further studied and the maximum removal efficiency of 89.34% was obtained at pH of 3, the decrease in removal efficiency with the increase in pH is a synergistic effect of Cr(VI) species, surface charge of mD-NZVI and OH⁻ amount at different pH.

Key words | Cr(VI), diatomite, nanoscale zero-valent iron (NZVI), response surface methodology (RSM)

INTRODUCTION
Chromium (Cr) is a heavy metal widely used in metallurgical activities and chemical engineering. Chromium exists in two stable oxidation states, Cr(III) and Cr(VI). Cr(III) is considered to be an essential micronutrient, while Cr(VI) is poisonous, easy to transport in soil and aquatic systems and absorbed by the human body (Gad 1989). Hexavalent chromium (Cr(VI)) contamination of soil and groundwater has become a prominent environmental problem around the globe (Kotaś & Stasicka 2000). The main methods for Cr(VI) removal are chemical precipitation (Ku & Jung 2001), membrane separation (Corvalán et al. 2004) and ion exchange resins (Fernández et al. 2005). However, these techniques are too expensive to remove a large amount of heavy metals.

In recent years, nanoscale zero-valent iron (NZVI) has been widely used for its effectiveness in treating chlorophenol (Jia & Wang 2012; Li et al. 2013; Hwang et al. 2013) and metal species (Liu et al. 2009; Dang et al. 2014) in water. The chemical reduction of Cr from hexavalent form Cr(VI) to trivalent form Cr(III) by NZVI is a competitive approach due to its smaller particle size, larger surface area, higher reactive surface sites, and greater reducibility (Li et al. 2006). However, NZVI particles have a strong tendency to agglomerate due to van der Waals and/or magnetic attraction forces and can also be easily oxidized, resulting in significant loss of reactivity (He & Zhao 2005). In order to overcome these limitations, NZVI is determined to be carried or encapsulated by organic/inorganic vehicles to improve dispersibility and anti-oxidativity (Stefaniuk et al. 2016).

Chitosan is a bioactive polymer made by treating the chitin shells of shrimp and other crustaceans with an alkaline medium. The presence of amino (-NH₂) and hydroxyl (-OH) in chitosan are beneficial to bind heavy metals (Monteiro & Airoldi 1999). However, the chitosan has weakness in mechanical strength and self-aggregation in water, it should be immobilized on scaffold material to improve its mechanical stability and to increase the effectiveness of its active sites (Han et al. 2013). Diatomite (SiO₂·nH₂O) is a lightweight sedimentary rock with a composition of diatom fossils. Diatomite’s high porosity, large
surface area, low density and chemical inertness resulted in applications as an adsorbent (Bailey et al. 1999) and filtration media (Li et al. 2014). The amino group in chitosan leads to a positive charge on the surface, while diatomite particles are negatively charged (Sheng et al. 2009). This makes chitosan readily bind to the diatomite surface by electrostatic attraction. Diatomite is less expensive than chitosan. Thus the chitosan can be immobilized on diatomite as a low-cost material to support the NZVI. In this research, a novel composite of chitosan modified diatomite supporting NZVI (mD-NZVI) for Cr(VI) removal was derived, an aspect that has been little reported in literature. mD-NZVI led to great promotion of Cr(VI) removal due to the significant synergistic effects of the chemical reduction by NZVI and the adsorption by the modified diatomite.

In order to overcome the weaknesses of the one-variable-at-a-time optimization technique in monitoring one factor response on an experiment, statistical approaches such as response surface methodology (RSM) are employed to study the interactive effects among the variables (Mason & Gunst 2003; Khosravi & Arabi 2016). Box-Behnken design (BBD) (Tripathi et al. 2009) and central composite design (CCD) (Desalegn et al. 2016) are the principal response surface methodologies used in optimization design. In this research, the optimum conditions for removing Cr(VI) by mD-NZVI were determined by means of a four factor (mD-NZVI dose, experimental temperature, contact time and initial pH of solution), three level Box-Behnken experimental design (BBD) combining with response surface modeling.

The major objectives of this study were: (1) to successfully synthesize novel mD-NZVI composites and to characterize them by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD); (2) to evaluate the effects of four factors on the removal of Cr(VI) by the RSM-BBD analysis with the consideration of previous studies about the effect of pH on the removal of Cr(VI) (Manuel et al. 1995; Hu et al. 2004); (3) to explore the reason why pH played a major role in the removal of Cr(VI) by mD-NZVI.

