

Preparation of wrapped nZVI particles and their application for the degradation of trichloroethylene (TCE) in aqueous solution

Wenjing Fan, Yue Cheng, Shuzhen Yu, Xiaofeng Fan and Yaqian Deng

ABSTRACT

Three types of wrapped nanoscale zero-valent iron (W-nZVI) with different coatings including agar, starch, and carboxyl methyl cellulose, were synthesized using a rheological phase reaction method. The structure and morphology of W-nZVI particles were characterized by scanning electron microscopy and transmission electron microscopy. Batch degradation experiments exhibited that W-nZVI dosage, initial trichloroethylene (TCE) concentration and solution pH had significant effects on TCE dechlorination. Experimental results proved that the highest dechlorination efficiency was obtained within 320 minutes for 10 mg/L of TCE at the optimal pH of 5.0 and W-nZVI dosage of 0.5 g/L. Kinetic study revealed that TCE dechlorination by W-nZVI in aqueous solution obeyed the quasi-first-order reaction kinetics. The product after the reaction could be easily separated by the permanent magnet for re-use.

Key words | agar-nZVI, CMC-nZVI, dechlorination, reaction kinetics, starch-nZVI, TCE, W-nZVI

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INTRODUCTION

Trichloroethylene (TCE)-contaminated aqueous solution has received extensive attention in environmental issues because of the extensive use of TCE in industry and its resistance to both biotic and abiotic degradation under natural subsurface conditions (Scottorth & Robert 1996). TCE is often categorized as dense non-aqueous phase liquid due to its low aqueous solubility and greater density than water. Once released into the subsurface environment, TCE would distribute between soil and water (Orphius & Tohren 2005).

Remediation technologies of TCE contamination include physical, chemical, and microbiological methods. Physical methods only transfer contaminants to another phase, which cannot completely remove the contaminants (Li *et al.* 2014). The microbiological method has more difficulty in developing bacteria. Therefore, removal of TCE by chemical reduction has been a challenging task. Among various chemical technologies for TCE dechlorination, zero-valent iron (ZVI) particles appear to be one of the most promising technologies (Amira *et al.* 2012).

Since the 1990s, ZVI has been used in environmental remediation. Researchers have paid attention to the performance and potential application of nanoscale ZVI (nZVI < 100 nm) (Hojeong *et al.* 2010). The high remediation efficiency of nZVI is mainly attributed to its high specific surface area, high levels of surface defects, high density of reactive surface sites and greater intrinsic reactivity of surface sites, which make the nanoparticles very reactive in degradation of contaminants (Singh *et al.* 2011). As a strong reductant, ZVI can effectively transform a wide variety of persistent organic and inorganic contaminants, such as chlorinated organic, nitroaromatic compounds, heavy metals, and organic dyes (Chen *et al.* 2011, 2012; Liu *et al.* 2012; Huang *et al.* 2013). Nowadays, nZVI has been frequently employed to achieve enhanced treatment of organic compounds (Welleyan *et al.* 2010). However, the mechanism of inhibition of dechlorination has not been explored further (Xiu *et al.* 2010). Conventional nZVI particles may react quickly with the surrounding media (e.g. dissolved oxygen, water, and other oxidizing agents), resulting in rapid

loss in reactivity (Alidokht *et al.* 2011). To prevent nanoparticle agglomeration, various particle stabilizing approaches have been reported (Brijesh & Rajeev 2013; Jia & Wang 2013). The stabilized nanoparticles exhibited markedly increased stability against aggregation, chemical reactivity, and soil transport.

In this work, to stabilize nZVI particles, wrapped nZVI (W-nZVI) was prepared using carboxyl methyl cellulose (CMC), agar or starch as surface modifier by rheological phase reaction method. The samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The effects of W-nZVI dosage, TCE initial concentration and solution pH value on TCE dechlorination were investigated. The reductive dechlorination of TCE was measured as a function of increasing chloride ion.

