

# Immobilization of bimetallic nanoparticles on microfiltration membranes for trichloroethylene dechlorination

G. K. Parshetti and R. A. Doong

## ABSTRACT

Highly reactive nanoscale Ni/Fe nanoparticles were synthesized on microfiltration membranes for dechlorination of 20 mg/L trichloroethylene (TCE). Complete degradation of TCE was achieved within 25 min by Nylon 66 membrane with the production of ethane as a major degradation product, depicting that hydrodechlorination is the major reaction mechanism for TCE dechlorination. In addition, the carbon mass balance can be reached to 93%. The surface-area-normalized rate constant ( $k_{SA}$ ) for TCE degradation by Ni/Fe immobilized on Nylon 66 was  $0.172 \text{ L h}^{-1} \text{ m}^{-2}$ , which is higher than that by Ni/Fe in solution. Further TEM and SEM-EDS analyses show that Nylon 66 can retain higher amounts of Ni on the surface of membrane. In addition, the efficiency and rate for TCE dechlorination increased upon increasing mass loading of Ni from 2.5 to 20 wt%. Results obtained in this study clearly demonstrate that the use of Nylon 66 as the support for immobilization of bimetallic Ni/Fe nanoparticles has a good catalytic activity for dechlorination of TCE.

**Key words** | bimetallic Ni/Fe nanoparticles, dechlorination, immobilization, microfiltration membranes, trichloroethylene (TCE)

G. K. Parshetti  
R. A. Doong  
Department of Biomedical Engineering and  
Environmental Sciences,  
National Tsing Hua University,  
Hsinchu 30013,  
Taiwan  
E-mail: radoong@mx.nthu.edu.tw

## INTRODUCTION

The small particle size and high surface area to mass ratio make nanoparticles highly reactive and extremely versatile for application. The use of nanomaterials to accelerate the degradation rate is a promising technology for the degradation of pollutants in contaminated water. The recent thrust to synthesize bimetallic nanoparticles has received the intensive attention in electronic, optical, magnetic, catalytic and biological fields (Kidambi & Bruening 2005; Xu & Bhattacharya 2005). More recently, the use of bimetallic nanoparticles, such as Ni/Fe and Pd/Fe for dechlorination of chlorinated hydrocarbons has received significantly attention due to the considerably faster reduction rate and the production of environmentally friendly end products (Xu & Bhattacharya 2005). However, the agglomeration of nanoparticles to reduce the surface area and the low recovery of nanoparticles in aqueous

solution limit the practical application of bimetallic nanoparticles to the treatment of priority pollutants in contaminated waters.

The long-term stability of the nanoparticles can be increased by the immobilization on support (Xu & Bhattacharya 2005). The immobilization of bimetallic nanoparticles onto microfiltration membranes is a novel strategy for environmental application because of the effectively reduction and less agglomeration of nanoparticles, long-term stability and protection of nanoparticles from oxidation. Nanoscale Ni/Fe particle is one of the important materials for degradation of chlorinated organic compounds since the dechlorination reactions of halogenated compounds is surface mediated, in the surface area of iron increases by introduction of some catalytic metals such as nickel, zinc and palladium (Li & Klabunde 1998; Zhang

*et al.* 1998). Therefore, the use of immobilized nanoscale bimetallic system is considered to be useful tool for the degradation of environmentally toxic chemical compounds with faster degradation rate and reduced toxic compound formation. Xu *et al.* (2005) synthesized the bimetallic Ni/Fe and Pd/Fe nanoparticles in the PAA/polyether sulfone (PES) composite membrane for the reductive dechlorination of TCE. The average particles sizes of the synthesized Ni/Fe nanoparticles were  $5 \pm 0.8$  nm, which is much small and narrow distribution compared with those in the absence of membrane matrix. In addition, the stability and reactivity of bimetallic nanoparticles also can be maintained using stabilizer. He *et al.* (2007) developed a new strategy for stabilizing palladized iron (Pd/Fe) nanoparticle with sodium carboxymethyl cellulose (CMC) as a stabilizer. The complexation between carboxylate groups with metals and the intermolecular hydrogen bond between CMC and the Fe particle surface were identified to be the major mechanisms for stabilizing bimetallic nanoparticles to yield stable dispersions with sizes smaller than 17.2 nm. However, the immobilization of bimetallic Ni/Pd nanoparticles on different microfiltration membranes for treatment of TCE has received less attention.

