Mesoporous silica supported bimetallic Pd/Fe for enhanced dechlorination of tetrachloroethylene†

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In this study, mesoporous silica (SiO₂) microspheres were hydrothermally synthesized in the presence of gelatin for the immobilization of bimetallic Pd/Fe nanoparticles (Pd–Fe/SiO₂) to enhance the dechlorination efficiency and dechlorination rate of tetrachloroethylene (PCE) under anoxic conditions. Scanning electron microscopy images and elemental mapping showed that the distribution of nanoscale zerovalent iron (NZVI, Fe) on SiO₂ was uniform and the density of Fe increased as the iron loading increased from 10 to 50 wt%. The optimized 30 wt% Fe/SiO₂ particles were used to fabricate Pd–Fe/SiO₂ microspheres by the electrochemical reduction of Pd ions to Pd⁰ for the enhanced dechlorination of PCE under anoxic conditions. The dechlorination efficiency and rate of PCE by Fe/SiO₂ was significantly enhanced in the presence of 0.5–3 wt% Pd and the pseudo-first-order rate constant (kₚₒₓ) for PCE dechlorination by the mesoporous Pd–Fe/SiO₂ microspheres increased by 2–3 orders of magnitude when compared with that of Fe/SiO₂ alone. Ethane was found as the only end product with a carbon mass balance of 95–100%, showing that hydrodechlorination was the main reaction mechanism for PCE dechlorination by the Pd–Fe/SiO₂ microspheres. Column experiments showed the good mobility and permeability of the mesoporous Pd–Fe/SiO₂ microspheres when compared with that of pure NZVI alone. The results obtained in this study clearly show that the immobilization of bimetallic Pd–Fe nanoparticles on the mesoporous SiO₂ microspheres not only increases the reactivity for the dechlorination of PCE but also enhances the mobility and permeability for in situ remediation of chlorinated hydrocarbons in porous media.

1. Introduction

The contamination of porous media such as soils and groundwater by dense non-aqueous phase liquids (DNAPLs) is becoming a serious environmental issue. DNAPLs such as tetrachloroethylene (PCE) and trichloroethylene (TCE) have been extensively used as cleaning solvents, aerosol propellants and refrigerants, and are released into aquatic environments as the priority pollutants in both surface water and groundwater.¹–³ These chemicals are possible carcinogens which pose a serious health concern to human beings because of their toxic and mutagenic behaviour.⁴–⁵ Therefore, there is an urgent need for the development of an effective strategy for the removal of chlorinated hydrocarbons in contaminated aquifers.

Several technologies have been developed for the detection⁶ and dechlorination of chlorinated hydrocarbons.⁷–¹⁰ Permeable reactive barriers (PRBs) packed with zerovalent metals have been demonstrated to be an effective method for the removal of organic and inorganic pollutants under anoxic conditions.¹¹–¹³ Various laboratory-scale and field applications have found that nanoscale zerovalent iron (NZVI) and bimetallic iron-based nanoparticles including Fe/Pd and Fe/Ni can transform the chlorinated compounds into less-chlorinated homologues and non-chlorinated end products through reductive dechlorination and hydrodechlorination.¹⁴–¹⁸ Several studies have shown that chlorinated hydrocarbons can be rapidly dechlorinated into non-chlorinated hydrocarbons by using nanoscale bimetallic Pd/Fe particles.¹⁸,¹⁹ However, the aggregation of NZVI decreases the dechlorination efficiency and dechlorination rate of chlorinated compounds. Several studies have demonstrated the effectiveness of using a stabilizer or support to homogeneously disperse NZVI nanoparticles to enhance their stability and mobility.²⁰–²⁸ Various organic polymers including carboxymethyl cellulose, polyacrylic acid (PAA) and electrospun PAA/polyvinyl alcohol nanofibers have been used to immobilize Pd/Fe for enhanced dechlorination efficiency and dechlorination rate of chlorinated compounds.²²,²³ In addition, the organic polymer-immobilized iron-based nanoparticles have high
mobility to facilitate the nanoparticles’ transport through soil columns.24,25