MATERIALS AND METHODS

Materials

All chemical reagents used (FeSO₄·7H₂O, NaBH₄, K₂Cr₂O₇, anhydrous ethanol, HNO₃, NaOH) in this study were analytical grade. The chitosan (degree of deacetylation ≥95%) and the raw diatomite were also obtained from Tianjin Fuchen Chemical Reagent Factory, Tianjin, China. All solutions were prepared using deionized water. Standard acid 0.1 M HNO₃ and 0.1 M NaOH solutions were used for the pH adjustment. Cr(VI) concentration was detected using an UV-visible spectrophotometer (Cary 100 Bio, Varian, Palo Alto, CA, USA) at 540 nm wavelength.

Synthesis of mD-NZVI

The chitosan modified diatomite (mD) composite was prepared by coating the diatomite with chitosan. Raw diatomite powder was added to 1 mol/L hydrochloric acid at room temperature for 30 minutes to remove any acid-soluble constituents of diatomite. After acid treatment, diatomite was washed three times with deionized water and dried at 80 °C for 6 h in an oven. An amount of chitosan was added slowly to 0.02 mol/L acetic acid solution, and the solution was stirred at room temperature for 1.5 h to form a viscous mixture. The acid treated diatomite was added to the chitosan solution and vigorously stirred for approximately 10 h to make a homogenous mixture of chitosan and diatomite in a 1:10 mass ratio. The mixture was filtered and washed with deionized water three times. The obtained mD was dried in an oven at 60 °C under vacuum for 24 h, and then sealed.

6.95 g of FeSO₄·7H₂O was dissolved in the deoxygenated deionized water and stirred for 30 min. The deoxygenated deionized water was prepared by purging with N₂ gas for 2 h before use. Then 1.4 g of mD was added to this solution under stirring for 2 h. 2.85 g of NaBH₄ dissolved in 200 mL of deoxygenated deionized water was subsequently added drop wise to the above solution under constant stirring. The solution was transferred to a black suspension, in which the mass ratio of mD to NZVI was 1:1. The reduction reaction can be expressed as:

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

Finally, the prepared mD-NZVI particles were filtered by solvent filter, and then washed with deionized water and ethanol several times, vacuum dried under 70 °C for 10 h, with sealed storage.

Characterization of diatomite and mD-NZVI

Scanning electron microscopy (JSM-7610 FPlus, JEOL Ltd, Japan) and transmission electron microscopy (JEM 2100, JEOL Ltd, Japan) were performed to observe the surface morphology of diatomite and mD-NZVI. X-ray diffraction
(BRUKER D8 Advance, Germany) was carried out to investigate the crystal structure of mD-NZVI.

**Batch experiments**

Under nitrogen gas atmosphere, 20 mg/L of Cr(VI) solution was prepared by dissolving K₂Cr₂O₇ with deionized water, different mD-NZVI dose was added into 200 mL Cr(VI) solution with a known initial pH, which was taken in a 250 mL stoppered conical flask. The mixture was shaken on a temperature controlled shaker at 250 rpm for the desired temperature and contact time. The Cr(VI) concentration after reaction was measured by a UV-visible spectrophotometer at λ of 540 nm.

The effects of initial pH were studied with a 200 ml solution of 20 mg/L Cr(VI) solution, mD-NZVI dose of 0.2 g/L, fixed temperature (30°C) and preset contact time (30 min). The initial pH of the solutions ranged from 2–12. The surface charge of mD-NZVI was measured by a Zeta potential analyzer (90plus Zeta, Brookhaven Instruments Corporation, USA).

**Experimental design by response surface methodology**

In the present work, the BBD was used to provide the experimental design and to evaluate the effects of four factors for Cr(VI) removal by mD-NZVI. The mD-NZVI dose (A), temperature (B), contact time (C), and initial pH (D) were considered as independent variables for the model, and the removal efficiency of Cr(VI) was considered as the dependent variable. The factor levels were coded as -1 (low), 0 (middle) and 1 (high) (Tripathi et al. 2009), which are given in Table 1. Twenty nine groups of experiments were performed in this work including five central point parallel experiments. The actual experimental design matrix is given in Table 2. The data obtained from the experiments was analyzed using (Design-Expert version 6.0.6) (Sohrabi et al. 2014). The results were analyzed using the coefficient of determination (R²), Pareto analysis of variance (ANOVA) and 3D response surface plots. The quadratic response model can be described as a non-linear regression equation:

\[
Y = X_0 + X_1A + X_2B + X_3C + X_4D + X_5AB + X_6AC + \ldots + X_{12}B^2 + X_{13}C^2 + X_{14}D^2
\]

where, Y is the removal efficiency of Cr(VI); X₀ is the intercept coefficient; X₁₋₁₄ are the estimated coefficients; A, B, C and D are coded factors.

