Degradation of simazine from aqueous solutions by diatomite-supported nanosized zero-valent iron composite materials

Zhiming Sun\textsuperscript{a,b}, Shuilin Zheng\textsuperscript{a}, Godwin A. Ayoko\textsuperscript{b}, Ray L. Frost\textsuperscript{b}, Yunfei Xi\textsuperscript{b,*}

\textsuperscript{a} School of Chemical and Environmental Engineering, China University of Mining & Technology, Beijing 100083, P.R. China

\textsuperscript{b} Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, Queensland 4001, Australia
Abstract: A novel composite material based on deposition of nanosized zero-valent iron (nZVI) particles on acid-leached diatomite was synthesised for the removal of a chlorinated contaminant in water. The nZVI /diatomite composites were characterized by X-ray diffraction, scanning electron microscopy, elemental analysis, transmission electron microscopy and X-ray photoelectron spectroscopy. Compared with the pure nZVI particles, better dispersion of nZVI particles on the surface or inside the pores of diatom shells was observed. The herbicide simazine was selected as the model chlorinated contaminant and the removal efficiency by nZVI /diatomite composite was compared with that of the pristine nZVI and commercial iron powder. It was found that the diatomite supported nZVI composite material prepared by centrifugation exhibits relatively better efficient activity in decomposition of simazine than commercial Fe, lab synthesized nZVI and composite material prepared via rotary evaporation, and the optimum experimental conditions were obtained based on a series of batch experiments. This study on immobilizing nZVI particles onto diatomite opens a new avenue for the practical application of nZVI and the diatomite-supported nanosized zero-valent iron composite materials have potential applications in environmental remediation.

Keywords: zero-valent iron, simazine, diatomite, composite material

* Corresponding author. Tel: +61 7 3138 1466(Y. Xi)
E-mail address: y.xi@qut.edu.au (Y. Xi)
1. Introduction

The nanoscale zero-valent iron (nZVI) can effectively degrade a wide range of persistent organic and inorganic pollutants, such as chlorinated organic compounds, heavy metals and organic dyes in aqueous solutions [1-6]. Compared with commercial iron powders, the nZVI materials have many advantages, such as larger surface area and higher reactivity. In the last decade, the nZVI materials have been extensively studied for ground water remediation and hazardous wastewater treatment [7]. However, the previous studies have demonstrated that there were several major limitations in nZVI materials practical applications including strong tendency to agglomerate, secondary iron pollution as well as separation and recovery problem after usage [8]. Agglomeration can significantly decrease the effective surface area of nanoparticles and thus reduces their catalytic performance. To solve these practical disadvantages, the nZVI particles have been proposed to be loaded on various supporters, such as rectorite [8], bentonite [9], palygorskite [10], silica materials [11-13], zeolite [14], porous carbon materials [15, 16], resin [17], starch [18] and carboxymethyl cellulose [19] and others. To some extent, these composite materials can improve the catalytic performance of nZVI through preventing agglomeration of iron nanoparticles and thus exposing highly reactive nano particles directly to the contaminants. Moreover, the porous structure of the matrix allows high hydraulic conductivity, which is in favour of faster degradation rates in water system [13].

Diatomite is a kind of natural amorphous siliceous mineral with porous structure composed of the fossilized skeletons of diatoms [20]. Diatomite possesses many unique properties, such as high permeability, high porosity and chemical inertness. Due to such characteristics, diatomite is widely used as filter agents, catalyst carriers, building materials and wastewater treatment agents [21, 22]. On the other hand, the diatomite maybe particularly suitable to be used as a carrier for nano-sized ZVI because of its macro/mesoporous structure and excellent thermal and mechanical stabilities [22]. The porous structure of the diatomite possesses high hydraulic conductivity, which should be in favour of conducting effluent to the reactive cites of the composite materials resulting in faster degradation rates. However, as reported in literatures, there were very few studies on diatomite supported nZVI [13]. To the best of our knowledge, there was no report using evaporative and centrifuge methods in synthesis of nZVI/diatomite composites. In this study, it was demonstrated that the particle sizes of nZVI on composite materials can be manipulated improving catalytic efficiency.
Simazine is a typical triazine-derivative herbicide, which is sparingly soluble in water. It has been reported in literatures that this compound is toxic to living organisms including human beings and can cause other serious environmental issues [23]. In this study, two diatomite-supported nano ZVI composite materials were synthesized and used as catalysts for the degradation of simazine in the aqueous phase. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), elemental analysis (EDS) and X-ray photoelectron spectroscopy (XPS). The degradation effect for simazine using the obtained nZVI composite materials was systematically studied compared with commercial iron powder and pristine nZVI; and initial pH, catalyst amount and equilibrium time were optimized by carrying out a series of batch experiments.