Another strategy for increasing the stability and reactivity of nanoparticles is the immobilization on supports such as membranes and carbon materials.26–31 Parshetti and Doong28 have immobilized bimetallic Ni/Fe nanoparticles in PVDF and nylon 66 membranes in the presence of polyethylene glycol for the dechlorination of TCE and found that the immobilization of the Fe/Ni nanoparticles in the hydrophilic membrane can retain the longevity and high reactivity of the nanoparticles towards TCE dechlorination. In addition, Su et al. used activated carbon-supported zerovalent iron (ZVI/AC) for the adsorption and dechlorination of TCE.32 The rate constant for TCE dechlorination by ZVI/AC was 7 times higher than that of AC only. More recently, silica has been used as a support to maintain the reactivity and stability of iron-based nanoparticles.33–34 The use of mesoporous SiO₂ microspheres as the support has several advantages including the prevention of NZVI agglomeration, environmental friendliness and increased reactivity and stability. Ensie and Samad have immobilized NZVI onto a SiO₂@FeOOH core using a reduction method to remove nitrate from drinking water and found that greater than 99% of the nitrate could be removed by the nano SiO₂@FeOOH@Fe core–shell material at pH 3.34 In addition, Xie et al. compared four different iron-based nanoparticles for the dechlorination of polybrominated diphenyl ethers.32 The results showed that the core–shell type SiO₂@FeOOH@Fe core–shell had higher usability and stability and a low Fe²⁺ leaching rate when compared to the other iron-based materials. It is noteworthy that a mesoporous SiO₂ microsphere is stable, environmentally friendly and can be transported with water in porous media. However, the use of mesoporous SiO₂ microspheres as a support for bimetallic Pd/Fe nanoparticles for the dechlorination of chlorinated hydrocarbons has received less attention. In addition, little information is available on the characterization and dechlorination efficiency of bimetallic Pd–Fe nanoparticles on mesoporous silica.

In this work, bimetallic Pd/Fe nanoparticles were immobilized onto mesoporous SiO₂ microspheres for PCE dechlorination under anoxic conditions. The mesoporous SiO₂ microspheres were hydrothermally fabricated in the presence of gelatin and then the bimetallic Pd/Fe nanoparticles were immobilized onto the surface of the mesoporous SiO₂. The properties of the microstructures of the Pd–Fe/SiO₂ microspheres including morphology, specific surface area, pore texture, and chemical species were characterized. The effect of the Fe and Pd loadings on the dechlorination efficiency and dechlorination rate of PCE was optimized. In addition, the longevity and stability of the mesoporous Pd–Fe/SiO₂ microspheres were investigated.

2. Materials and methods

2.1. Reagents

The chlorinated hydrocarbons including PCE and TCE (99.8%, GC grade) used in this study were purchased from Merck Co. (Darmstadt, Germany). Palladium acetate (Pd(CH₃CO₂)₂, 98%) was obtained from Fluka Co. (Tokyo, Japan). HEPES (N-[2-hydroxyethyl]piperazine-N’-[2-ethanesulfonic acid] (C₈H₁ₘN₂O₄S) and ferrous sulfate-7-hydrate (FeSO₄·7H₂O) were purchased from Sigma Co. (St. Louis, MI). All other reagents were of analytical grade and were used as received without further treatment. In addition, deoxygenated water was prepared by vacuuming well-mixed deionized bidistilled water (18.3 MΩ cm, Millipore Co.) in serum bottles for 20 min and then purging with nitrogen for 5.0 min at 12.5 psi. The above procedure was repeated several times to remove the oxygen in the solutions.9

2.2. Synthesis of mesoporous silica

A stock solution of silicate was obtained upon mixing 20 g of sodium silicate, 250 mL of deionized bidistilled water and 250 mL of 0.1 M H₂SO₄ solution at 40 °C. The final pH of the solutions was then adjusted to 5. The fresh gelatine solution, prepared by adding 10 g of gelatin into 125 mL of water at 40 °C, was poured directly to the acidic solution of sodium silicate and stirred for several minutes. The solutions were hydrothermally treated at 100 °C for 1 d to form mesoporous silica. After cooling down to room temperature, the products were harvested by filtration, washed with water, dried in air and calcined at 550 °C.

