Performance of iron nano particles and bimetallic Ni/Fe nanoparticles in removal of amoxicillin trihydrate from synthetic wastewater
Ahmad Reza Yazdanbakhsh, Hasti Daraei, Mohamad Rafiee and Hosein Kamali

ABSTRACT
In the present study, the degradation of amoxicillin trihydrate (AMT), using synthesized nanoscale zero-valent iron (nZVI) and bimetallic Fe and Ni nanoparticles stabilized with chitosan (Cs-Fe/Ni), in water was investigated. A central composite design combined with response surface methodology and optimization was utilized for maximizing the AMT reduction by the nanoparticles-water system. The importance of the various variables and their interactions were analyzed using analysis of variance and t-test. The effects of independent parameters were tested and the results showed that the initial concentration of AMT, pH, and nanoparticles dosage were all significant factors. Field-emission scanning electron microscopy images indicated that chitosan acts as a stabilizer preventing the agglomeration of nanoparticles. Also, chitosan and Ni increased the specific surface area of Cs-Fe/Ni. X-ray diffraction confirmed the existence of Fe⁰ in fresh samples and the presence of Fe(II) and Fe(III) after the reaction with AMT. This study demonstrates that the nZVI technology could be a promising approach for antibiotic wastewater treatment.

Key words | amoxicillin, central composite design, chitosan, nZVI

INTRODUCTION
In recent years, antibiotics have been widely used for medicine and therapy. Amoxicillin is one of the main antibiotics that benefits humans and animals. Unfortunately, these antibiotics are discharged into the aquatic environment and have emerged as a potential risk to the environment and organisms. Some of the harmful effects caused by discharged antibiotics include aquatic toxicity, resistance in pathogenic bacteria, and genotoxicity (Nawi et al. 2011). Some studies have recently reported on the effective degradation of amoxicillin trihydrate (AMT) under different treatment processes. Many methods have been applied to remove amoxicillin and other antibiotics, including ozonation, sorption, advanced oxidation processes, chemical precipitation, ion exchange, and electrolysis (Homem & Santos 2011).

Iron is one of the metals which can be profusely found on the earth. Zero-valent iron is one type of iron which is a strong reducing element. Zero-valent iron is used for pollution demolition because of advantages such as its easy access, effective degradation, and low waste. Lately, the synthesis of iron nanoparticles has been of specific interest to researchers. Iron nanoparticles and iron powder have been widely investigated in the removal of phenol and other organic matters (Kassae et al. 2011). Nanoscale zero-valent iron (nZVI) was also used in the elimination of metals (Ponder et al. 2000), herbicide (Joo et al. 2004), aromatic compounds (Choe et al. 2001), and arsenic (Kanel et al. 2005). In rather comparable conditions, such a process allows contaminant removal in a short time compared to a conventional process like biodegradation (Gotpagar et al. 1998). Elimination of contaminants occurs on the surface of iron nanoparticles (Wang & Zhang 1997). In most studies, the particles perform best when the size is typically around 1–100 nm (Lu et al. 2007; Xu & Wang 2011).

Chitosan is one of the special natural polymers that exhibit many advantages such as antimicrobial activity, excellent biocompatibility, good mechanical strength, bioadhesiveness, biodegradability, and low toxicity (Liu et al. 2012). Lately, this natural biopolymer has been used with other nanoparticles in a sorbent technology, including its use as a stabilizer, a recovery agent, and as a secondary coagulant.
to increase the efficiency of adsorbent in the removal of pollutants (Nawi et al. 2011). Previous studies have indicated that nZVI stabilized by chitosan increases its dispersal and stability for the removal of heavy metals (Geng et al. 2009).

Iron-based bimetallic nanoparticles have received attention for removal of pollutants. Ni has a catalytic effect, which can provide better corrosion stability, and lower cost for site remediation. Thus, this catalyst makes iron-based bimetallic nanoparticles more stable in the air, preventing oxidation (Weng et al. 2014).