MATERIALS AND METHODS

Chemicals

Chemicals of analytical grade or better were used in this study, including $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (CAS No.7782-63-0), KBH_4 (CAS No.13762-51-1), C_2HCl_3 (CAS No.79-01-6), HNO_3 (CAS No.13587-52-5), AgNO_3 (CAS No.7761-88-8), ethanol (CAS NO. 64-17-5), CMC (CAS No. 9004-32-4), agar (CAS No. 9002-18-0), and starch (CAS No. 9005-84-9). All the reagents were prepared with deionized water. Deionized water was used throughout this study. All solvents were degassed and saturated with N_2 before use.

Preparation of W-nZVI

The wrapped ZVI nanoparticles were prepared in aqueous solution by reducing Fe (II) to Fe (0) using KBH_4 in the presence of CMC, agar or starch as a parcel agent. Briefly, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and KBH_4 were mixed by grinding in a molar ratio of 1:2. The solid mixture was then added to 0.06 g/mL CMC, agar or starch solution to obtain a rheological body, and the mixture was transferred into a three-necked round-bottom flask. The reaction was conducted under continuous stirring at room temperature. The resulting solid product was collected by filtration, washed with deionized water and ethanol, and finally dried under vacuum. The reaction involved was as follows: $\text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow \text{Fe} + 2\text{B}(\text{OH})_3 + 7\text{H}_2$.

Characterization of W-nZVI

The structure and morphology of W-nZVI particles were investigated by SEM on a high-resolution SEM (JEOL-JMS-6700F, Tokyo, Japan) with an acceleration voltage of 10–30 kV. The micromorphology was characterized by TEM on a high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010, Tokyo, Japan) with an acceleration voltage of 200 kV.

Batch experiments with TCE

The dechlorination experiments of TCE were carried out in batch conditions at room temperature and atmospheric pressure in 250 mL stoppered conical flasks, containing a certain amount of W-nZVI and 100 mL TCE solution on a temperature-controlled shaker with continuous stirring at 150 rpm. After a desired time, the solutions were filtered using a 0.22 μm filter membrane to separate the solid particles and solution. To confirm TCE degradation, chloride ion was measured with a 722 UV-V is spectrophotometer (Shanghai Instrument Analysis Instrument Co., Ltd, Shanghai, China) using the silver chloride turbidimetry method operated at 450 nm.

The data obtained from the experiments were then used to calculate the dechlorination efficiency using Equation (1)

$$E = C_t/C_0 \quad (1)$$

where C_0 and C_t are the concentrations of chlorine atom concentration in solution at time $t = 0$ and $t = t$, respectively.

Kinetics study

It is known that the reductive dechlorination of TCE by ZVI follows pseudo-first-order kinetics as shown in the following equation (Meyer *et al.* 2004):

$$\text{d}C/\text{d}t = -k_{\text{obs}} \times C \quad (2)$$

where C is the aqueous contaminant concentration and k_{obs} is the observed pseudo-first-order rate constant (h^{-1}).

All experiments in this study were performed in triplicate to obtain reliable data, and the results presented here

represent the mean values of three independent measurements \pm standard deviations.

RESULTS AND DISCUSSION

SEM analysis

SEM images of freshly synthesized W-nZVI are presented in Figure 1. The white spots in Figure 1(a)–1(c) represent nZVI particles wrapped with CMC, agar, and starch, respectively. Figure 1(a) is the SEM spectrum of CMC-nZVI prepared by the rheological phase reaction method with a magnification of 10,000 times. As can be seen from Figure 1(a), the particles have good dispersibility. This may be because the package agent CMC layer has good dispersion function with nano iron ions. Figure 1(b) is the SEM spectrum of agar-nZVI prepared by the rheological phase reaction method with a magnification of 10,000 times. No agglomeration occurs. This may be because agar prevents particles from

agglomeration. Figure 1(c) is the SEM spectrum of starch-nZVI prepared by the rheological phase reaction method with a magnification of 10,000 times. It is shown that the particles were distributed evenly, had good dispersion and did not have particle agglomeration due to the good dispersion properties of particles or starch layer preventing particles from agglomeration (Jiao 2013).