2.3. Immobilization of Pd–Fe nanoparticles onto mesoporous silica

Fe/SiO₂ was synthesized by dispersing 0.3 g of mesoporous silica microspheres in 100 mL of bidistilled deionized water. 0.3 g of FeSO₄·7H₂O was added into the mesoporous SiO₂ solution and the Fe/SiO₂ microspheres were synthesized by the dropwise addition of 30 mL of 0.2 M ice-bathed NaBH₄ solution to reduce the ferrous ions into NZVI at pH 4 under stirring conditions. The mesoporous Fe/SiO₂ microspheres were collected by centrifugation at 14 000 rpm for 10 min and then dried in N₂. In addition, the bimetallic Pd–Fe/SiO₂ microspheres were fabricated using an electrochemical reduction method by the addition of deoxygenated 0.1–3 wt% Pd(CH₂COO)₂ solutions into the Fe/SiO₂ solutions under anoxic conditions. The Pd concentration in the Pd–Fe/SiO₂ microspheres was also examined by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500ce). The measured Pd concentrations were in the range of 0.095–2.86 wt%, which corresponded to a recovery of 94–97%.

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Pd^{2+} + Fe^{0} \rightarrow Pd^{0} + Fe^{2+} \quad (1)
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2.4. Dechlorination of PCE by Pd–Fe/SiO₂ microspheres

The dechlorination of PCE by mesoporous Pd–Fe/SiO₂ microspheres was performed by using batch experimental systems. N₂-purged serum bottles containing 0.1 g of Pd–Fe/SiO₂ or pure NZVI were filled with 50 mL of 25 mM HEPES buffer solution at pH 7.2 in a glove box. After being capped with Teflon-lined rubber septa and aluminium caps, the stock solutions of PCE were introduced into the bottles to get the final concentration of 5 mg L⁻¹. The serum bottles were then incubated in an orbital
shaker at 120 rpm and at 25 °C in the dark. Control experiments were also performed in the absence of the mesoporous Pd–Fe/SiO2 microspheres.

The column experiments were performed by using a 15 mL glass burette packed with 0.4–0.6 mm glass beads to investigate the mobility and water permeability of the Pd–Fe/SiO2 microspheres and NZVI. The column diameter was 1.5 cm and the total pore volume was 11.9 cm³. The columns were saturated with deoxygenated deionized water before the addition of 2 g L⁻¹ NZVI or Pd–Fe/SiO2 suspensions. The flow rate of the feeding solution was 4.8 mL min⁻¹.

2.5. Analysis and characterization

The chlorinated as well as non-chlorinated hydrocarbons were determined by injecting 40 μL of headspace gas from the serum bottles into a Perkin-Elmer gas chromatograph (GC) equipped with an electron capture detector (ECD) and a flame ionization detector (FID). A VOCOL fused-silica megabore capillary column was used to separate the chlorinated and non-chlorinated compounds by isothermally maintaining 120 °C and using ultra high purity nitrogen (>99.9995%) as the carrier gas. The temperatures of the ECD and FID were maintained at 325 and 250 °C, respectively. Blank controls were also performed to examine the possible loss of chlorinated compounds during the dechlorination periods. In addition, the aqueous concentrations of chlorinated hydrocarbons were calculated using the external standard method by preparing known concentrations of chlorinated hydrocarbons in aqueous solutions.

The crystallite size and crystal phase of the Pd–Fe/SiO2 microspheres were examined using a Scintag X1 advanced X-ray diffractometer (XRD) with Ni-filtered Cu Kα radiation (λ = 0.1541 nm). The XRD patterns were obtained from 2θ = 20° to 70° 2θ with a sampling step width of 0.05° and a step time of 0.5 s. The specific surface area, pore volume and pore size distribution were determined by the N₂ adsorption–desorption isotherms at 77 K using a ASAP 2020 surface area and porosimetry system manufactured by Micromeritics Co. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_BET) using the adsorption data in a relative pressure (P/Po) range of 0.02 to 0.2. By using the Barrett–Joyner–Halenda (BJH) model, the pore volumes and pore size distributions in the mesopore range (>2 nm) could be derived from the adsorption branches of the isotherms, and the total pore volumes (V_t) were calculated from the adsorbed amount at a relative pressure of 0.995.