Given the findings of previous research, this study set out to use a catalytic metal, Ni, with nZVI to form bimetallic nanoparticles and use chitosan polymer to stabilize them. Afterwards, the characterizations of nZVI and bimetallic Fe and Ni nanoparticles stabilized with chitosan (Cs-Fe/Ni) for the removal of AMT were studied.

**MATERIALS AND METHOD**

**Synthesis of nZVI**

In this research, nanoparticles were generated by reducing ferric iron in the presence of sodium borohydride. These particles were synthesized with 1:1 volume ratio of NaBH₄ and FeCl₃⋅6H₂O. Then, a solution (0.16 M) was added dropwise into FeCl₃⋅6H₂O (0.1 M) under vigorous magnetic stirring in atmospheric conditions for 1 hour (Daraei & kamali 2014). Finally, fine black particles were obtained and precipitated according to the following reaction:

\[
4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^{0} + 3\text{H}_2\text{BO}_3^- + 12\ \text{H}^+ + 6\text{H}_2
\]

**Synthesis of Cs-Fe/Ni nanoparticles**

Cs-Fe/Ni nanoparticles were synthesized by the reduction method in presence of chitosan as a stabilizer agent. The deoxygenated water was deoxygenated by nitrogen gas for 30 minutes. Other reagents were prepared using this deoxygenated deionized water.

For this purpose, first, a solution of chitosan (0.5%) in 0.05 M of acetic acid and distilled water was prepared, and then was placed in a shaker for 15 minutes. In the next step, FeCl₃⋅6H₂O (0.36 mol) was dissolved in a 3/1 (v/v) absolute ethanol/deionized water solution (7 mL ethanol + 3 mL water). Also, NiSO₄⋅6H₂O (0.34 mol) was dissolved in 10 mL of distilled water. Finally, these two solutions were added into the chitosan solution. Then 100 mL of NaBH₄ was added dropwise into the mixture and stirred strongly and constantly for 60 minutes. Black solids of nanoparticles were formed after addition of NaBH₄ solution. After the 1 hour, vacuum filtration was applied to collect the bimetallic nanoparticles. During the filtration process, solid particles were repeatedly washed with 99% absolute ethanol. Then, nanoparticles were dried at 80 °C under vacuum overnight (Weng et al. 2013, 2014).

**Chemicals and batch experiments**

The stock solution containing 1,000 mg/L of amoxicillin was provided by dissolving this antibiotic into deionized water. Batch experiments were performed by adding nanoparticles in 250 mL bottles containing amoxicillin, and the following parameters were examined: the contact time (5, 25, 45, 65 and 85 min), the amoxicillin concentration (5, 15, 25, 35 and 45 mg/L), the pH (2, 4, 6, 8 and 10), and the sorbent dosage (0.25, 0.5, 0.75, 1 and 1.25 g). The concentration of residual amoxicillin was spectrophotometrically determined at \( \lambda = 228\ \text{nm} \) (Weng et al. 2013; Pouretedal & Sadegh 2014).

The response surface method was used to analyze the data. To this end, a central composite design (CCD) was applied to delve into the effect of the operating variables such as pH, sorbent dosage, and amoxicillin concentration on the performance of the sorption process. Thus, to optimize the parameters and investigate the interactions between these independent parameters for amoxicillin biosorption, response surface modeling (RSM) was utilized.

**Experimental design**

RSM is an experiential statistical method that uses quantitative data collected from appropriately designed experiments to define a regression model and operating conditions. The main purpose of RSM is to assess the optimum set of operational variables of the experiment. This method has widely been used in chemical and sorption reaction optimization (Kunwar et al. 2011).

A statistical experimental design based on CCD was contrived (Kunwar et al. 2011) and the output was measured for alternative variables of initial concentration, pH, time, and nanoparticles dosage coded as \( x_1, x_2, x_3 \), and \( x_4 \), respectively. These variables were studied at five levels (−2, −1, 0, 1, 2) and the dependent variable was \( Y \) (response). The Minitab software package (version 16.2) was used to design and estimate these five independent
variables at five levels on the responses according to Equation (2). The ranges of the variables are shown in Table 1. The experimental efficiency for different levels of variables is indicated for 31 runs.

\[ Y = \beta_0 + \sum \beta_j \cdot X_i + \sum \beta_{jj} \cdot X_i^2 + \sum \beta_{jk} \cdot X_i \cdot X_k \]  

(2)

where \( Y \) = response, \( \beta_0 \) = intercept, \( \beta_j \) = linear coefficients, \( \beta_{jj} \) = squared coefficients, \( \beta_{jk} \) = interaction coefficients, \( X_i, \) \( X_i^2, \) \( X_i, \) \( X_k \) = level of independent variables.