2. Materials and methods

2.1. Chemical

Original diatomite was obtained from the Liudaogou area of Linjiang, Jilin province in China. Commercial iron powder (Fe-Com) and iron (II) chloride tetrahydrate (FeCl₂·4H₂O) were purchased from Chem-Supply Co. Sodium borohydride (NaBH₄) and simazine (C₇H₁₂N₅Cl) were obtained from Merck Schuchardt and Sigma-Aldrich Co. as analytical grade, respectively. The chemical structure of simazine is showed in Fig. 1.

![Figure 1. Chemical structure of simazine. Molar mass 201.66 g/mol. Solubility in water: 5 ppm (25 °C). Acid dissociation constant (pKa): 1.7.](image)

2.2. Preparation and characterization of acid-leached diatomite and iron samples

The raw diatomite was firstly physically purified in a centrifugal field in order to remove some impurities, such as sand and clay minerals. And then the sample was processed by acid-leaching in 5 M HCl solutions at 80 °C for 24 h. During the acid-leaching, 20 g of diatomite
sample was weighed and poured into 500 ml of solution, the solution was then stirred continuously using a magnetic stirrer in a water bath. After a predetermined period of time, the solid product was filtered and washed with distilled water. The final product was denoted as DE.

The nZVI/diatomite composites were synthesized through the following two techniques, similar to some previous studies [9, 24]. Briefly, 5 g of FeCl₂·4H₂O was dissolved in a mixture of 95% ethanol and deoxygenated de-ionised water (75 ml ethanol plus 25 ml H₂O) using a ultrasonic instrument for 15 min and stirred for another 5 min. The deoxygenated de-ionised water was prepared by purging with N₂ gas for 2 h before use. Then 5 g of diatomite was added to this solution under stirring for overnight, which is denoted as solution A₁. The solution A₁ was centrifuged at 3000 rpm for 15 min at room temperature (Thermo scientific, heraeus mutifuge X1) in order to remove the excess Fe²⁺ and the residue was noted as A₁-R.

Then, 6.1 g of NaBH₄ was dissolved in 800 ml of deoxygenated de-ionised water to form 0.2 M solution, denoted as solution B₁. Then solution B₁ was added dropwise to A₁-R in a fume hood under constant stirring. The A₁-R was transferred from red sediment to black suspension. The resulting reaction can be expressed as:

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

Afterwards, the solid was centrifuged and wished twice with about 500 ml of 95% ethanol. The sediment was dried in an oven at 50 °C. The final mixture was denoted as nZVI/DE-C. Similarly, 1 g of FeCl₂·4H₂O was dissolved in a mixture of 95% ethanol and de-ionised water (150 ml ethanol plus 50 ml H₂O) using an ultrasonic instrument for 15 min and stirred for overnight. Then 5 g of diatomite was added to this solution under stirring for 2 h, which was denoted as solution A₂. Solution A₂ was concentrated through rotary evaporation at 40 °C. Then, 1.5 g of NaBH₄ was dissolved in 200 ml of H₂O to form 0.2 M solution, denoted as solution B₂ and the residue was labelled as A₂-R. Then solution B₂ was added drop by drop to A₂-R in a fume hood under constant stirring. Afterwards, the solid was washed using the above method. The solid was denoted as nZVI/DE-E. For comparison, the unsupported nZVI sample was prepared by a similar procedure as described above, except that no A-DE was added in solution A. The final product was labelled as nZVI-Lab. Fig. 1 shows a schematic diagram of the possible pathways of Fe⁰ particles deposited onto diatom in the synthesis process.
Figure 2. A schematic diagram of the possible pathways of Fe⁰ particles deposited onto diatom.