### Table 1 | Levels of variables for RSM

<table>
<thead>
<tr>
<th>Variables</th>
<th>Unit</th>
<th>Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low(-1)</td>
<td>Middle(0)</td>
</tr>
<tr>
<td>mD-NZVI dose</td>
<td>g/L</td>
<td>A</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>B</td>
</tr>
<tr>
<td>Contact time</td>
<td>min</td>
<td>C</td>
</tr>
<tr>
<td>Initial pH</td>
<td>/</td>
<td>D</td>
</tr>
</tbody>
</table>

### Table 2 | Experimental and predicted values of Cr(VI) removal

<table>
<thead>
<tr>
<th>Run</th>
<th>A (g/L)</th>
<th>B (°C)</th>
<th>C (min)</th>
<th>D /</th>
<th>Experimental (%)</th>
<th>Predicted (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>37.83</td>
<td>42.72</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>88.29</td>
<td>81.87</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>26.83</td>
<td>34.50</td>
</tr>
<tr>
<td>4</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>51.17</td>
<td>53.81</td>
</tr>
<tr>
<td>5</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>18.25</td>
<td>9.21</td>
</tr>
<tr>
<td>6</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>59.29</td>
<td>59.55</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>41.38</td>
<td>46.50</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>91.29</td>
<td>90.25</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>29.77</td>
<td>30.71</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>76.58</td>
<td>71.69</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>87.41</td>
<td>77.20</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>22.76</td>
<td>13.18</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>93.98</td>
<td>96.73</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>38.46</td>
<td>43.92</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>52.33</td>
<td>55.08</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>93.77</td>
<td>95.81</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>32.42</td>
<td>40.36</td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>89.50</td>
<td>82.23</td>
</tr>
<tr>
<td>19</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48.67</td>
<td>48.14</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>46.04</td>
<td>48.14</td>
</tr>
<tr>
<td>21</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>47.50</td>
<td>48.14</td>
</tr>
<tr>
<td>22</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>47.42</td>
<td>48.14</td>
</tr>
<tr>
<td>23</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>51.08</td>
<td>48.14</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>88.04</td>
<td>83.03</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>56.42</td>
<td>60.68</td>
</tr>
<tr>
<td>26</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>94.82</td>
<td>98.71</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>51.17</td>
<td>55.45</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>94.48</td>
<td>93.71</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>94.96</td>
<td>85.32</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Characterization of diatomite and mD-NZVI

The SEM and TEM images were used to investigate the surface morphology of diatomite, modified diatomite and mD-NZVI, which are shown in Figures 1 and 2. From Figure 1(a), the surface of raw diatomite was covered and pores blocked by a lot of impurities. On the contrary, it is shown in Figure 1(b) that obviously less impurities and more open pores were on the surface of the disc-shaped diatomite. NZVI particles tend to aggregate and display a chain-like structure as shown in Figures 1(c) and 2(a), which was caused by magnetic attraction and/or van der Waals. When NZVI were supported onto diatomite, there were several particles dispersed in the pores or on the surface of diatomite, and the porous structure remained clearly visible as shown in Figures 1(d) and 2(b). Therefore we can know that the aggregation of NZVI can significantly decrease after being supported on the surface of diatomite, thus keeping a larger surface area and ensuring the removal of Cr(VI) from aqueous solution.

Figure 1 | SEM image of raw diatomite (a), modified diatomite (b), NZVI (c) and mD-NZVI (d).

Figure 2 | TEM image of NZVI (a) and mD-NZVI (b).
The XRD was carried out to investigate the chemical component of mD-NZVI, which is shown in Figure 3. It is apparent that SiO₂ mainly existed in the samples with a minor component of Al. Fe was found to have a cubic structure as the characteristic peak appears at 2θ of 44.7° was observed, which indicated that zero valent iron was successfully supported by the diatomite.