**RESULTS AND DISCUSSION**

**Characterization of nZVI and Cs-Fe/Ni particles**

**FESEM**

Synthesized nanoparticles were analyzed to identify the size and characteristics of these nanoparticles. Accordingly, field-emission scanning electron microscopy (FESEM) was used to scrutinize the morphology and the size diffusion of synthesized nanoparticles. Figure 1(a) and 1(b) show FESEM micrographs of these fresh particles. Synthesized nanoparticles were in the size range of 25–50 nm. These micrographs showed that these synthesized particles are not discrete. The results indicated that these nanoparticles are spherical and interconnected in chains of beads. As shown in Figure 1, on the spherical particles there were string-like structures. These structures increased the active and available surface area of reaction (Rasheed et al. 2011). Good dispersibility of the iron nanoparticles and bimetallic nanoparticles were attributed to the performance of chitosan. Metallic nanoparticles tended to agglomerate in aqua solution to form larger hunks, thus losing their reactivity and mobility (Su et al. 2011). To prevent aggregation and to improve the surface of nanoparticles, stabilizers (such as bentonite and Chitosan) have been added onto the nanoparticles during the synthesis process (Su et al. 2011). In fact, these stabilizers, by reducing the potential for electrostatic hindrance, made the nanoparticles stable.

**EDX**

Localized Cs-Fe/Ni and nZVI information from the chosen region was obtained with energy-dispersive X-ray spectroscopy (EDX). EDX analysis of nZVI and Cs-Fe/Ni is presented in Figure 2(a) and 2(b). The presence of Fe and Ni ions on the surface of fresh CS-Fe/Ni nanoparticles is confirmed by EDX. The elemental compositions of Fe, Ni, O, S, and Na in these nanoparticles were 70.32, 13.78, 4.97, 1, and 9.72 wt%, respectively (Figure 2(a)). The presence of elements such as sulfur and sodium, along with particles, was due to the presence of these elements of chitosan polymer. Also,

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Process variables and their limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variables</td>
<td>-2</td>
</tr>
<tr>
<td>Amoxicillin concentration (mg/L)</td>
<td>5</td>
</tr>
<tr>
<td>pH</td>
<td>2</td>
</tr>
<tr>
<td>Time (min)</td>
<td>5</td>
</tr>
<tr>
<td>Dosage (g)</td>
<td>0.25</td>
</tr>
</tbody>
</table>
EDX analysis of nZVI confirmed the presence of metal element and it was apparent that these synthesized nanoparticles contain high amounts of Fe (81.72%).

XRD

Figure 3 and Figure 4 show the X-ray diffraction (XRD) pattern of the synthesized nanoparticles. XRD patterns for nZVI and Cs-Fe/Ni nanoparticles before and after reacting with AMT were done at 2θ angles ranging from 10 to 80°. A significant peak of 2θ = 45° illustrates the crystallization of Fe⁰ and Ni⁰ in fresh Cs-Fe/Ni before the removal of AMT. An obvious peak for chitosan was not found because its amount was little. The XRD pattern displays several characteristic peaks at 2θ = 21°, 32.8°, 35°, and 58° after reaction. These peaks illustrate the presence of magnetite (Fe₃O₄ and Fe₂O₃) on nanoparticles (Fang et al. 2011; Lin et al. 2012). This can be demonstrated by
the corrosion of Fe as a reductant to form iron oxides (Fe$^{2+}$ and Fe$^{3+}$).