The samples were pressed in stainless steel sample holders. X-ray diffraction (XRD) patterns were recorded using Iron filtered CoKα radiation (x = 1.789010 Å) on a PANalytical X’Pert PRO 240 mm radius diffractometer operating at 40 kV and 40 mA with 0.5° fixed divergence slit between 3.5 and 90° (2θ) at a step size of 0.0167°. Incident beam and diffracted beam have 0.04 rad Soller slit. The sample was spun at 30 rpm. The detector is an X’Celerator RTMS set to 2.122°. A Zeiss Sigma field scanning electron microscope (FESEM) with integrated energy dispersive X-ray analyser (EDX) system was used for morphological studies. All samples were dried at room temperature and coated with carbon for the SEM studies. The microstructure of all samples was observed by JEOL 1400 transmission electron microscope (TEM). The X-ray photoelectron spectroscopy (XPS) was applied using a Kratos AXIS Ultra with a monochromatic Al X-ray source at 225 W. A survey scan was run for each analysis from 0 to 1200 eV with a dwell time of 100 ms, pass energy of 160 eV at step of 1 eV with one sweep. Additionally, a high resolution analysis was undertaken at 40 eV at steps of 50 meV. The obtained spectra were analysed using Casa XPS version 2.3.14 software, which enabled the baseline (Shirley baseline applied) and various data handling procedures.

2.3. Batch experiments for the removal of simazine

Each iron sample (commercial iron powder, nZVI-Lab or nZVI/DE composites) was added into a 100 ml beaker containing 50 mL of simazine solution of 4 mg/L (C₀) under stirring for pre-set time. The natural pH of simazine solution was about 5. Then, the mixture was centrifuged at 3000 rpm for 15 min at room temperature and the supernatants were analysed by a high-performance liquid chromatography (HPLC, Agilent HP 1100) system coupled with a Luna 5µ C18 column (Phenomenex Pty Ltd) and a UV absorbance detector. A
mobile phase of methanol-water mixture (50:50, V/V) at a flow rate of 1 mL/min and 40 µL of injection volume was used for this experiment and the analysis wavelength was 222 nm. The effect of solution pH on the removal of simazine (with initial concentration of 4 ppm) was studied by adjusting the pH of simazine solution (using 1 M HCl). The solution pH was measured with a pH meter (TPS Pty Ltd, WP-80). Similarly, to undertake the degradation kinetics, the iron samples were added into 50 mL of simazine solution with an initial concentration (4 mg/L) at room temperature in order to determine the minimum time to reach the equilibrium concentration. The concentrations of simazine were measured at different time intervals from 5 min to 420 min. The quantity of the removed simazine was calculated using the following equation.

\[ q_e = \frac{V(C_i - C_e)}{M \times 1000} \]  

(1)

Where, \( q_e \) is the removal amount of simazine (mg/g), \( C_i \) is the initial concentration of the solution (mg/L), \( C_e \) is the equilibrium concentration of simazine (mg/L), \( V \) is the solution volume (mL), and \( M \) is the mass of the iron samples (g). All the removal data for the batch experiments were obtained in triplicates.

3. Results and discussion

3.1. Characterizations

3.1.1. X-ray diffraction analysis
Fig. 3 shows XRD patterns of commercial Fe, nZVI-Lab, DE and nZVI/DE samples. Both the commercial Fe sample and laboratory synthesized nZVI show a pure cubic $\alpha$-Fe crystalline structure with two characteristic reflections at $2\theta=52.4^\circ$ and $77.3^\circ$ corresponding to Fe (110) and Fe (200) respectively. No obvious reflections of Fe oxides were observed in the XRD pattern of Fe-Com and nZVI-Lab suggesting that their major surface species are Fe$^0$. The previous studies have indicated that the Fe nanoparticles may possess “core-shell” structure including the existence of Fe$^0$ (core) and iron oxides (shell) [25-27]. However, no such observations are found in this study using XRD, which may be due to the low crystallinity of iron oxides phases in both samples [9]. The XRD pattern of acid-leached diatomite is in good agreement with that of the referenced amorphous opal-A, which is characteristic of a broad reflection centred at around $21.8^\circ$ ($2\theta$). The XRD patterns of diatomite-supported nZVI particles prepared via centrifugation and rotary evaporation are
also displayed in Fig. 3. Only low-crystalline Fe species were observed in both samples, indicating that the iron species were well dispersed, forming very small crystallites with size below the detection limit of X-ray diffraction [9, 28].

