Evaluation of trichloroethylene degradation by starch supported Fe/Ni nanoparticles via response surface methodology

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ABSTRACT

In this study, degradation of trichloroethylene (TCE), a chlorinated hydrocarbon, using starch supported Fe/Ni nanoparticles was investigated. The scanning electron microscope images showed applying water soluble starch as a stabilizer for the Fe/Ni nanoparticles tended to reduce agglomeration and discrete particle. Also the mean particle diameter reduced from about 70 nm (unsupported Fe/Ni nanoparticle) to about 30 nm. Effects of three key independent operating parameters including initial TCE concentration (10.0 – 300.0 mg L⁻¹), initial pH (4.00 – 10.00) and Fe⁰ dosage (0.10 – 2.00) g L⁻¹ on TCE dechlorination efficiency in 1 hour were analysed by employing response surface methodology (RSM). Based on a five-level three-factor central composite design, TCE removal efficiency was examined and optimized. The obtained RSM model fitted the experimental data to a second order polynomial equation. The optimum dechlorination conditions at initial TCE concentration 100.0 mgL⁻¹ were initial pH 5.77, Fe⁰ dosage 1.67 g L⁻¹. At these conditions TCE removal concentration reached 94.87%, which is in close acceptance with predicted value by the RSM model.

Key words | degradation, response surface methodology, starch supported Fe/Ni nanoparticles, trichloroethylene

INTRODUCTION

One of the most hazardous contaminants is trichloroethylene (TCE), which is widely used in industry and has great dielectric properties and can resist chemical and thermal degradation. Due to its hydrophobic nature, it forms dense non-aqueous phase liquids in groundwater (He et al. 2010; Wang & Zhou 2010) and is one of the greatest environmental concerns.

Recently, nanotechnology and especially nano-scale zero valent iron (nZVI) have received significant attention (Su et al. 2011; Zhang et al. 2012). Laboratories and researchers have demonstrated high efficiency of nZVI in dechlorination treatment by directly injecting nZVI into the contaminated aquifer (Elliott & Zhang 2001; He et al. 2010; Zhang et al. 2011). This technology is available and economical (Kim & Carraway 2003). But due to the large concern of subsurface microbiology (Kumar et al. 2014b), it cannot be considered environmentally accepted yet.

Scientists reported that nZVI reactivity will enhance by incorporating another zero valent metal with less standard reduction potential than iron, such as Ni⁰, Pd⁰ or Pt⁰ on the iron surface (Elliott & Zhang 2001; Su et al. 2011). Numerous studies have proven that a second metal compels Fe⁰ to release more electrons and also this metal plays a role as a catalyst in reactions by utilizing released electrons and hydrogen gas (Kim & Carraway 2003; Wu & Ritchie 2006). The second metal increases nZVI activity and dechlorination rate and will reduce formation of toxic byproducts (Wang & Zhang 1997; lien & Zhang 1999).

On the other hand, because of high reactivity of nanoparticles, they are very prone to agglomeration and oxidation when they are exposed to dissolved oxygen (DO) (Grieger et al. 2010; Li et al. 2013). Therefore a thin layer will settle on the surface and will decrease its active surface area. The results of studies showed coating of
nanoparticles leads to reduced particle diameter, less agglomeration and increased settling time and stability (Xiu et al. 2010; Kaifas et al. 2014). Coating nanoparticles by several polymers such as guar gum (Tiraferrri et al. 2008), alginate (Kim et al. 2010), carboxyl methyl cellulose (He et al. 2010), xanthan (Comba & Sethi 2009), cellulose acetate (Wu & Ritchie 2006), polyaspartate (Phenrat et al. 2009) and potato starch (Dong & Lo 2013) has been studied. Among the hydrophilic polymers, water soluble starch makes promising results because not only is it cost effective, available, biodegradable and nontoxic (Alidokht et al. 2011), but also it can improve dispersibility and stability of nanoparticles (Xiong et al. 2007). Raveendran et al. suggested that Fe0 is formed in starch matrix as cluster in starch supported nanoparticles. The binding interaction between starch and nanoparticles is weak and breaks down in the presence of contaminants (Alidokht et al. 2011), and hydroxyl groups of starch act as passivation contacts for stabilization (Raveendran et al. 2003).