**BET**

Nitrogen adsorption measurement was conducted at liquid nitrogen temperature at 77 K using a surface area analyzer. The textural properties and specific surface areas for nanoscale iron and nanoscale Cs-Fe/Ni were estimated through the Brunauer–Emmett–Teller (BET) equation. The BET surface area for nZVI and Cs-Fe/Ni was 103.56 m$^2$/g and 152.58 m$^2$/g, respectively. The properties of nZVI and Cs-Fe/Ni obtained from N$_2$ adsorption–desorption isotherms are displayed in Table 2. Compared to nZVI, the perceived specific surface area of Cs-Fe/Ni has increased, which relates to the presence of nickel on the surface of the iron nanoparticles. Also, the pore volumes of nZVI and Cs-Fe/Ni are 0.316 and 0.45 cm$^3$/g, respectively. Compared to nZVI, a slight increase in the porosity of Cs-Fe/Ni is possibly caused by the presence of some of the pores in Ni with iron nanoparticles.

**FTIR**

The nanoparticles were also characterized by using Fourier-transform infrared spectroscopy (FTIR). To discern the structure of nZVI and Cs-Fe/Ni, the synthesized nanoparticles before and after reacting with AMT were investigated using the FTIR technique. Figure 5 exhibits the FTIR spectra of chitosan (a), nZVI (b), Cs-Fe/Ni (c), nZVI (d) and Cs-Fe/Ni (e) after removing AMT respectively. As seen in Figure 5(a), the strong broad peak at 3,453.73 cm$^{-1}$ corresponds to stretching vibration of O–H and N–H. The C–H bending vibration of the chitosan polymer is definite through apparent peaks at 2,875.46 and 1,031.50 cm$^{-1}$ signifies bend of C–O. The adsorption bands observed around 1,655.26 and 1,383.12 cm$^{-1}$ were implied as amide I and II, respectively. The adsorption peak of O stretching and a C–O–C and C–N stretching also appears at round 663.65 or 592.59 cm$^{-1}$ and 1081 cm$^{-1}$. As shown in FTIR spectra of Cs-Fe/Ni (Figure 5(b)), changes in peaks of the Cs-Fe/Ni are observed, and the band of O–H and N–H shifts from 3433.73 cm$^{-1}$ to 3417.67 cm$^{-1}$. Decrease in band number or broad (approximately 16 cm$^{-1}$) illustrates the interaction of the iron and nickel with these bonds on the chitosan polymer (Su et al. 2011). Figure 5(d) and 5(e) confirms the changes created in the waves from Cs-Fe/Ni and nZVI after reacting with AMT. Peaks around 689.68 cm$^{-1}$ and 527 cm$^{-1}$ broadly show evidence of Fe–O stretches of Fe$_2$O$_3$ and Fe$_3$O$_4$, which was confirmed by the results obtained from XRD in this research (Yuan et al. 2008; Chen et al. 2011; Fang et al. 2011).

**Optimum conditions**

For the best AMT removal efficiency, initial AMT concentration, pH, time, and nanoparticle dosage were 29.45 mg/L, 2, 76.32 min, and 0.58 g in the case of Cs-Fe/Ni and 30 mg/L, 2, 80 min, and 1.25 g in the case of nZVI. The optimal
conditions might provide the design basis for an industrial-scale process. A second-order polynomial equation is proposed for the prediction of the yield for nZVI (Equation (3)) and Cs-Fe/Ni (Equation (4)) as a function of the different variables as follows (Daraei et al. 2014):

\[
Y = 57.4605 - 5.1017C_{\text{AMT}} - 20.0017pH + 3.5775t
\]

\[
+ 3.1400D_{nZVI} - 4.2569pH^2 - 3.3569t^2 + 2.2712pH \times C_{\text{AMT}} - 2.2913C_{\text{AMT}} \times D_{nZVI} - 1.8787pH \times D_{nZVI}
\]

(3)

\[
Y = 50.4455 - 3.150C_{\text{AMT}} - 17.1733pH + 3.9417t
\]

\[
+ 3.2917D_{\text{Fe/Ni}} - 4.7437pH^2 - 3.6163t^2 + 2.2712pH \times C_{\text{AMT}} - 2.0500pH \times D_{\text{Fe/Ni}}
\]