RSM-BBD analysis

In order to investigate the effects of four factors on the removal of Cr(VI) by mD-NZVI, 29 experiments designed by RSM have been performed, as shown in Table 2 along with the predicted Cr(VI) removal values. The predicted values obtained from RSM were fitted well to the experimental values with a coefficient of determination (R² = 0.956) and adjusted coefficient determination (adjusted R² = 0.904) as can be seen from Figure 4, which illustrates that the RSM model is precise in describing the significance of different factors and able to provide a proper prediction for the removal efficiency.

Table 3 summarizes the results of ANOVA, F-values and P-values were used to estimate statistical significance of the model, individual factors, as well as their squares and interactions (Tripathi et al. 2009; Shi et al. 2017). F-value and P-value are opposite indicators; the less the amount of P-value gets, the more the amount of F value goes. If the amount of P-value is less than 0.05, that factor will be meaningful and the model terms are significant at 95% of probability level (Tripathi et al. 2009; Sohrabi et al. 2014). As listed in Table 3, the F-value of 19.83 is gived by the response surface quadratic model, which indicated that terms have a significant effects on the response of the model. The p-values are all less than 0.0001 for four factors except B (temperature). Particularly, initial pH is the most significant factor as the F-value of 166.93 is much bigger than the others. According to the results, a second-order polynomial equation was gained for the relationship of
Cr(VI) removal efficiency and four factors:

\[ Y = 48.14 + 16.52A + 4.78B + 13.09C - 29.75D - 3.65AB + 5.43AC + 6.60AD + 0.49BC + 0.043BD + 2.28CD + 8.16A^2 + 11.36B^2 + 4.37C^2 + 5.76D^2 \]

The ANOVA was done to examine the availability of the model. Regression coefficients have two aspects including amount and sign (Sohrabi et al. 2014). The sign of the regression coefficients determines its effect direction, a positive sign of the coefficient represents a synergistic effect, while a negative sign decreases the response (Singh et al. 2011). The initial pH (D), mD-NZVI dose and temperature (AB) have negative effects and others have positive effects. The percent contribution (PC) of each of the individual terms in the final model was obtained using the sum of squares (SS) values of the corresponding term, which are listed in Table 4 and calculated by the following equations:

\[ PC = \frac{SS}{\sum SS} \times 100 \]

As it is obvious, presented in Table 4, the initial pH made the greatest contribution on Cr(VI) removal as the PC value of 58.55.

The three-dimensional response surface plots were used to evaluate the interaction between the four factors on Cr(VI) removal, as shown in Figure 5. It is evident that initial pH has a crucial effect on the removal of Cr(VI). Figure 5(c), 5(e) and 5(f) show the interactive effects between the initial pH and mD-NZVI dose, temperature, and contact time, respectively. It is obvious that the removal efficiency of Cr(VI) decreases with increase of initial pH.

The optimum removal conditions obtained from the RSM model were mD-NZVI dose of 0.60 g/L, temperature of 34.96 °C, contact time of 59.47 min, and initial pH of 4.00, respectively. Under these optimal conditions the removal efficiency of 97.79% was observed; in order to verify the model’s accuracy for predicting Cr(VI) removal, three additional experiments were carried out and the result was 96.02%, 95.66%, and 95.96%, respectively, which was compatible with the experimental values, and the absolute error was 1.91%, indicating that the RSM model is reliable to provide a proper prediction for the removal of Cr(VI).

**Effects of initial pH**

The acidity of the aqueous solution is a key parameter in the adsorption process because it can be an influence on the property of metal ions as well as the state of functional groups on the surface of its (Karaer & Kaya 2017). In the present study, variance analysis, PC values and 3D response surface plots all indicated that initial pH played the greatest role on the removal of Cr(VI).