TEM analysis

The distinct iron asthenospheres could be observed clearly from the TEM image of W-nZVI (Figure 2). In Figure 2(a)–2(c), spherical asthenospheres were covered by a thin white layer. The W-nZVI particles were encapsulated into the microspheres by coating agents and were isolated from each other and displayed core-shell type (Luo *et al.* 2013). Measurements can be obtained from the figure: CMC-nZVI size of approximately 50–125 nm, agar-nZVI size of approximately 60–130 nm, starch-nZVI size of approximately 5–15 nm.

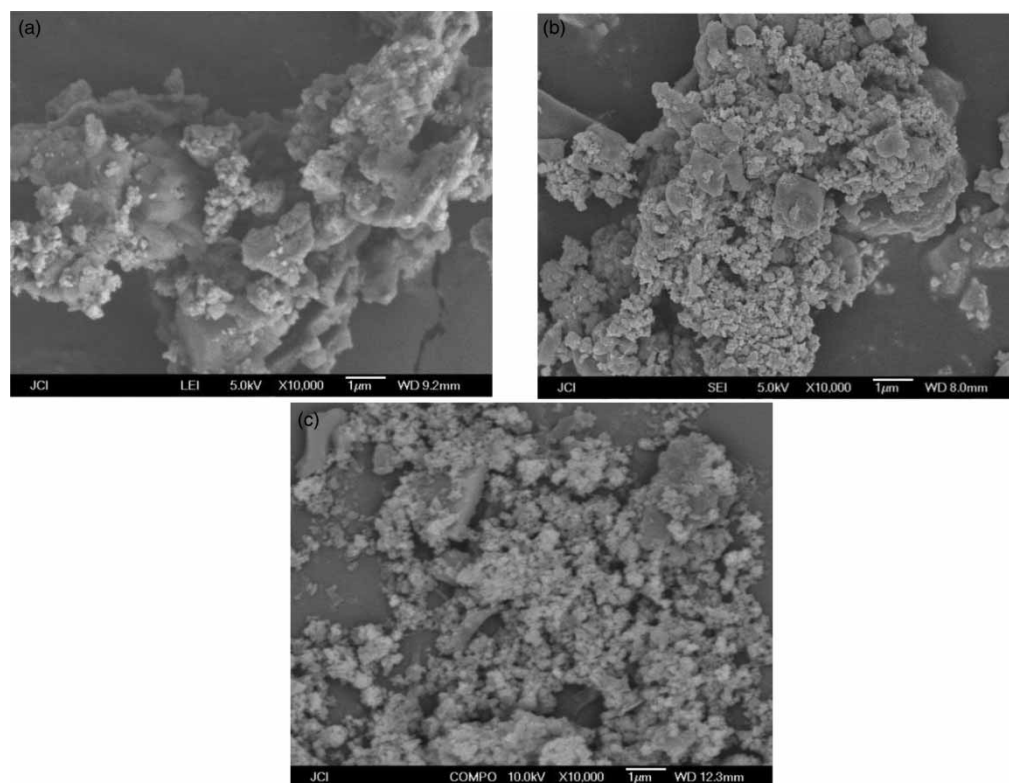


Figure 1 | The SEM spectrogram of samples: (a) CMC-nZVI; (b) agar-nZVI; (c) starch-nZVI.