Response surface methodology (RSM) is a statistical approach used to understand the interactive effects and seek optimum conditions for multivariable systems. Recently, some researchers have used RSM for optimization of nZVI technology (Abbassi et al. 2013; Fakhrí & Adami 2013). To the best of our knowledge, there are barely any reports regarding the optimization of the process of TCE degradation by applying starch supported Fe/Ni nanoparticles in aqueous phase. In this study, synthesized starch supported Fe/Ni nanoparticles are applied to treat TCE contaminated water. Central composite design (CCD) of RSM was used to study the degradation process, and evaluate the interactive effects of individual factors including initial concentration of TCE, initial pH of the solution and injected amount of nanoparticles and then optimize them in order to maximize TCE removal yield.

**MATERIALS AND METHODS**

**Materials**

The following chemicals were used as received: ferric chloride (FeCl3·6H2O, Merck Co.); sodium borohydride (NaBH4, Merck Co.); TCE (Merck Co.); nickel chloride (NiCl2·2H2O, Aldrich Co.); water soluble starch (Merck Co.); acetone (99.9%, high-performance liquid chromatography (HPLC) grade, Merck Co.); ethanol (99.9%, HPLC grade, Merck Co.); n-hexane (99.9%, HPLC grade, Merck Co.). All water used in every section was deionized (DI) distilled water.

**Nanoparticle preparation**

Stabilized and non-stabilized nZVI were synthesized using liquid phase reduction method as described previously (Wang & Zhang 1997; He & Zhao 2005). In brief, the synthesis was carried out according to the following reaction in Equation (1); ferric iron was reduced to zero valent iron (Glavee et al. 1995).

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

The mixture of starch solution and freshly prepared FeCl3·6H2O stock solution with desired Fe and starch concentration was sparged with N2 gas for 1 h to purge out DO. Fe concentration varied from 0.10 g L\(^{-1}\) to 2.00 g L\(^{-1}\) and, respectively, starch concentration was 0.2% (w/w) for 0.10 g L\(^{-1}\) Fe or 1% (w/w) for 2.00 g L\(^{-1}\) Fe. Then NaBH\(_4\) solution (BH\(_4^- /\text{Fe}^{3+} = 2\)) was added drop by drop into ferric solution at a rate of 0.004 L/min and mixed by using magnetic stirring at high speed and under N2-purging to enhance dispersity. The suspension was turned to dark ink as the nanoparticles formed. The fresh nanoparticles were washed three times with DI water and two times with ethanol and acetone to remove excess chemicals and water. Bare nZVI was synthesized in the same process without starch solution.

In order to prepare Fe/Ni nanoparticles, in an ultrasonic bath (Parsonic mini, Iran) the fresh nZVI soaked in ethanol solution containing nickel chloride 25 wt%. Tee et al. reported optimum catalytic effect of nickel was reached at 25 wt% Ni (Tee et al. 2005). This caused Fe\(^0\) oxidation and deposition of Ni\(^0\) on the nZVI surface afterwards. Bimetallic nanoparticles were obtained as indicated in Equation (2) (Bokare et al. 2007).

\[
\text{Ni}^{2+} + \text{Fe}^0 \rightarrow \text{Fe}^{2+} + \text{Ni}^0 \\
\]

Coating of Fe/Ni nanoparticles keeps the second metal (Ni) at the surface of nZVI, so Ni can catalyse the reactions (Savage et al. 2008).