In this study, a highly efficient method for immobilization of Ni/Fe nanoparticles on different microfiltration membranes was developed for dechlorination of trichloroethylene (TCE) in contaminated waters. The highly reactive bimetallic Ni/Fe nanoparticles were synthesized on polyvinylidene fluoride (PVDF), Nylon 66, Millex GS, and mixed cellulose ester polymer (MCEP) membranes by using polyethylene glycol (PEG) as cross linking agent. In addition, the reaction kinetics and mechanisms for TCE dechlorination were calculated and determined.

## MATERIALS AND METHODS

### Synthesis of immobilized Ni/Fe nanoparticles on microfiltration membranes

Bimetallic Ni/Fe nanoparticles were prepared on different microfiltration membranes including hydrophilized PVDF membrane (13 mm, 0.45  $\mu$ m pore size, Millipore), Nylon 66 (47 mm, 0.45  $\mu$ m pore size, Supelco, USA), Millex GS (20 mm, 0.45  $\mu$ m pore size, Millipore) and mixed cellulose

ester polymer (MCEP) (47 mm, 0.45  $\mu$ m pore size, Advantech MFS, Inc. USA) according to the previous procedures with minor modification (Xu & Bhattacharya 2005). An aqueous coating solution was prepared with 10.5% of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  precursor for zerovalent iron (Riedel-De Haen, Germany) and 2.3% polyethylene glycol (Aldrich) in deionized deoxygenated water. All the microfiltration membranes were dipped in a 200-mL coating solution for 10 min, and then followed by thermally heating the membrane at 110°C for 3 h for grafting polyethylene glycol (PEG) to the membranes. Zerovalent iron on membranes was prepared by soaking the membranes into the 300 mL solution containing 0.5 M  $\text{NaBH}_4$  for 10 min. For synthesis of bimetallic Ni/Fe, membranes were dipped in to the 2.5%  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Merck, Germany) solution for 10 min followed by immersing into 0.5 M  $\text{NaBH}_4$  for another 10 min. The zerovalent nickel was then precipitated on iron surface, leading to the formation of immobilized Ni/Fe bimetallic nanoparticles on microfiltration membranes. The immobilized membranes were washed with ethanol twice, and then stored in organic solvent containing methanol:isopropanol:ethanol (90:5:5) to prevent the oxidation of zerovalent metals. The content of Fe and Ni on the immobilized membranes were determined by AAS (Perkin-Elmer AA100) by digesting membranes using 20 mL of 1 N sulphuric acid for 1 h (Xu *et al.* 2005). The determined Fe content were 10.0, 6.04, 5.7 and 3.0 mg in PVDF, Nylon 66, MCEP and Millex GS membranes, respectively, while the Ni contents were 0.173, 1.15, 0.987 and 0.628 mg, respectively.

To understand the effect of support on dechlorination of TCE, aqueous phase of Ni/Fe nanoparticles in the absence of membrane were synthesized by dissolving 0.2 M  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in deoxygenated deionized water at pH adjusted to 8.0 followed by dropwise addition of 0.5 M  $\text{NaBH}_4$ . The black precipitates was then washed with ethanol and stored in organic solvent as mentioned above. The synthetic procedures of bimetallic Ni/Fe nanoparticles were similar to that of zerovalent iron except dissolving 0.01 M  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in solution.

### Dechlorination of TCE

The dechlorination of trichloroethylene (Sigma 99.9%) by immobilized bimetallic Ni/Fe membrane was investigated

using 40 mL N<sub>2</sub> purged serum glass vials with Teflon septa. PVDF and Millex GS membranes immobilized with 10.173 and 3.629 mg of Ni/Fe nanoparticles, respectively, were loaded into the vial containing 10 mg/L TCE in 20 mL of deoxygenated HEPES buffer, and membranes of Nylon 66 and MCEP, loading with 7.19 and 6.687 mg Ni/Fe, respectively, were amended to the batch solution for TCE dechlorination. 50 mM HEPES was used to control the pH value at 7.2 to avoid the increase in pH after reaction. Deoxygenated solutions were prepared by purging nitrogen gas (N<sub>2</sub>, 99.99%) at a flow rate of 42 L/min in vacuum-sealed bottles, this process was repeated 4–5 times to remove trace amount of oxygen in the solution (Doong & Lai 2005). All sets for dechlorination vials were sealed with Teflon septa and placed on shaker at 150 rpm and at 25 °C in dark throughout the duration of experiment. In addition, parallel control experiments were carried out by adding support membranes in the absence of Ni/Fe nanoparticles to the buffered TCE solution. All the experiments were run in duplicate and only the average values were reported.