(4)

where \(C_{\text{AMT}}\) is the AMT concentration, \(t\) the time, and \(D\) the nanoparticle dosage. The response surface model which was obtained from an experimental design was evaluated using analysis of variance (ANOVA) and analysis of residuals. The results of the statistical analysis including the estimated regression coefficients, \(t\)-test, and \(p\)-values of the yield are tabulated in Tables 3 and 4. The obtained \(R^2\) were 0.9836 and 0.9894 for nZVI and Cs-Fe/Ni, respectively, showing the accuracy of the developed models to fully predict the yield. The linear regression coefficients, \(R^2\), for nZVI and Cs-Fe/Ni for the yield were 0.9947 and 0.9801, showing good performance of the model based on the observed and predicted yields. The value of significance of each coefficient determined by \(t\)-test and \(p\)-values is listed in Tables 3 and 4. The larger the \(t\)-value and the smaller the \(p\)-value, the more significant the corresponding coefficient. Based on the statistical results (ANOVA) with confidence level of 95%, the effect of each term in the models could be significant provided that its \(p\)-value is smaller than 0.05.

**Effect of the different parameters**

Initial concentrations of different reactants, i.e. AMT, nZVI and Cs-Fe/Ni, time and pH would significantly affect the AMT degradation. To investigate these initial parameters, a series of comparative experiments were conducted.

The degradation of AMT by Cs-Fe/Ni and nZVI was conducted at pH values of 2, 4, 6, 8 and 10 as exhibited in Figures 6(a) and 7(a). The removal of AMT was also monitored in the initial concentration range of 5 to 45 mg/L. Figures 6(a) and 7(b) show that increasing the AMT concentration led to a decrease in the degradation percentage. The
pH of the solution was adjusted using dilute HCl and NaOH. Removal was optimal at acidic pH.

The degradation efficiency reached the maximum value of 69% at pH 4 and the AMT concentration of 30 mg/L with nZVI. The results also show that a higher uptake efficiency (85%) was achieved at pH 2 and the AMT concentration of 29.45 mg/L with Cs-Fe/Ni. Hence, it was clear that acid conditions suit the degradation of AMT process and this pollutant could be adsorbed onto the Fe particle surface more easily at acidic pH.

The removal of AMT by iron nanoparticles directly depends on the contact between the organic contaminant and reactive site on the nanoparticle surface. Amoxicillin first spread through the solution to the nanoparticle surface and then was adsorbed on the reactive surface of iron particles. When the impressive contact between molecular AMT and iron nanoparticles occurred, iron nanoparticles, as an electron donor, were corroded. After the iron corrosion process, the produced hydrogen ions were adsorbed onto the catalytic Ni²⁺ surface and a

![FTIR spectra](image)

**Figure 5** | FTIR spectra. (a) Chitosan; (b) fresh Cs-Fe/Ni; (c) fresh nZVI; (d) nZVI after reaction with AMT; and (e) Cs-Fe/Ni after reaction with AMT.