**Degradation of TCE**

Different concentrations of TCE (10.0–300.0 mg L\(^{-1}\)) in aqueous solution were prepared by adding quantities of TCE based on experimental design in DI water and purged by Argon to omit DO. Batch tests were conducted in a
50 ml serum bottle capped with a Teflon Mininert valve filled with a 50 ml sample of selected TCE concentration. Initial pH solution also based on experimental design was adjusted by using 1 M HCl or 1 M NaOH solutions. Degradation was initiated by injecting a quantity of nanoparticles which were prepared just before each experiment based on TCE concentration and experimental design. Then the mixture was mixed on a rotary shaker operated at 40 rpm at ambient temperature (25°C). Parallel control experiments also were conducted. At selected time 60 min, 0.1 ml of sample was withdrawn from the bottle and mixed with 1 ml n-hexane. Then the extracted upon phase, which contained TCE and n-hexane, was transferred to a 2 ml gas chromatography (GC) vial. The extracts were analysed to identify TCE by using an Agilent 7890A GC coupled with an Agilent 5975C mass selective detector (MSD) (Agilent Technologies, Santa Clara, CA, USA), a capillary column (30 m × 250 μm × 0.25 μm) and an ion trap mass spectrometer. The sample (4 μl) was injected in split mode with split ratio of 100:1 and carrier gas was helium at 1 ml min⁻¹. The oven temperature was programmed to start at 40°C, hold 1 min, ramp up to 90°C at a rate of 5°C min⁻¹ and hold 1 min. The temperature of the injector and the detector were 250°C and 300°C, respectively. For the accuracy of data, all experiments were prepared in triplicate.

The TCE removal efficiency (%) is calculated as follows (3):

\[
\text{TCE removal efficiency} = \left( \frac{C - C_0}{C_0} \right) \times 100 \tag{3}
\]

where \( C \) is TCE concentration at selected time and \( C_0 \) is the initial TCE concentration.

There are two main mechanisms for dechlorination by nZVI—direct electron transferring from nZVI to the chlorinated adsorbed molecule on ZVI surface, and hydrogenation of chlorinated hydrocarbons with adsorbed hydrogen (Cheng & Wu 2000; Lin et al. 2004). Schrick et al. (2002) proposed that on bimetallic particles such as Fe/Ni nanoparticles, the main mechanism is catalysed hydrodechlorination by second metal. In fact, Ni on the surface chemisorbs hydrogen ions, which are produced from iron corrosion. Then TCE will be adsorbed to the Ni surface and hydrogenated. This mechanism results in fast reaction and formation of non-chlorinated compounds such as ethane and ethylene as products, although trace amounts of hazardous chlorinated by-products may be formed (Schrick et al. 2002; Kaifas et al. 2014).

### Experimental design and statistical analysis

In this study, a five-level three-factor CCD was employed which required 20 experiments to evaluate the chosen variables. The variables and their ranges were based on preliminary experiments (Nikroo 2015) and the results of other literatures. The variables and their levels are listed in Table 1. The experiments were carried out in run order. To fit the experimental data and explain the behaviour of the system, the following second-order polynomial equation was developed, which is the most commonly used for RSM:

\[
Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_i^2 \tag{4}
\]

\( Y \) is the predicted response function, \( \beta_0 \) is constant coefficient, \( \beta_i, \beta_{ij} \) and \( \beta_{ii} \) are the coefficients of linear, quadratic and interactive terms, respectively, for input factors \( X \) (\( i = 1 - 3, j = 1 - 3 \) and \( i \neq j \)). This function represented and visualized the relationship between the independent variables and predicted response as surface and contour plots.

### Data analysis

The obtained data were analysed using Design-Expert® software (trial version 7.0.0 Stat-Ease, Inc., Minneapolis, USA) and then results were interpreted. Analysis of variance (ANOVA), regression analysis and plotting of response surface were performed to reach optimum conditions for maximum TCE removal efficiency.