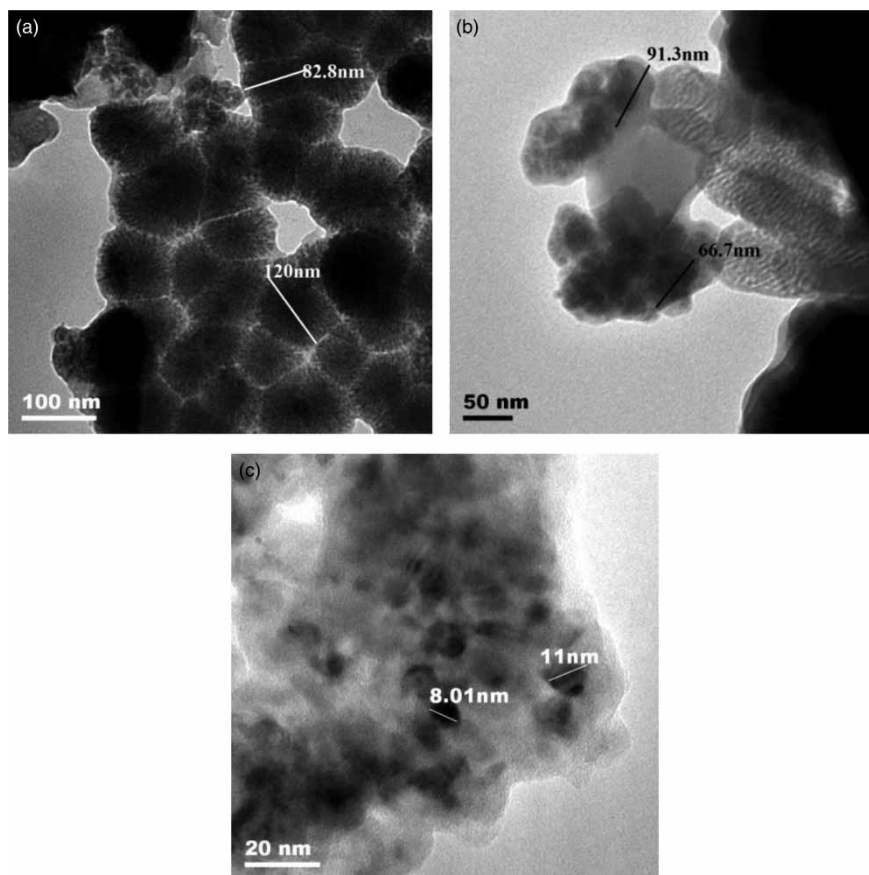


Figure 2 | The TEM spectrogram of samples: (a) CMC-nZVI; (b) agar-nZVI; (c) starch-nZVI.

The dechlorination of TCE

Wrapping effects on TCE dechlorination

As a reductant, nZVI properties play an important role in TCE dechlorination reaction. To compare the effects of different coatings to TCE dechlorination, agar-nZVI, CMC-nZVI, and starch-nZVI, each with a dosage of 0.5 g/L applied. Concentration of TCE was 10 mg/L and pH was adjusted to 5.0 for all cases. The solutions were then stirred at 200 rpm at room temperature. Solutions were sampled at certain time points (30, 90, 150, 210, 270, and 330 minutes), the generated chloride concentrations were examined and compared between different warping agents.

Figure 3 shows the dechlorination efficiency using three types of wrapped nZVI (agar-nZVI, CMC-nZVI, and starch-nZVI). Over a period of 330 minutes, dechlorination

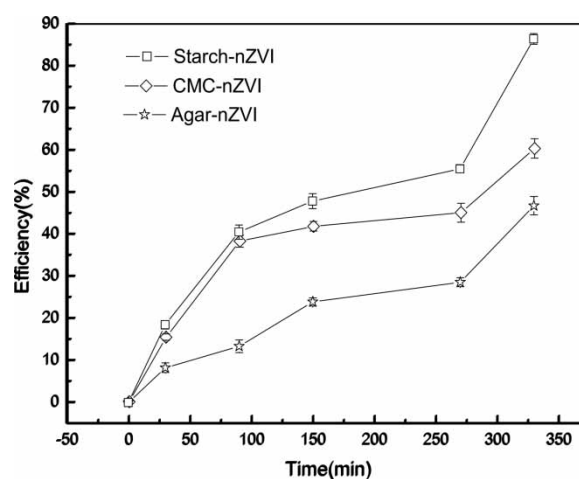


Figure 3 | Dechlorination efficiency in the presence of different wrapped iron nanoparticles.

efficiencies reached 47.41%, 60.15% and 86.16% for agar-nZVI, CMC-nZVI, and starch-nZVI, respectively.

The best performance of starch coating can be attributed to the following reason: starch-nZVI has the highest resistance to oxidation and has the highest stability. This is mainly due to starch having a higher wrapping capability for nZVI particles than the other substances. Similar results were also found in the literature (Feng & Zhao 2005; Zhang *et al.* 2007). Wang *et al.* (2010) demonstrated that, as coating agents, starch, dextrin, and CMC could increase the dispersion of nZVI particles, and effectively control the oxidation of nZVI particles during their exposure to air, but did not affect the chemical activity. Starch had the highest dispersion ability for nZVI particles, the best concentration ratio of starch to nZVI is 0.7%, and the obtained particles had the minimum average size.