**Table 3** | Observed regression coefficients, t-test, and p-values for AMT removal by nZVI

<table>
<thead>
<tr>
<th>Regression coefficients</th>
<th>t-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>41.000</td>
<td>112.979</td>
</tr>
<tr>
<td>CAMT (mg/L)</td>
<td>−2.3750</td>
<td>−12.118</td>
</tr>
<tr>
<td>pH</td>
<td>−13.0417</td>
<td>−66.543</td>
</tr>
<tr>
<td>t (min)</td>
<td>4.3750</td>
<td>22.323</td>
</tr>
<tr>
<td>D (g)</td>
<td>3.2917</td>
<td>16.795</td>
</tr>
<tr>
<td>CAMT (mg/L)²</td>
<td>1.1979</td>
<td>6.672</td>
</tr>
<tr>
<td>pH²</td>
<td>0.5729</td>
<td>3.191</td>
</tr>
<tr>
<td>t² (min)²</td>
<td>−1.1771</td>
<td>−6.556</td>
</tr>
<tr>
<td>D² (g)²</td>
<td>1.4479</td>
<td>8.064</td>
</tr>
<tr>
<td>pH × CAMT (mg/L)</td>
<td>0.5625</td>
<td>2.343</td>
</tr>
<tr>
<td>CAMT (mg/L) × t (min)</td>
<td>0.1875</td>
<td>0.781</td>
</tr>
<tr>
<td>CAMT (mg/L) × D (g)</td>
<td>−0.0625</td>
<td>−0.260</td>
</tr>
<tr>
<td>pH × t (min)</td>
<td>−2.1875</td>
<td>−9.113</td>
</tr>
<tr>
<td>pH × D (g)</td>
<td>−0.3125</td>
<td>−1.302</td>
</tr>
<tr>
<td>t (min) × D (g)</td>
<td>1.0325</td>
<td>1.936</td>
</tr>
</tbody>
</table>
strong oxidant such as hydroxyl radical (OH) was created. Once the AMT was adsorbed onto the surface of the nanoparticles, this organic pollutant degraded via the hydroxyl radical, breaking the \( \beta \)-lactam bond of AMT. This is demonstrated by Equations (5)–(10) (Bokare et al. 2008; Weng et al. 2015).

\[
\text{Fe}^0 \rightarrow \text{Fe}^{+2} + 2e^- \quad (5)
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{Ni}^5\text{H}_0 + 2\text{OH}^- \quad (6)
\]

\[
\text{Ni} + \text{H}^0 \rightarrow \text{Ni-H} \quad (7)
\]

\[
\text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + e^- \quad (8)
\]

\[
\text{Fe}^{+3} + \text{H}_2\text{O} \rightarrow \text{Fe}^{+2} + \text{OH}^0 + \text{H}^+ \quad (9)
\]

\[
\text{Ni-H} + \text{AMT} \rightarrow \text{Ni} + \text{AMT}\text{reduced} + \text{H}_2\text{O} \quad (10)
\]

Also, at high pH the degradation of AMT decreased. In the alkaline condition, low generation of H\(_2\) blocked the degradation of AMT, and ferrous hydroxide precipitates also produced an inactive layer on the catalyst and ZVI particle surface. These layers cover the reactive sites and make these nanoparticles ineffective (Ghauch et al. 2009; Weng et al. 2013). In addition, with pH increase, electrostatic repulsive force becomes operative, which thereby retards diffusion and adsorption. Also, the iron corrosion in the presence of oxygen can create hydrogen peroxide (Equation (11)). This hydrogen peroxide could react with the \( \text{Fe}^{+2} \) Equation (11) and create strong oxidants such as OH\(^{+}\) and ferryl (iron(IV)) species (He et al. 2012).

\[
\text{Fe}^0 + 2\text{H}^+ + \text{O}_2 \rightarrow \text{Fe}^{+2} + \text{H}_2\text{O}_2 \quad (11)
\]

\[
\text{Fe}^{+2} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{+3} + \text{OH}^0 + \text{OH}^- \quad (12)
\]

\[
\text{Fe}^0 + \text{Fe}^{+3} \rightarrow \text{Fe}^{+2} \quad (13)
\]

It is observed from Figures 6 and 7 that the degradation of AMT by nZVI and Cs-Fe/Ni increased with increase in the initial concentration to 30 mg/L and 29.45 mg/L, respectively, while it is observed that after this amount, there was reduction in the AMT removal efficiency. In high concentrations, amoxicillin occupies a greater number of active sites on the nanoparticle surface. Thus, higher initial AMT concentration would lead to the decrease of produced OH on the iron surface.