In order to study the effects of initial pH, the variation of pH value during the removal process was measured as shown in Figure 6. It was found that, for initial pH of 4 the pH value increased to 6.3 gradually, which might be caused by the consumption of H⁺ and generation of OH⁻ as presented in Equations (5)–(7). For initial pH of 8, the pH value decreased to 6.9, which could be explained as the generation of H⁺ on the formation of Hydroxide by Fe(III) and Cr(III) as described in Equations (8) and (9).

\[ 3\text{Fe}^0 + \text{Cr}_2\text{O}_7^{2-} + 7\text{H}_2\text{O} \rightarrow 3\text{Fe}^{2+} + 2\text{Cr(OH)}_3^- + 8\text{OH}^- \]  
\[ \text{Fe}^0 + \text{HCrO}_4^- + 7\text{H}^+ \rightarrow 3\text{Fe}^{3+} + 5\text{Cr}^{3+} + 4\text{H}_2\text{O} \]  
\[ \equiv \text{Fe(OH)} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \equiv \text{Fe} - \text{Cr}_2\text{O}_7^- + \text{OH}^- \]  
\[ (1 - x)\text{Fe}^{3+} + (x)\text{Cr}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Fe}_{1-x}\text{Cr}_x\text{OOH} + 3\text{H}^+ \]  
\[ (1 - x)\text{Fe}^{3+} + (x)\text{Cr}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_{1-x}\text{Cr}_x\text{OH}_3^- + 3\text{H}^+ \]

Batch experiments were carried out at different initial pH values adjusted in the range of 2–12 and keeping other factors constant, mD-NZVI dose (0.2 g/L), temperature (30 °C) and contact time (30 min), respectively. The blue
line in Figure 7 shows the removal efficiency of Cr(VI) by mD-NZVI at different initial pH, there is a high removal efficiency when pH values in the range of 2–5 and the maximum removal efficiency of 89.34% was obtained at pH value of 3. It is evident that the Cr(VI) removal efficiency decreased sharply with elevated pH in the range of 5–8.

Existing species of Cr(VI) at different pH value is distinguishing. Figure 7 shows the Cr(VI) species at different pH values obtained from the Visual MINTEQ, which is consistent with the previous report (Manuel et al. 1993). The predominant Cr(VI) species is HCrO₄⁻ at pH of 2–5, which can explain the higher removal efficiency of Cr(VI) at the
pH values of 2–5, because the HCrO$_4^-$ ion has a lower adsorption free energy than the CrO$_4^{2-}$ ion and is more favorably be adsorbed (Manuel et al. 1995; Hu et al. 2004). With the increase of pH from 5 to 8, the amount of HCrO$_4^-$ decreased and CrO$_4^{2-}$ increased, CrO$_4^{2-}$ is mainly existed as the pH values at the range of 8–12. The variation of Cr(VI) species is highly consistent with the removal efficiency at different initial pH values, which indicates that the removal efficiency of Cr(VI) is existing species dependent.

The zeta potential of mD-NZVI at aqueous suspension was measured at different pH values to determine the pH$_{ZPC}$ (zero point of charge), as can be seen from Figure 8, the surface charge of mD-NZVI is neutral when pH value of 8.5 is reached. The reason why Cr(VI) removal efficiency is highly pH-dependent can also be explained as the surfaces of mD-NZVI in aqueous solution with pH below the pH$_{ZPC}$ are positively charged and Cr(VI) adsorption favored, with pH value increasing, the surface of mD-NZVI are negatively charged thus increased electrostatic repulsion with also negatively charged Cr(VI) species (CrO$_4^{2-}$). Moreover, the increase of pH value bring an increment concentration of OH$^-$ ions presenting in the reaction mixture, which compete with CrO$_4^{2-}$ for the adsorption sites and thus obtained a declined removal efficiency of Cr(VI). Hence, the removal efficiency of Cr(VI) have a close relationship with the surface charge of mD-NZVI in aqueous solution.

CONCLUSIONS

The modified diatomite supported NZVI was employed in this study to investigate the removal capacities of Cr(VI) in aqueous solution. The synthesized materials were characterized by SEM, TEM and XRD. The RSM model was used to examine the effects of four factors on the removal of Cr(VI), the accuracy of the model was depicted by the comparison of predicted and experimental values ($R^2 = 0.956$), as well as analysis of variance with high F-value (19.83), very low P-value(<0.0001). Variance analysis, PC values and 3D response surface plots all indicated that initial pH was the most significant factor in the removal process; the removal efficiency decreased with the increase in pH value, that is from synergistic effects of Cr(VI) species, surface charge of mD-NZVI and OH$^-$ concentration at different pH value. Consequently useful information about this alternative wastewater technology was obtained by studing the removal of Cr(VI) by modified diatomite supported NZVI.

ACKNOWLEDGEMENTS

This work was supported by National key research and development program of China under No. 2016YFC0401404.
REFERENCES


First received 5 May 2019; accepted in revised form 1 August 2019. Available online 12 August 2019