The surface morphology of the mesoporous Pd–Fe/SiO2 microspheres was observed using a JOEL field-emission scanning electron microscope (FE-SEM). The TEM images and particle sizes of Pd–Fe/SiO2 were obtained using a Hitachi H-7500 transmission electron microscope at an acceleration voltage of 80 kV by suspending one drop of the microsphere suspension on a 300-mesh carbon coated Cu grid. The X-ray photoelectron spectroscopic (XPS) measurements were performed on a ESCA PHI 1600 photoelectron spectrometer using an Al Kα X-ray source (1486.6 eV). The binding energies of the photoelectrons were determined by assuming that the carbon 1s electron has a binding energy of 284.8 eV. During the data acquisition, the pressure in the sample chamber did not exceed 2.5 × 10⁻⁹ Torr.

3. Results and discussion

3.1. Microstructures of Fe/SiO2 microspheres

The morphology and specific surface area of the mesoporous SiO2 microspheres were first characterized. Fig. S1 (ESI†) shows the TEM images of mesoporous SiO₂ fabricated at various hydrothermal times ranging from 1 to 7 d. It is clear that the particle sizes of mesoporous SiO₂ increased with the increase in hydrothermal time and the particle diameters were in the range of 1–5 μm. In addition, the mesoporous silica showed typical type IV isotherms with a hysteresis loop in the P/P₀ range of 0.5–0.95, clearly showing the mesoporous characteristics of SiO₂ (Fig. S2, ESI†). The specific surface area of the mesoporous SiO₂ microspheres decreased from 312 m² g⁻¹ at 1 d to 164 m² g⁻¹ at 7 d, while the average pore diameter increased slightly from 6.9 to 8.6 nm when the hydrothermal time increased from 1 to 7 d. Since the role of the mesoporous SiO₂ microspheres used in this study is to serve as a support, the hydrothermal time of 1 d was selected because of the high surface area and similar pore diameter for the immobilization of NZVI.

Fig. 1 shows the SEM and TEM images of 10–50 wt% Fe/SiO2 prepared by adding 50 mL of 0.2 M NaBH₄ into the mesoporous
SiO₂ solutions containing ferrous ions. It is clear that the particle number as well as the size of the NZVI on the SiO₂ microspheres increased with the increase in Fe loading. No obvious aggregation of NZVI was observed when the loading of Fe was lower than 30 wt% (Fig. 1a and b). However, the NZVI aggregated into large particles at 50 wt% Fe and some NZVI nanoparticles were agglomerated into long chains outside of the SiO₂ microspheres (Fig. 1c). The EDS analysis indicated that the atomic ratios of Fe to Si were 0.122 for 10 wt% Fe/SiO₂, 0.316 for 30 wt% Fe/SiO₂ and 0.575 for 50 wt% Fe/SiO₂. In addition, the ICP-MS analysis showed similar results and the Fe concentration was 12.5 wt% for 10 wt% Fe/SiO₂, 30.3 wt% for 30 wt% Fe/SiO₂, and 45.1 wt% for 50 wt% Fe/SiO₂. These results clearly indicate the nearly complete reduction of ferrous ions to NZVI on the surface of mesoporous SiO₂ by NaBH₄.

Similar to the SEM images, the TEM images clearly showed the formation of discrete NZVI nanoparticles on the surface of the mesoporous SiO₂ microspheres when the Fe loadings were in the range 10–30 wt% (Fig. 1d and e). In contrast, the agglomeration of long-chained NZVI was clearly observed at 50 wt% Fe/SiO₂ (Fig. 1f). Fig. 2 shows a histogram of the particle sizes of NZVI on Fe/SiO₂ at various iron loadings of 10–50 wt%.

The particle size distribution of NZVI at 10 wt% Fe/SiO₂ was in the range of 60–160 nm, and then increased to 120–240 nm at 50 wt% Fe/SiO₂. In addition, the average particle sizes of NZVI were 85 ± 27 nm, 150 ± 21 nm and 165 ± 30 nm for 10, 30, and 50 wt% Fe/SiO₂, respectively. No obvious difference in the mean diameter of NZVI between 30 and 50 wt% Fe/SiO₂ reflected the fact that 30 wt% could be the optimal iron loading for the mesoporous SiO₂ microspheres.