#### Table 1 | Independent variables and levels

<table>
<thead>
<tr>
<th>Factor</th>
<th>Symbol</th>
<th>Factor levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial TCE concentration (mg L⁻¹)</td>
<td>( X_1 )</td>
<td>(-2)</td>
</tr>
<tr>
<td>Initial pH</td>
<td>( X_2 )</td>
<td>10.0</td>
</tr>
<tr>
<td>Fe⁰ dosage (g L⁻¹)</td>
<td>( X_3 )</td>
<td>0.10</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Characterization of nanoparticles

Starch supported Fe/Ni nanoparticles and nonstabilized Fe/Ni nanoparticles were prepared and their characterizations were acquired using scanning electron microscope (SEM) and stability test. SEM samples were prepared by depositing two droplets of nanoparticle suspension on a flat surface under Argon atmosphere in order to avoid oxidation and then they were coated by gold to prevent charging. SEM image of Fe/Ni nanoparticles in Figure 1 shows the comparisons between the particle distribution and their morphologies in (a) absence and (b) presence of 0.2% (w/w) of the starch stabilizer. The SEM images were obtained using an SEM (KYKY EM 3200, KYKY Co.)

![SEM image of Fe/Ni nanoparticles](image-url)

Figure 1 | SEM image of Fe/Ni nanoparticles (a) without starch stabilizer and (b) in presence of starch (0.2% w/w).
 Images were obtained at an operating voltage 26 kV. As seen in Figure 1, nZVI particles had a spherical shape and Figure 1(a) indicates Fe/Ni nanoparticle aggregation and that the diameters of particle were mostly in a range of 60–85 nm. Figure 1(b) shows coating starch on Fe/Ni nanoparticles tended to reduce diameter of particles (to a range of 30–45 nm) and increase the particle dispersity. Based on similar reported data (Tiraferri et al. 2008), SEM results could be described: unsupported Fe/Ni nanoparticles were inclined to sediment due to their high surface energies and intrinsic magnetic interactions. When interactions of supporting polymer are enough to overcome inter-particle magnetic and van der Waals attraction forces (Bezbarua et al. 2009), polymer coating will inhibit nZVI particle aggregation by electrostatic and repulsion forces (He & Zhao 2005).

Stability test was utilized to demonstrate more characterizations. It was based on evaluating qualitatively by observing the turbidity of suspension. Figure 2(a) shows unsupported Fe/Ni nanoparticles only remained in suspension for less than 30 minutes, whereas Figure 2(b) shows starch supported Fe/Ni nanoparticles remained in a good suspension for less than 30 minutes, whereas Figure 2(b) shows starch supported Fe/Ni nanoparticles only remained in suspension.

Model fitting and ANOVA

Experimental data of TCE removal experiments are given in Table 2. Fitting the data to various models (linear, quadratic and cubic) and the results showed quadratic polynomial model, given in Equation (5), described properly the TCE degradation by applying stabilized Fe/Ni nanoparticles,

\[
Y = 32.81 - 0.101X_1 + 14.243X_2 + 35.985X_3 \\
+ 8.88 \times 10^{-4}X_1X_2 + 0.047X_1X_3 - 1.134X_2X_3 \\
- 5.31 \times 10^{-4}X_1^2 - 1.077X_2^2 - 8.56X_3^2
\]

where Y is the TCE removal; X1, X2 and X3 are, respectively, initial TCE concentration, initial pH and dosage of iron loading.

In order to verify the significance and adequacy of the model, an ANOVA analysis was performed and the results are given in Table 3. A high F-value of 23.41 and a very low probability value (p-value < 0.0001) declared the model was significant. According to Table 3, the high value coefficient of determination R squared (approaches unity), adjusted R-squared and predicted R-squared verified the reliability of regression model. Estimated coefficients and effects of model are listed in Table 4. The corresponding p-value of each parameter was used as a reference in order to examine the significance of them.

![Figure 2](https://iwaponline.com/wst/article-pdf/73/4/935/464137/wst073040935.pdf)
The comparison between experimental data and predicted value from regression model of TCE removal efficiency as shown in Figure 3, proved that the fitted regression equation has shown a good fit of the obtained model from CCD and also that this model can be used as a predictor for the optimization of TCE removal condition.