To compare the effects of different parcel agents to TCE adsorption, agar, CMC, starch, and nZVI, each with a dosage of 0.5 g/L were applied. The concentration of TCE was 10 mg/L and pH was adjusted to 5.0 for all cases. Figure 4 shows the efficiency of three types of parcel agent (agar, CMC, and starch) and nZVI. Within 330 minutes, dechlorination efficiencies reached 35.12%, 4.13%, 5.23%, and 5.77% for nZVI, agar, CMC, and starch, respectively.

Effect of W-nZVI dosage

To study the effect of dosage of W-nZVI on TCE dechlorination, five levels of sample dosages (0.3, 0.5, 0.7, 1.0, and 1.5 g/L) were initially tested with pH 5.0, TCE concentration of 10 mg/L and reaction time of 330 minutes.

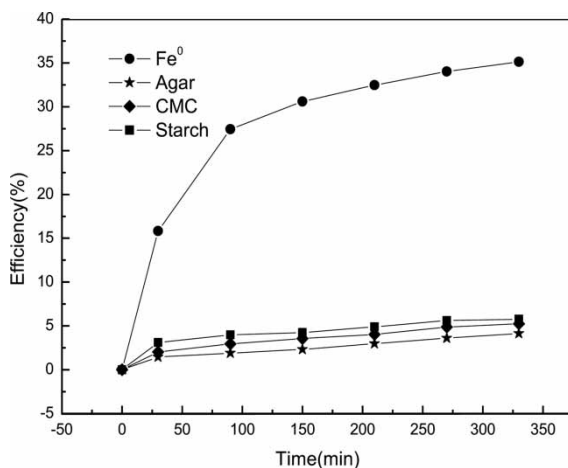


Figure 4 | Dechlorination efficiency in the presence of nZVI, agar, CMC, and starch.

As shown in Figure 5, TCE dechlorination efficiency was increased when sample dosages increased within the tested range. This is because the higher the dosage, the more active sites on W-nZVI surface and the greater the surface area (Wang 2008).

Effect of different initial TCE concentration

Different initial TCE concentrations will affect the contact between the reactants and thus affect the result. To examine the effects of initial TCE concentration on dechlorination efficiency by agar-nZVI, CMC-nZVI, and starch-nZVI, the initial pH of the solution and the dosage of the W-nZVI were set to 5.0 g/L and 0.5 g/L, respectively, and the initial TCE concentrations were set to 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L, respectively.

Figure 6 shows that TCE dechlorination efficiency decreased along with the initial concentration of TCE, increasing with three types of W-nZVI. This is due to the degradation of TCE accompanied the generation of iron oxides and hydroxides (Xu 2012). The higher TCE initial concentration, the more generation of such materials. They occupy the active point on the surface of W-nZVI, hinder further reaction and reduce the reaction rate.

Effect of pH

To investigate whether the pH value could affect the TCE dechlorination, batch experiments were carried out at

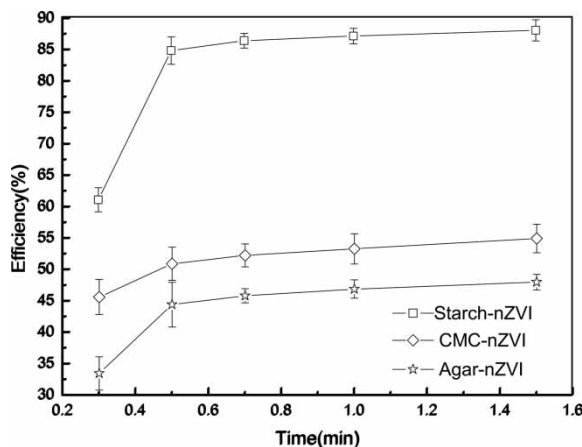


Figure 5 | Dechlorination efficiency at various dosages.