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Fig. 3 shows the XRD patterns and specific surface areas of the Fe/SiO₂ microspheres with various Fe loading. As shown in Fig. 3a, the XRD pattern of pure NZVI showed peaks centered at 44.6° and 65.0° 2θ, which can be assigned to the (110) and (200) planes of body-centered cubic Fe (JCPDS 06-0696) respectively. The broad peak at 20° for the Fe/SiO₂ microspheres was mainly attributed to the amorphous characteristics of SiO₂. In addition, the small and broad peak at 44.6° 2θ appeared when the iron loading increased from 10 to 50 wt%, indicating the successful immobilization of NZVI onto the surface of SiO₂.

Fig. 3b shows the BET surface area of the 10–50 wt% Fe/SiO₂ microspheres. Similar to the pure mesoporous SiO₂ microspheres, the N₂ adsorption–desorption isotherms of Fe/SiO₂ with varying Fe loadings followed a type IV physisorption isotherm with a H3 hysteresis loop in the P/P₀ range of 0.4–0.95, which is mainly attributed to capillary condensation in the mesopores of the silica substrate. The specific surface areas of 10 and 30 wt% Fe/SiO₂ were in the range of 196–209 m² g⁻¹ and then decreased to 143 m² g⁻¹ when the Fe loading increased to 50 wt%. In addition, the pore size distributions of 10–50 wt% Fe/SiO₂ were similar and the average pore diameters were in the range of 5.7–6.0 nm, which indicate that the decrease in the specific surface area of 50 wt% Fe/SiO₂ is mainly attributed to the formation of large and excess NZVI nanoparticles on and outside of the mesoporous SiO₂ microspheres.

The average pore diameter of the Fe/SiO₂ microspheres is smaller than that of the pure SiO₂ microspheres, presumably attributed to the formation of NZVI on the surface of SiO₂ microspheres.

3.2 Microstructures of Pd–Fe/SiO₂ nanoparticles

After the successful fabrication of Fe/SiO₂, the Pd precursor was added to Fe/SiO₂ for the electrochemical formation of
bimetallic Pd–Fe nanoparticles on the mesoporous SiO2 microspheres. The 30 wt% Fe/SiO2 microspheres were selected as the support because of the homogenous Fe nanoparticles on the SiO2 surface and the large specific surface area. Fig. S3 (ESI†) shows the XRD patterns of the 0.5–3 wt% Pd–Fe nanoparticles on the mesoporous SiO2 microspheres. The XRD patterns of the Pd–Fe/SiO2 microspheres (with various Pd loadings) showed broad peaks at 20–25° 2θ, which were similar to the results obtained by the Fe/SiO2 microspheres. No Fe peak at 44.6° 2θ was observed, presumably attributed to the transformation of NZVI into iron oxides by providing electrons to electrochemically reduce Pd2+ into Pd0. The TEM images of the 1–3 wt% Pd–Fe/SiO2 microspheres clearly showed the formation of a thin layer on the surface of the NZVI with some needle-like structures (Fig. S4, ESI†), indicating the formation of iron oxides after the addition of the Pd ions. However, no characteristic Pd peak was observed because of the low amount of Pd added onto Fe/SiO2.