### Effect of parameters

Three dimensional (3D) and contour (2D) plots based on the quadratic model for the predicted response were formed to evaluate the change of response surface and the relationship between TCE removal efficiency and independent variables.

Interaction effects of initial TCE concentration and pH on TCE removal at constant Fe⁰ dosage equal to 1.05 is shown in Figure 4. As seen, maximum TCE removal efficiency was attained at low TCE concentration and pH range 5.00–7.00. As the initial TCE concentration increases, the effect of pH will contribute to greater removal efficiency. TCE removal efficiency increases with the increase of pH from 5.03 to 7.50, but removal efficiency gradually decreases, beyond initial pH 7.50.

All the response surfaces indicated TCE removal efficiency is much higher in acidic pH (5.03–6.90) and as pH increases to alkaline pH, the removal efficiency decreases. The maximum and minimum TCE removal efficiency were attained at initial pH 6.00 and 9.00, respectively. This effect is due to the fact which was reported previously (Chen et al. 2014) in alkaline pH, the layer formed in iron corrosion, inhibits nZVI reduction and decreases nanoparticle activity. Indeed, iron corrosion is strongly a function of pH solution and the formed layer on nZVI nanoparticles will be dissolved in acidic condition and prepare more active site on nZVI surface (Yang & Lee 2005). So, in acidic condition, Fe⁰ corrosion accelerates and enhances the removal reaction rate.

As seen in Figure 5, the removal efficiency of TCE is inversely affected by the initial TCE concentration, but it is apparent that removal efficiency is not linear function of initial TCE concentration. According to Tables 1 and 2, the removal efficiency was 99.90, 76.98 (average) and 41.63% at initial TCE concentration of 10.0, 155.0 and 300.0 mg L⁻¹, respectively, after 1 hour at same conditions with initial pH 7.00 and Fe⁰ dosage 1.05 g L⁻¹. This trend was in agreement with similar studies of nZVI (Arnold & Roberts 2000; Wang & Zhou 2010) and according to their results, when TCE concentration increases, rate constant decreases as a result of completion for a finite number of surface reactive sites. Mass transfer limitations may be responsible for this effect. Although TCE may act as an electron acceptor and enhance electron transport from nZVI core to oxide shell (Kumar et al. 2014a), if the amount of injected nanoparticles is not sufficient at high initial TCE concentration, residual TCE and the degradation products

### Table 3 | ANOVA results of the response surface quadratic model for TCE removal efficiency

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>7351.70</td>
<td>9</td>
<td>816.86</td>
<td>23.41</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>348.89</td>
<td>10</td>
<td>34.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of fit</td>
<td>229.30</td>
<td>5</td>
<td>45.86</td>
<td>1.92</td>
<td>0.2461</td>
</tr>
<tr>
<td>Pure error</td>
<td>119.59</td>
<td>5</td>
<td>23.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>7700.59</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-squared = 0.9547; adjusted R-squared = 0.9139; predicted R-squared = 0.7559.

### Table 4 | ANOVA results for the model and coefficients of variables

<table>
<thead>
<tr>
<th>Variables</th>
<th>Coefficient</th>
<th>Standard error</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial TCE Conc. (A)</td>
<td>-19.99</td>
<td>1.66</td>
<td>144.85</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Initial pH (B)</td>
<td>-3.72</td>
<td>1.66</td>
<td>5.03</td>
<td>0.0488</td>
</tr>
<tr>
<td>Fe⁰ dosage (C)</td>
<td>10.84</td>
<td>1.66</td>
<td>42.61</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>AB</td>
<td>0.17</td>
<td>2.09</td>
<td>0.0063</td>
<td>0.9381</td>
</tr>
<tr>
<td>AC</td>
<td>2.80</td>
<td>2.09</td>
<td>1.80</td>
<td>0.2091</td>
</tr>
<tr>
<td>BC</td>
<td>-1.39</td>
<td>2.09</td>
<td>0.44</td>
<td>0.5204</td>
</tr>
<tr>
<td>A²</td>
<td>-4.81</td>
<td>1.80</td>
<td>7.17</td>
<td>0.0232</td>
</tr>
<tr>
<td>B²</td>
<td>-4.17</td>
<td>1.80</td>
<td>5.39</td>
<td>0.0427</td>
</tr>
<tr>
<td>C²</td>
<td>-3.32</td>
<td>1.80</td>
<td>3.42</td>
<td>0.0941</td>
</tr>
</tbody>
</table>