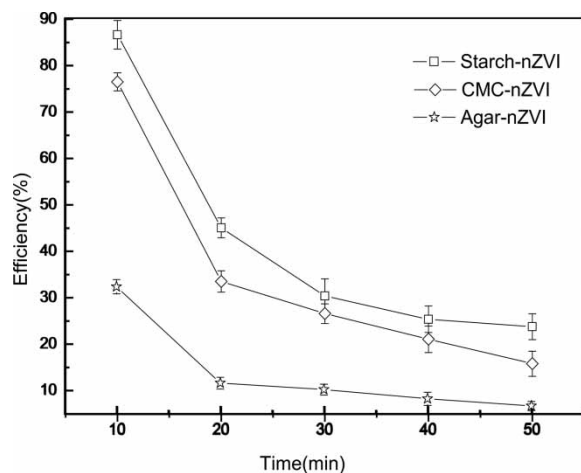


Figure 6 | Dechlorination efficiency at various initial TCE concentrations.

various values of pH from 1 to 11, with TCE initial concentrations of 10 mg/L and W-nZVI dosage of 0.5 g/L. As shown in Figure 7, TCE dechlorination efficiencies using agar-nZVI, CMC-nZVI, and starch-nZVI were affected by initial pH. At lower pH, a large amount of hydrogen is generated to form 'gas film' that inhibits the adsorption of TCE, and the nano-iron is consumed too quickly, thereby inhibiting the reaction of dechlorination of TCE. At a higher pH, hydrogen ion concentration is lower, nanoscale iron corrosion reaction is suppressed and not conducive to electron transfer, thus reducing the efficiency of the dechlorination of TCE (Wang 2013).

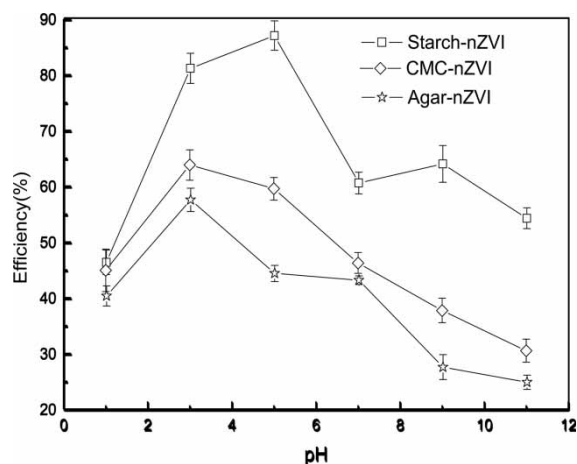


Figure 7 | Dechlorination efficiency of TCE in the aqueous phase at various pH values.

TCE dechlorination reaction kinetics study

TCE dechlorination kinetics with agar-nZVI, CMC-nZVI, and starch-nZVI were studied when the pH was 5.0, initial TCE concentration was 10 mg/L and sample dosages were all 0.5 g/L. The reaction rate can be calculated by the Johnson *et al.* (1996) equation. To determine reaction constant, logarithm of TCE concentrations was plotted versus

$$dC/dt = -K_{obs}C$$

where C is aqueous contaminant concentration, and K_{obs} is observed pseudo-first-order rate constant (h^{-1}).

It can be seen from Figure 8 that, for all types of nZVI samples, a good linear relationship was shown between $\ln(C/C_0)$ and time t , in which C and C_0 are the final and initial TCE concentrations, respectively.

It shows that the wrapping materials examined in this study increase the reaction rate constant (Table 1). The reaction rate constants (k_{obs}) of agar-nZVI, CMC-nZVI, and starch-nZVI were 0.00332 min^{-1} , 0.00552 min^{-1} , and 0.00582 min^{-1} , respectively.

Reaction product of SEM and energy dispersive spectrometer

Figure 9 shows the complete reaction product of SEM images. It can be seen that iron nanoparticles were in an accumulated state and the particles significantly became larger, and the oxide material was on the surface of Fe^0

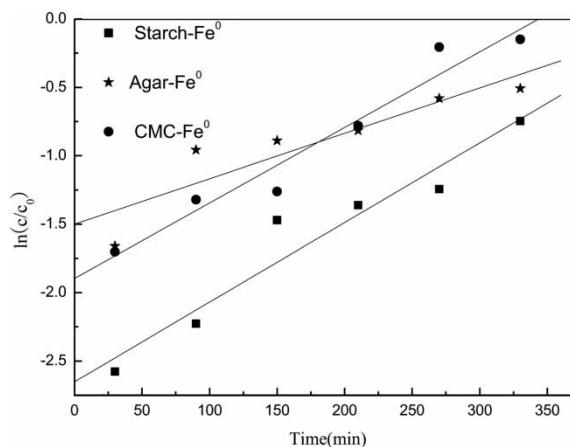


Figure 8 | Dynamics curve for dechlorination of TCE by W-nZVI.