3.1.2. Morphology analysis

Figure 4. SEM images of DE (a), nZVI/DE-C (b), nZVI/DE-E (c), and nZVI-Lab (d) and Fe-Com (e).

From the SEM image of acid-leached diatomite, as shown in Fig. 4 (a), the characteristic disc-shaped porous structure of diatom particles was clearly observed with the
diameter of about 50 μm. The diameter of pores on the surface of diatom varied from 440 to 560 nm, while that on the edge was about 130-150 nm. There were fewer impurities in the pores of diatomite after acid leaching process which is similar to that in previous studies [29, 30]. SEM was also applied to study the morphology and morphological changes of diatomite and their ZVI modified samples as shown in Fig. 4 (b) and (c). ZVI nanoparticles were observed on the surface of diatom disc and the porous structure of diatomite remained clearly visible. The SEM image of nZVI-Lab (Fig. 4 (d)) shows that the synthesized ZVI nanoparticles dramatically assemble together and displays a chain-like structure, which was caused by magnetostatic attraction between the Fe particles. The morphology of commercial iron powder is shown in Fig. 4 (e). The iron powders exhibit large particles with size at around several tens of microns with irregular shapes.
Figure 5. TEM images of nZVI (a), nZVI/DE-C (b, c and d) and nZVI/DE-E (e).

In order to confirm the observations obtained from SEM and observe the morphology on the surface of the prepared samples more precisely, TEM was also applied in this study. A TEM image of nZVI-Lab is shown in Fig. 5 (a), where chain-like structures were exhibited similar to that observed in Fig. 4 (d). It is observed that the average diameter of nZVI-lab particles is about 40 nm with regular shapes. On the other hand, when nZVI particles were loaded onto the surface of diatom, significant differences can be observed as shown in Fig. 5 (b and e), which showed that the nanoparticles were separated and presented as individual spherical shaped particles. The detailed morphologies of nanoparticles on the surface and in the pores of diatom in nZVI/DE-C are shown in Fig. 5 (c) and (d), respectively. The particle size of nZVI on the surface of diatom is around 45-60 nm, which is larger than that of nZVI in the pores of diatom in range of 20-40 nm. On the other hand, nZVI/DE-E sample exhibits larger particles with size in the range of 70-150 nm, which is almost twice larger than that in nZVI/DE-C sample. The larger ZVI particle size was caused by the rotary evaporation process, which favours the growth of ZVI particles at a relative higher temperature and higher iron ions concentration. The larger nZVI particles are hard to load into the pores of diatom and most of them are well dispersed on the surface. It can be concluded from the above observations that the nZVI particles loaded onto diatomite can be controlled by varying the preparation conditions. Imaging of EDX spectrum (not shown here) was conducted to determine the iron loading amount in two nZVI/DE samples. The quantitative analysis results reveal that the content of Fe in nZVI/DE-C sample is 6.48 w%, which is slightly smaller than that in nZVI/DE-E sample (8.19 w%). On the other hand, there is only a small quantity of iron in the diatomite after acid leaching (0.17 w%), which confirms that Fe⁰ was successfully loaded onto the diatomite with the procedures used.

3.1.3. X-ray photoelectron analysis
Figure 6. Fe 2p XPS spectra of nZVI-Lab (a) and nZVI/DE samples (b).
Figure 7. O 1s XPS spectra of nZVI-Lab (a) and nZVI/DE samples (b).