### Table 4

<table>
<thead>
<tr>
<th>Regression coefficients</th>
<th>t-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>55.5357</td>
<td>68.889</td>
</tr>
<tr>
<td>( C_{\text{AMT}} ) (mg/L)</td>
<td>-3.3967</td>
<td>-7.802</td>
</tr>
<tr>
<td>pH</td>
<td>-14.8492</td>
<td>-34.107</td>
</tr>
<tr>
<td>( t ) (min)</td>
<td>5.2925</td>
<td>12.156</td>
</tr>
<tr>
<td>( D ) (g)</td>
<td>2.0175</td>
<td>4.634</td>
</tr>
<tr>
<td>( C_{\text{AMT}}^2 ) (mg/L)(^2)</td>
<td>1.2798</td>
<td>3.209</td>
</tr>
<tr>
<td>( \text{pH}^2 )</td>
<td>0.3673</td>
<td>0.921</td>
</tr>
<tr>
<td>( t^2 ) (min)(^2)</td>
<td>-2.1202</td>
<td>-5.316</td>
</tr>
<tr>
<td>( D^2 ) (g)(^2)</td>
<td>1.5673</td>
<td>3.930</td>
</tr>
<tr>
<td>( \text{pH} \times C_{\text{AMT}} ) (mg/L)</td>
<td>0.6863</td>
<td>1.287</td>
</tr>
<tr>
<td>( C_{\text{AMT}} \times t ) (min)</td>
<td>0.7612</td>
<td>1.428</td>
</tr>
<tr>
<td>( C_{\text{AMT}}^2 \times D ) (g)</td>
<td>-0.7763</td>
<td>-1.456</td>
</tr>
<tr>
<td>( \text{pH} \times t ) (min)</td>
<td>-2.9800</td>
<td>-5.589</td>
</tr>
<tr>
<td>( \text{pH} \times D ) (g)</td>
<td>-0.3300</td>
<td>-0.619</td>
</tr>
<tr>
<td>( t \times D ) (g)</td>
<td>1.0523</td>
<td>1.936</td>
</tr>
</tbody>
</table>

**Figure 6** | Response surface for AMT removal with nZVI as a function of (a) pH and concentration, (b) time and dosage.
and thus prolong the reaction time. The $p$-value is used to determine the effect of each parameter; it should be less than 0.05. The ANOVA statistical test shows that there was a statistically significant difference between the removal efficiency by pH and concentration ($p$-value $< 0.05$).

The change in removal efficiency under various nanoparticle dosages is shown in Figures 6(b) and 7(a). The results show that an increase in nZVI and Cs-Fe/Ni dosage increased the reduction in AMT, as the remaining AMT decreased. Also, as seen from these figures, by increasing nanoparticle dosage, removal efficiency did not change. Usually, the reduction of organic contaminants with Fe particles is a surface function. This can be attributed to an increase in the surface area of nanoparticles available for this organic pollutant (Weng et al. 2013, 2014). The results indicated that increasing fresh iron dosage could increase the iron surface and could accelerate the reactions of iron corrosion and production of OH'. Due to its high specific surface and high reactivity, nano-iron particle has a remarkable potential for elimination of organic ions.

Regarding contact time, the results showed that the optimal times to remove AMT by nZVI and Cs-Fe/Ni were 80 min and 76.23 min, respectively; AMT removal was found to increase with time up to the optimum value, and then a plateau was reached up to 85 min as shown in Figures 6(b) and 7(b). The AMT removal in the given time was attributed to the site junction between active surface groups and AMT. Also, the further sorption at the times above can be explained by an increased availability in the active bonding sites on the sorbent surface area (Joo et al. 2004). Finally, the results of this study are presented in Table 5.

### CONCLUSION

In this study, chitosan has been applied as a stabilizer for bimetallic nanoparticles, inhibiting the agglomeration of nanoscale metals. These metals disperse well on the surface of this polymer, providing more effective sites for degradation of AMT. Results of batch experiments demonstrate that Cs-Fe/Ni can more effectively remove AMT from aqueous solution compared with non-supported nZVI. According to the results, nanoscale iron can be used to remove organic pollutants in water, under reduction reactions, and adsorption and precipitation processes. Because of its quick reaction, low cost, and convenience to obtain, this material has gained interest for removal of pollutants in environment. The theoretical treatment by CCD gave interactive influence of various parameters on the efficiency of AMT removal. Taken together, it can be safely concluded, based on experimental and theoretical data, that nanoscale iron can be efficiently used as a low-cost suitable sorbent for the removal of AMT.

### REFERENCES

Bokare, A. D., Chikate, R. C., Rode, C. V. & Paknikar, K. M. 2008
Iron–nickel bimetallic nanoparticles for reductive


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