Table 1 | The apparent reaction rate constant of the dechlorination of TCE by W-nZVI

Samples	$K_{obs}/(\text{min})$	R^2
agar-nZVI	0.00332	0.9062
CMC-nZVI	0.00552	0.9769
starch-nZVI	0.00582	0.9672

particles. TCE removal by nano-iron reduction occurs mainly early, but flocculation substance iron oxides formed also have some effect on the adsorption of pollutants. So there were iron oxides, as well as some product. After the reduction, Fe^0 itself was oxidized to iron oxides, which no longer existed in the form of elemental iron. Meanwhile, since the reaction was in the presence of oxygen in solution, elemental iron was oxidized into iron oxides, hydroxides and carbonates of substances, covering the surface of the iron particles, thereby preventing further reaction.

Table 2 lists energy dispersive spectrometer after complete reaction. It is mainly comprised of three elements

C, O, and Fe, the main material on the surface was Fe and small amounts of iron oxides and hydroxides. The C element was on the one hand from the nZVI in contact with TCE degradation process, and on the other hand from the solution in contact with the CO_2 (Ren 2013). Table 2 shows the element analysis of W-nZVI after reaction, the weight percentage of oxygen and iron were large, indicating that the main substance after the reaction was iron oxide.

Recycling performance of W-nZVI after reaction

The product after the reaction could be easily separated by the permanent magnet for recovery, as shown in Figure 10. It shows that the product could be well recovered magnetically. The main substance after the reaction was iron oxide, which was weakly magnetic and easily adsorbed by permanent magnet.

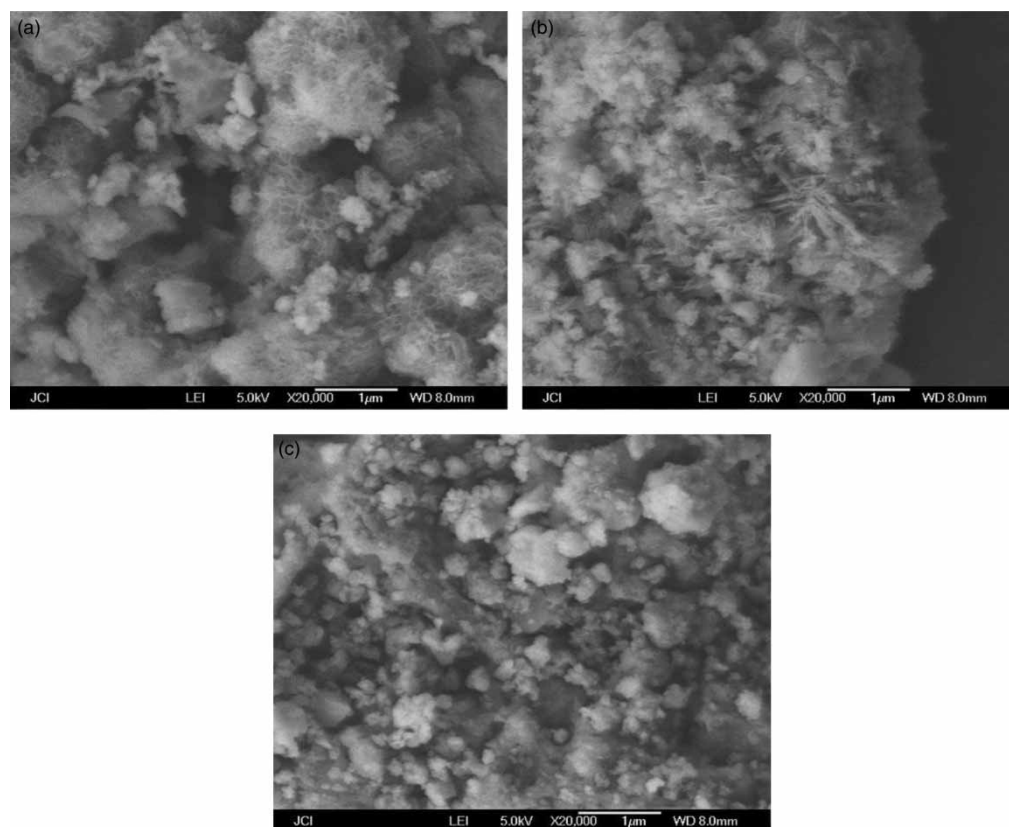
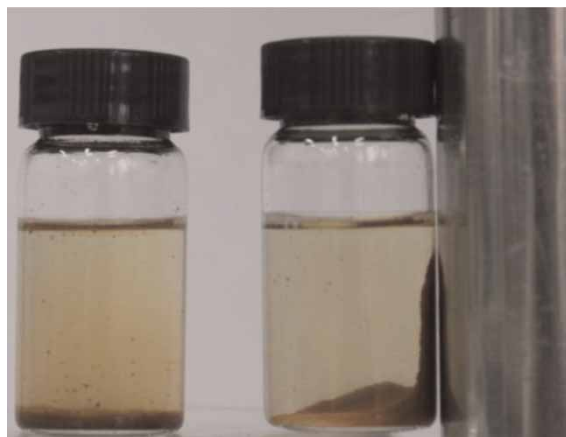
**Figure 9** | The SEM images after reaction: (a) CMC-nZVI; (b) agar-nZVI; (c) starch-nZVI.