The comparison between experimental data and predicted value from regression model of TCE removal efficiency as shown in Figure 3, proved that the fitted regression equation has shown a good fit of the obtained
of TCE and iron corrosion will cover the reactive sites of nanoparticles and tend to reduce reaction rate.

The effect of different dosages of Fe\(^0\) nanoparticles ranging from 0.10 to 2.00 g L\(^{-1}\) on TCE removal efficiency can be inferred from Figure 6, which presents the effect of Fe dosage in a range of 0.43 to 1.67 g L\(^{-1}\) on TCE removal efficiency. TCE removal efficiency increased at higher nanoparticle dosage, which is similar to previous results (Yang & Lee 2005; Wang & Zhou 2010). As the nanoparticle dosage increases, the reactive sites on nZVI surface steadily increase and TCE removal will increase. Also Figure 6 represents an optimum range of nanoparticle dosage to maximize TCE removal efficiency.
Optimization and verification of results

In order to maximize TCE removal efficiency, the obtained quadratic model was utilized to optimize the operating parameters. Since the model is empirical, it needs to impose a restriction on the levels of parameters ($X_i$), as defined in Equation (6) in order to avoid extrapolation.

$$-2 < X_i < +2, \quad i = 1, 2, 3$$  (6)
The optimum conditions for the maximum possible efficiency of TCE degradation under the described limitations and initial TCE concentration 100.0 mg L$^{-1}$ (a mean value just for a common comparison) were found out to be initial pH 5.77, Fe$^0$ dosage 1.67 g L$^{-1}$. At these conditions, the model predicted the TCE removal efficiency to be 97.41%. Also interaction effects of initial pH and Fe$^0$ dosage at constant initial TCE concentration 100.0 mg L$^{-1}$ on TCE removal efficiency are shown in Figure 7. This optimization verified our explanations for effects of each parameter as discussed previously.
To verify the validity of proposed model, three replicate confirmation experiments were conducted under these optimum conditions. The mean experimental TCE removal efficiency was 94.87%, which is very close to predicted value of 97.41%. Hence the results indicated this model was adequate for TCE removal process (Table 5). In order to compare the effect of starch coating on TCE removal, comparative experiment was done with unsupported Fe/Ni nanoparticles and under optimum conditions. The mean TCE removal efficiency yielded 87.55%, which indicated

Figure 7 | Surface and contour plot of interaction effects of initial pH and Fe⁰ dosage on TCE removal efficiency at constant initial TCE concentration equal to 100.0 mg L⁻¹.
enhanced stability of nanoparticles has improved TCE degradation.

CONCLUSIONS

In this study, starch supported Fe/Ni nanoparticles were synthesized to treat TCE contaminated water. The optimization and modeling of TCE removal efficiency by starch supported Fe/Ni nanoparticles were evaluated by using CCD of RSM. The well-fitted second order polynomial indicated the model would be useful in determining the optimum conditions for maximizing TCE treatment. The optimum conditions to obtain maximum TCE removal efficiency at initial TCE concentration 100.0 mg L$^{-1}$ were initial pH equals 5.77, Fe$^{0}$ dosage equals 1.67 g L$^{-1}$. Under these conditions, the experimental efficiency of TCE removal was 94.87%, which was close to predicted value (97.41%).

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