The XPS technique was applied to study the binding energy of element in order to distinguish the oxidation states of certain elements. In order to observe the existence of Fe and O more precisely, the high resolution XPS spectra of the Fe 2p and O 1s for nZVI-Lab and nZVI/DE composites are displayed in Fig. 6 and Fig. 7, respectively. As shown in Fig. 6, the primary Fe 2p3/2 photoelectron peaks at binding energy of around 710.3 eV are associated to iron oxides. Due to the low content of Fe, the Fe 2p signals are relatively weak in nZVI/DE composites. On the other hand, the peaks at 712.2-712.8 eV are assigned to the Fe 2p3/2 satellite. In addition, small shoulders at around 706.6-706.8 eV in three samples are also observed, which represent the 2p3/2 peaks of Fe$^0$. The Fe$^0$ signals are very weak, which is probably because the XPS is a surface analysis technique with only 2-5 nm probing depth. However, the XPS results prove the existence of Fe$^0$ and iron oxide, which is in line with the previous results reported in the literatures [8, 31]. From the Fig. 7, for nZVI-lab, the photoelectron peaks of O1s can be decomposed into four peaks at 529.6, 530.9, 531.8 and 532.9 eV, which represent binding energies of Fe$_3$O$_4$, FeOOH, OH and O-C, respectively. While for nZVI/DE-C composites, the peaks of O1s are located at 529.9, 531.1 and 532.5 eV,
which are associated to binding energies of Fe$_2$O$_3$, OH and O-Si (O-C), respectively. Similar observations are obtained in O 1s spectrum of nZVI/DE-E composites. This above observation combined with XRD analysis results confirms the “core-shell” structure for nZVI materials. Moreover, compared to the nZVI/DE-E composites, the intensity of Fe 2p in the nZVI/DE-C sample was obviously enhanced, indicating that iron species grow during rotary evaporation process. The results are in line with morphology analysis, which confirms that the iron particle size of nZVI/DE-E composites is larger than that of nZVI/DE-C composites.

3.2. Batch experiments

![Graph showing the effect of initial pH on simazine degradation](image)

Figure 8. Effect of initial pH on the degradation of simazine using DE, nZVI-Lab, Fe-Com and nZVI/DE samples (sample amount: 2.0 g L$^{-1}$; concentration of simazine solution: 4 ppm; volume of simazine solution: 40 ml; reaction time: 5h).

The solution pH is one of the critical factors controlling the degradation effect of chlorinated organic contaminants [32]. The decomposition of simazine by DE, nZVI-Lab, Fe-Com or nZVI/DE composite materials was conducted at different initial pH values from 2 to 8, and the experimental results are displayed in Fig. 8. For pure DE, no obvious removal effect is observed at different solution pH indicating that pure diatomite does not have any
adsorption capacity for simazine. The hydrophilic surface of diatomite should be the main reason for low adsorption of simazine. On the other hand, the removal efficiencies of simazine by nZVI-Lab, Fe-Com, and nZVI/DE composite materials are improved with decreasing solution pH, which are similar to the previous reported results [6, 33]. Moreover, as shown in Fig. 8, the removal efficiencies of nZVI-Lab, Fe-Com, nZVI/DE-C and nZVI/DE-E composite materials reach the highest value at lower pH of around 2.3-2.5, which are 16.51%, 36.23%, 80.19% and 31.30%, respectively. Therefore, it can be assumed that the removal efficiency of simazine by nZVI/DE-C is much higher than the other samples in the pH range studied.

\[
\text{Fe}^0(\text{s}) + \text{H}^+ + \text{R-Cl} \rightarrow \text{R-H} + \text{Fe}^{2+} + \text{Cl}^{-} \quad (2)
\]

It is reported that Eq. (2) is the dechlorination reaction between iron and chlorinated organic contaminants [6, 32, 33]. It is obvious that this reaction occurs more quickly under acid conditions. With the decrease of solution pH, the shell of ZVI particles (oxide and hydroxide coatings) would dissociate under acid conditions which benefit the accessibility of simazine on reaction activity sites of Fe\(^0\) and therefore accelerate the dechlorination process. However, with further decreasing in the solution pH, the removal efficiency decreases rapidly which may be due to the further ionization of Fe\(^0\) under strong acid conditions. Under higher pH values, iron oxide and hydroxide coating undoubtedly form on the surface of these activity cites which hinder access to the Fe\(^0\) surface [6].
Figure 9. Effect of catalysts amount on the degradation of simazine using DE, Fe-Com, nZVI-Lab and nZVI/DE samples (initial pH: 2.35; concentration of simazine solution: 4 ppm; volume of simazine solution: 40 ml; reaction time: 5h).