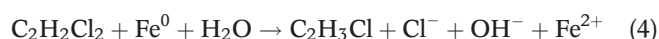
Table 2 | Element analysis of W-nZVI after reaction

W-nZVI	Element	Weight percentage	Atomic percentage
CMC-nZVI	C	12.88	21.18
	Fe	41.06	18.23
	O	43.24	60.59
Agar-nZVI	C	19.08	28.35
	Fe	23.38	7.47
	O	57.54	64.18
Starch-nZVI	C	12.88	22.88
	Fe	41.06	15.69
	O	46.07	61.44

**Figure 10** | The product of magnetic separation and recovery.

The proposed TCE dechlorination reactions mechanism

The dechlorination reactions occur at the iron surface and require excess electrons produced from the corrosion of the ZVI in water. Through this process, the target chemicals undergo sequential dechlorination steps, resulting in the formation of non-chlorinated hydrocarbon products. The degradation of TCE by W-nZVI is believed to take place via both reductive dechlorination and β -elimination. The reaction equations are as follows (Dirk & Ralf 2003):



Recently, environmentally friendly and edible compounds such as agar, CMC, and starch are used for the preparation of high stability and dispersibility nZVI. They are macromolecular chemical substances, the molecule contains a considerable amount of carboxyl groups and a large number of hydroxyl groups, these groups may be among the nZVI and with adsorption itself (Cao 2011). Owing to their amphiphilic nature, parcel agents are known to enhance the solubilization and mobilization of contaminants. As seen in Figures 1 and 2, the smaller the particle size of nZVI, the greater the surface area of nZVI, leading to more opportunities for contact with TCE and thus a higher dechlorination rate (Xue *et al.* 2006).

CONCLUSIONS

nZVI was efficiently wrapped with agar, CMC or starch. From SEM and TEM analysis, it is observed that the size of W-nZVI was within 150 nm and the structure was core-shell type where the inner core was composed of Fe^0 and the outer shell consisted of starch. W-nZVI by the synthesis of rheological phase method has good dispersion and stability. Experimental results show that the optimum conditions were pH 5, starch-nZVI dosage 0.5 g/L and initial TCE concentration 10 mg/L achieved the highest dechlorination efficiency. Because of the small quantity of W-nZVI used in the degradation of TCE, the rate constant was low. Therefore, W-nZVI can be used efficiently in the degradation of chlorinated solvent in aqueous solution. The product after the reaction could be easily separated by the permanent magnet for recovery.

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