To further elucidate the immobilization of Pd onto the Fe/SiO2 surfaces, XPS was used to characterize the change in the chemical species of the elements in the Pd–Fe/SiO2 microspheres. Fig. 4 shows the XPS spectra of the Si 2p, Fe 2p and Pd 3d species in the 3 wt% Pd–Fe/SiO2 microspheres. The XP spectrum of Si 2p showed a broad peak at 100–105 eV, indicating the formation of SiO2 (Fig. 4a). After Ar sputtering for 1 min to remove the top 27 nm of the particle surface, the Si 2p peak still remained at the same position, indicating the stability of SiO2 as the support. The XPS of Fe 2p showed two peaks centered at 711 and 724 eV, which were the characteristic Fe 2p3/2 and Fe 2p1/2 peaks of iron oxides (Fig. 4b). Additional zerovalent iron peaks at 707 and 720 eV appeared after Ar sputtering for 1 min, clearly indicating the transformation of NZVI to iron oxides after the addition of Pd2+. This result also supports the XRD results, that no iron species was identified in the Pd–Fe/SiO2 microspheres. In addition, the XPS peak of the iron oxides shifted from 711.8 eV to 710.4 eV. After peak deconvolution, the major species of the iron oxides changed from goethite (FeOOH) to magnetite (Fe3O4) after Ar sputtering (Fig. S5, ESI†), which reflected the fact that the reduction of Pd2+ to Pd0 changed the species of the iron oxides on the surface of NZVI. The XPS spectra of the 3 wt% Pd loaded Fe/SiO2 showed Pd 3d peaks at 334.9 and 340.2 eV, which belonged to Pd0 3d5/2 and Pd0 3d3/2, respectively (Fig. 4c). The peak positions of the Pd species did not change after Ar sputtering for 1 min, clearly indicating the formation of zerovalent Pd. In addition, no other peak related to the oxidation state of Pd2+ was observed, confirming the complete reduction of the immobilized Pd2+ to Pd0 through the electrochemical Pd2+-Fe0 reduction reaction.

3.3. Dechlorination of PCE by Pd–Fe/SiO2 microspheres

Since the SiO2 microspheres are mesoporous materials and can adsorb organic contaminants, the adsorption of PCE by the mesoporous SiO2 microspheres was examined first. Fig. S6 (ESI†) shows the adsorption of 5 mg L−1 PCE onto the mesoporous SiO2 microspheres. No obvious decrease in the PCE concentration was observed after 50 h of incubation, indicating that the adsorption of PCE onto the mesoporous SiO2 microspheres can be neglected. In addition, the PCE dechlorination efficiency of pure NZVI and Fe/SiO2 was compared at pH 5.5. As shown in Fig. S7 (ESI†), the PCE dechlorination efficiency of Fe/SiO2 after 575 h of incubation was higher than that of pure NZVI. The dechlorination followed pseudo-first-order rate kinetics and the pseudo-first-order rate constants (kobs) for PCE dechlorination were 0.0061 and 0.0042 h−1 for the Fe/SiO2 microspheres and pure NZVI, respectively. Since SiO2 has no reactivity in PCE dechlorination, the dechlorination of PCE is mainly contributed by the NZVI on the SiO2 microspheres and the rate constant for PCE dechlorination can be normalized to
the unit mass of NZVI to reflect the reactivity of NZVI on the Fe/SiO₂. After normalization to the unit mass of NZVI, the mass-normalized rate constant (kₘₐ) for PCE dechlorination by Fe/SiO₂ was 0.01 L h⁻¹ g⁻¹. This value is 4.8 times higher than that by pure NZVI, presumably attributed to the well-dispersed NZVI on the surface of the SiO₂ microspheres.

The addition of second catalytic metal ions such as Pd, Ni and Pt onto the iron surface can significantly enhance the dechlorination efficiency and dechlorination rate of chlorinated compounds. Fig. 5a shows the PCE dechlorination efficiency of SiO₂-supported Pd–Fe nanoparticles at various Pd loadings of 0.1–3 wt%. The PCE dechlorination efficiency of Pd–Fe/SiO₂ increased significantly from 33% at 0.1 wt% Pd to 99.5% at 0.3 wt% Pd and nearly complete PCE dechlorination was observed with Pd loadings >0.5 wt%. Fig. 5b shows the kₘₐ values for PCE dechlorination as a function of Pd loading. The kₘₐ values increased positively from 0.011 ± 0.004 min⁻¹ at 0.1 wt% Pd to 0.267 ± 0.021 min⁻¹ at 0.5 wt% Pd and then slightly decreased to 0.253 ± 0.023 min⁻¹ when the Pd concentration increased to 3 wt%. These values are 2–3 orders of magnitude higher than that of the pure Fe/SiO₂ microspheres at pH 5.5, showing that the addition of low amounts of Pd ions can significantly enhance the dechlorination efficiency and dechlorination rate of PCE by mesoporous SiO₂-supported NZVI.