Catalysts amount in the treatment system is another key factor during the dechlorination process. The effect of catalysts amount on the dechlorination effect is shown in Fig. 9. From Fig. 9, with increasing the catalysts amount, the removal percentage is increased firstly and then gradually reduced. The first improvement of dechlorination effect is probably due to the increase in the number of available adsorption and active sites with increase in the catalysts amount [34]. The optimum catalysts amounts for nZVI-Lab, Fe-Com and two nZVI/DE composite materials are 0.5 g/L, 1.0 g/L and 2.0 g/L, respectively. It is easy to understand that the nZVI/DE composite materials possess much less Fe⁰ content than nZVI-Lab and Fe-Com, which may be why the composite materials need more amounts in the treatment system. However, if the catalysts in the treatment system are too much, the solution pH will be increased dramatically during the reaction process according to Eq. (3), which in reverse reduces the dechlorination effect. Therefore, the dechlorination effect of pure nZVI samples is unsatisfactory.

$$\text{Fe}^0(s) + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 2\text{OH}^{-}$$  \hspace{1cm} (3)
Figure 10. (a) Effect of reaction time on degradation of simazine using Fe-Com, nZVI-Lab and nZVI/DE samples (initial pH: 2.35; concentration of simazine solution: 4 ppm; volume of simazine solution: 200 ml); (b) The pseudo-second equation for degradation of simazine.
The relationship between reaction time and removal effect of simazine by Fe-Com, nZVI-Lab and nZVI/DE samples are described in Fig. 10 (a). As can be seen, the maximum removal capacities by nZVI/DE-C and nZVI/DE-E for simazine were about 0.97 mg/g and 0.80 mg/g, respectively, while the maximum removal capacities by commercial iron and nZVI-Lab were 0.79 and 0.24 mg/g, respectively. Apparently, the removal percentage of simazine by composite materials was higher than that by two bare iron samples. According to the previous morphology analysis, the nZVI particles immobilized on diatomite were well dispersed on the supports without aggregation. Hence, compared with bare nZVI samples, the reactive activity of the obtained composite materials was higher, leading to the enhanced removal percentage [35, 36]. For nZVI-Lab and nZVI/DE-C, simazine was more rapidly removed within 5 minutes and slowly reached the maximum within 30 minutes. While for Fe-Com and nZVI/DE-E, the reaction rate is apparently lower than the former two materials. The pseudo-second order rate expressed by Ho and Mckay is the most widely used for the kinetic study of liquid/solid reaction system based on solid capacity [37, 38]. The rate equation is expressed in the following form:

\[
\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e}
\]  

(3)

Where \( k \) is the rate constant of pseudo-first order reaction (min\(^{-1}\)), \( Q_e \) is the removal amount of simazine at equilibrium (mg/g) and \( Q_t \) is the removal amount of simazine at any time \( t \) (mg/g). Hence, the constants can be determined from the linear plot \( t/Q_t \) against \( t \) as shown in Fig. 10 (b). The parameters of pseudo-second model were obtained and summarised in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pseudo-second order</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k ) (min(^{-1}))</td>
<td>( Q_e ) (mg/g)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Fe-Com</td>
<td>0.01</td>
<td>0.81</td>
<td>0.99</td>
</tr>
<tr>
<td>nZVI-Lab</td>
<td>37.25</td>
<td>0.24</td>
<td>1.00</td>
</tr>
<tr>
<td>ZVI/DE-C</td>
<td>10.61</td>
<td>0.97</td>
<td>1.00</td>
</tr>
<tr>
<td>ZVI/DE-E</td>
<td>0.10</td>
<td>0.81</td>
<td>1.00</td>
</tr>
</tbody>
</table>

From Table 1, the reaction rate decreases in the following order: nZVI-Lab > nZVI/DE-C > nZVI/DE-E > Fe-Com. Combined with the morphology analysis, it is logical
to suggest the smaller nZVI particles in nZVI-Lab and nZVI/DE-C causes the faster removal rate for simazine. However, the Fe$^0$ particles in nZVI-Lab may be too reactive to control the solution pH, which results in the unsatisfactory simazine removal effect. Moreover, the reactive exhaustion during storage and transportation is difficult to be avoided which limits the practical application of pure nZVI particles [7]. While for nZVI/DE composite materials, the pore structure of the diatomite facilitates the mass transfer, which can accelerate the decomposition of simazine in a synergetic way [35]. Although the removal effect of the commercial Fe is also very good, the reaction rate is too slow due to its relatively larger particle size. Similar limitation also exists in nZVI/DE-E. In conclusion, nZVI/DE-C shows a better efficient activity in decomposition of simazine than the other three samples. Advanced oxidation processes (AOPs) have been proved to be an effective way for the removal of simazine from water. The removal of simazine based on typical AOPs previously reported in the literatures are summarised in Table 2.

Table 2. Removal of simazine by nZVI/DE composite materials in comparison to AOPs.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Initial concentration of simazine</th>
<th>pH</th>
<th>Reaction time</th>
<th>Removal percentage (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton oxidation</td>
<td>3 ppm</td>
<td>3.5</td>
<td>15 min</td>
<td>100</td>
<td>[39]</td>
</tr>
<tr>
<td>Photocatalytic oxidation</td>
<td>70 ppb</td>
<td>4.6-4.9</td>
<td>180 min</td>
<td>100</td>
<td>[40]</td>
</tr>
<tr>
<td>Photo-Fenton oxidation</td>
<td>0.5 ppm</td>
<td>3</td>
<td>60 min</td>
<td>100</td>
<td>[41]</td>
</tr>
<tr>
<td>Ozonation</td>
<td>4 ppm</td>
<td>7.2</td>
<td>15 min</td>
<td>100</td>
<td>[42]</td>
</tr>
<tr>
<td>Ozone/H$_2$O$_2$ oxidation</td>
<td>0.5 ppm</td>
<td>11</td>
<td>60 min</td>
<td>94</td>
<td>[43]</td>
</tr>
<tr>
<td>nZVI/DE composite</td>
<td>4 ppm</td>
<td>2.35</td>
<td>5 min</td>
<td>80</td>
<td>Present study</td>
</tr>
</tbody>
</table>

The removal effect of simazine by nZVI/DE composite materials in the present study is relatively lower compared with that by AOPs. However, compared with AOPs process, no extra oxidizing reagents, such as O$_3$, H$_2$O$_2$, were applied in present study, which has characteristics of low cost, simple operation and higher degree of safety. The naturally abundant diatomite is more desirable for industrial applications due to their low cost. By comparison with conventional Fenton’ reagent, since the release of iron ions could cause a secondary environmental pollution in the environment, the negative effect on the
environment is relatively smaller because of the low Fe loading amount in nZVI/DE composite materials [36].

4. Conclusion

The nanosized zero-valent iron (nZVI) particles were successfully loaded onto acid leached diatomite by a simple reduction method. XRD and XPS analysis confirmed the Fe$^0$ particles existed in the obtained composite materials. In addition, SEM and TEM studies indicated a good distribution of these Fe$^0$ particles on surface of disc diatom and into the porous structure. Compared with the centrifugation process, the relative higher temperature and higher iron ions concentration during the rotary evaporation process are in favour of the growth of ZVI particles, which results in the larger Fe$^0$ particles size on the nZVI/DE composite material prepared by rotary evaporation. Hence, it indicates that the nZVI particles loaded onto diatomite can be controlled by varying the preparation conditions. The particular porous structure of diatomite facilitated a good Fe$^0$ dispersion and high hydraulic conductivity, which should be in favour of conducting effluent to the reactive cites of the composite materials resulting in faster degradation rates. Two nZVI/DE composite materials with different Fe$^0$ particle size, pure lab synthesized nZVI and commercial Fe as well as acid leached diatomite (as a reference) were used for the decomposition of simazine. The solution pH is one of the critical factors to control the degradation effect of simazine and the optimum solution pH is around 2.3-2.5. Moreover, the support diatomite has low adsorption capacity for simazine, which indicates that the simazine removal by nZVI/DE composites is dominantly attributed to the reduction by nZVI rather than the adsorption by diatomite. The catalysts amount in the treatment system should be controlled, which may reduce the dechlorination effect since it can greatly affect the solution pH during the dechlorination process. The sample nZVI/DE-C exhibits relatively better efficient activity in decomposition of simazine than the other three samples, which shows good potential for application in water purification.

Acknowledgments
This research was supported by the Queensland University of Technology’s Vice Chancellor’s research grant. We acknowledge Dr Barry Wood from the University of Queensland for XPS characterisation. The first author also thanks the China Scholarship Council (CSC) for financial support.
Reference