Several studies have addressed the effect of additive loadings on the dechlorination efficiency of zerovalent metals toward chlorinated hydrocarbons. An optimal mass loading often exists for a wide variety of bimetallic catalysts including Ni/Fe, Pd/Fe, Ni/Si and Ru/Fe. Lin et al. reported that the dechlorination rate of TCE by bimetallic Ru/Fe increased as the Ru loading increased from 0.25 to 1.5 wt%. A decrease in kₘₐ was also observed when the Ru loading increased to 2.0 wt%. In this study, an optimal dosage of 0.5 wt% Pd ions was obtained for the dechlorination of PCE by the Fe/SiO₂ microspheres. The addition of catalytic Pd ions prevents the formation of toxic products by the dechlorination of chlorinated hydrocarbons via hydrogen reduction rather than through electron transfer. As shown in Fig. 5c, ethane was the only detected product for the dechlorination of PCE by 0.5–3 wt% Pd–Fe/SiO₂ and the carbon mass balances were all greater than 95%, showing that hydrodechlorination is the major reaction mechanism for the dechlorination of PCE by the mesoporous Pd–Fe/SiO₂ microspheres. In addition, several studies have reported the hydrodechlorination of gaseous PCE over Pd-based catalysts in the presence of hydrogen under high temperature conditions. Bueres et al. immobilized 1 wt% Pd catalysts on three different carbonaceous materials and found that 68–97% of the gaseous PCE was converted to ethane and trace amounts of TCE by the carbon supported Pd at 525 K after 30 h of incubation. This indicates that Pd only can show its dechlorination ability at high temperature and the Pd–Fe/SiO₂ microspheres are excellent catalysts for the hydrodechlorination of PCE in aqueous solutions.

The long-term performance of 0.5 wt% Pd–Fe/SiO₂ in the dechlorination of PCE was further investigated by repeatedly injecting 5 mg L⁻¹ PCE into the solution containing Pd–Fe/SiO₂ microspheres. Fig. 7 shows the stability and longevity of Pd–Fe/SiO₂ microspheres. A fast PCE dechlorination process was observed and the Pd–Fe/SiO₂ microspheres can be reused for at least 10 times, all with
a stable dechlorination efficiency of >99%. Several studies have reported the repeated use of Pd/Fe nanoparticles for dechlorination. Nagpal et al. have used bimetallic Fe–Pd nanoparticles for lindane degradation under anoxic conditions and found that the dechlorination efficiency of the recycled Fe–Pd dropped slightly to 92% after the 10th cycle. In this study, the $k_{obs}$ values and initial rate for PCE dechlorination were in the range 0.207–0.271 min$^{-1}$ and 8.96–11.5 μM min$^{-1}$, respectively, showing that the 0.5 wt% Pd–Fe/SiO$_2$ microspheres are a promising material for the dechlorination of chlorinated hydrocarbons. The stability of Pd–Fe/SiO$_2$ is mainly attributed to the introduction of SiO$_2$ as the support. Reardon et al. have proposed that the presence of silica may slow down iron corrosion by adsorbing silicate, the dissolved form of SiO$_2$ after reaction, to the anodic surface. In this study, the solution pH after dechlorination in the presence of the Fe/SiO$_2$ microspheres increased by 0.4–0.8 units which is lower than that in the presence of pure NZVI (1–1.5 units). This result supports the hypothesis that the introduction of the SiO$_2$ microspheres could maintain the reactivity of NZVI with >99% dechlorination efficiency of PCE.

### 3.4. Column experiments

One of the advantages of using mesoporous SiO$_2$ microspheres as the support is the high mobility and water permeability during the dechlorination processes. To prove the merits of mesoporous SiO$_2$ microspheres, column experiments were conducted to understand the water permeability in the presence of the Pd–Fe/SiO$_2$ microspheres. As shown in Fig. S8 (ESI†), pure NZVI was retained at the top of the column, which was similar to reported data. In contrast, the Pd–Fe/SiO$_2$ microspheres could transport along with the water through the whole column, which indicates the good transportability of Pd–Fe/SiO$_2$. Fig. 8 shows the breakthrough curves of pure NZVI and Pd–Fe/SiO$_2$. It is clear that the mass ratios of pure NZVI in the effluent were in the range of 0.01–0.06 in the first 6 pore volumes, showing that NZVI would be aggregated into large particles and then retained in the column. On the contrary, the mass of the Pd–Fe/SiO$_2$ microspheres in the effluent started to increase after 3 pore volumes and 90% of Pd–Fe/SiO$_2$ was eluted from the column after 6 pore volumes. Zhan et al. compared the mobility of Fe/ethylsilica and NZVI using a column packed with standard Ottawa sand and found that most NZVI was trapped within the first few centimeters of the column, while the Fe/ethylsilica particles reached the bottom of the column, which is consistent with the results obtained in this study.

Fig. 8b shows the water permeability of pure NZVI and Pd–Fe/SiO$_2$ by packing 1 cm of different materials in the middle of the column. In the absence of Fe-based particles, the average water flow in the glass bead packed column was 82–90 mL h$^{-1}$, and slightly decreased to 72–80 mL h$^{-1}$ in the presence of the mesoporous Pd–Fe/SiO$_2$ microspheres. However, the water flow decreased to 58–70 mL h$^{-1}$ when pure NZVI was packed in the column, showing that the mesoporous SiO$_2$ microspheres are a good support with good permeability to disperse NZVI for the remediation of chlorinated compounds in porous media.

Fig. 9 shows the possible reaction mechanism for PCE dechlorination by the mesoporous Pd–Fe/SiO$_2$ microspheres under anoxic conditions. The negatively charged silica surface can adsorb Fe$^{2+}$ ions and then convert them to NZVI in the presence of NaBH$_4$, which can be well dispersed on the surface of the SiO$_2$ microspheres to enhance the reactivity of Fe/SiO$_2$. 

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**Fig. 7** The stability and longevity of mesoporous Pd–Fe/SiO$_2$ microspheres with repeated spiking of 5 mg L$^{-1}$ PCE.

**Fig. 8** (a) The breakthrough curves and (b) permeability of pure NZVI and mesoporous 0.5 wt% Pd–Fe/SiO$_2$ microspheres. M/M$_0$ represents the fraction of particles that are eluted in the effluent.
The silica-supported Pd–Fe nanoparticles were electrochemically generated when the Pd\(^{2+}\) ions were adsorbed onto the NZVI surfaces. The hydrodechlorination of PCE by the bimetallic Pd–Fe nanoparticles involves the oxidation of NZVI to galvanically protect the Pd metal and the Pd metal provides active sites for hydrodechlorination.\(^{22}\) As the corrosion of NZVI increases, protons from water are reduced to adsorbed H atoms and to molecular hydrogen at the catalytic Pd surface, resulting in the formation of ethane during the hydrodechlorination of PCE.

4. Conclusions

In this study, we have first demonstrated the use of mesoporous SiO\(_2\) microspheres as a support to well disperse bimetallic Pd–Fe nanoparticles for the hydrodechlorination of PCE under anoxic conditions. TEM images and surface area analysis showed that the poorly crystalline SiO\(_2\) provided large specific surface areas for the immobilization of Pd–Fe nanoparticles. The dechlorination reaction by Fe/SiO\(_2\) followed a pseudo-first-order reaction and the Fe mass normalized rate constant of Fe/SiO\(_2\) was 5.2 times higher than that of pure NZVI at pH 5.5. The addition of Pd ions enhanced the efficiency and dechlorination rate and the \(k_{\text{obs}}\) for PCE dechlorination by Fe/SiO\(_2\) was significantly enhanced by 2–3 orders of magnitude after the addition of 0.5–3 wt% Pd ions. The Pd–Fe/SiO\(_2\) microspheres showed excellent reusability for PCE dechlorination, and they can be recycled at least 10 times. The mesoporous silica plays an important role in immobilizing and well dispersing NZVI on the surface, which can provide the maximum number of active sites for the dechlorination of PCE. The column experiments prove that mesoporous silica is a good carrier for bimetallic Pd–Fe nanoparticles; to pass through the bed of glass beads and helping them have better permeability than bare NZVI. The results obtained in this study clearly indicate that the mesoporous Pd–Fe/SiO\(_2\) microspheres are environmentally friendly composites for the effective and efficient dechlorination of chlorinated hydrocarbons and can open an avenue to tailor mesoporous nanocomposites for the long-term dechlorination of chlorinated compounds in porous media.

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Notes and references