The headspace analytical technique was used for the determination of chlorinated hydrocarbons and non-chlorinated hydrocarbons. The concentrations of TCE and the byproducts in the headspace of the test bottles were monitored by withdrawing 40 µL of gas in the headspace using a 50-µL gas-tight syringe. The headspace sample was immediately injected into a gas chromatograph (GC) equipped with an electron capture detector (ECD) and a flame ionization detector (FID) (Perkin-Elmer, Autosystem, Norwalk, CT). A 60-m VOCOL fused-silica megabore capillary column (0.545 mm × 3.0 µm, Supelco Co.) was employed to separate the organic compounds. The column was connected to the FID and ECD simultaneously by a Y-splitter; and optimal sensitivity for chlorinated hydrocarbons was achieved with 40% of the flow (1.85 ml min<sup>-1</sup>) to the ECD. The column temperature was isothermally maintained at 120°C using ultra-high-purity nitrogen (>99.9995%) as the carrier gas. The temperatures of the ECD and FID were maintained at 350 and 250°C, respectively. The relative standard deviations (RSD) of the ECD analyses were within 10% and those for the FID analyses were within 5%. The concentration of total acid extractable Fe (II) in the serum bottle after dechlorination was determined by withdrawing 0.5 ml of suspension using

N<sub>2</sub>-purged syringe, and were then immediately acidified with 1 N HCl. After mixing vigorously, the acidified sample was centrifuged at 8,000 rpm for 10 min to remove the particles, and Fe (II) content in supernatant was determined by the Ferrozine method at 562 nm (Doong *et al.* 2003).

### Characterization of immobilized nanoparticles on membranes

The morphology of immobilized Ni/Fe membranes was determined by SEM image. The SEM image was obtained using Hitachi S-4700 type α and image is secondary electron image. Before placed sample into vacuum chamber, the surface of sample were coated with Pt using Ion Sputter ε-1030 Hitachi, Japan) to increase the conduction of sample surface. After coating with Pt, the sample was placed under high vacuum (10<sup>-3</sup>–10<sup>-7</sup> mbar) condition. An acceleration electron voltage of 5 kV was typically used. In addition, the dimensions and morphology of Ni/Fe nanoparticles were examined by transmission electron microscopy (TEM) at accelerating voltages of 300 kV. The specimen was prepared by dispersing of titanate nanostructures on a Cu grid.

The specific surface area and pore size distribution studies were carried out by nitrogen adsorption and desorption at 77 K using a surface area and porosimetry system (ASAP 2020, Micromeritics). The specific surface area was obtained by Brunauer, Emmett and Teller (BET) model which uses low-temperature gas adsorption method to determine the specific surface area of the porous solids.

## RESULTS AND DISCUSSION

### Characterization of membrane and immobilized nanoparticles

A dip coating method was used to prepare the immobilized Ni/Fe nanoparticles (Xu & Bhattacharya 2005). A typical method for formation of nanoparticles onto membranes involves thermolysis of organometallic compounds within a polymer membrane to produce the reduced metal nanoparticles (Meyer *et al.* 2003). In the present study we combined the coating and thermal graft polymerization procedure for the immobilization of bimetallic nanoparticles on different

microfiltration membranes by using polyethylene glycol (PEG) polymer to trap metal ions, which can be subsequently reduced to form stable nanosized zerovalent metal particles. Grafting is referred to immobilization or introduction of polymer or copolymer on membranes to give surface modification. Covalent immobilization of hydrophilic species onto the membranes can be achieved by surface graft copolymerizations of membranes with monomers or macromolecules in solutions (Iwata *et al.* 1991; Ulbricht *et al.* 1996). Previous studies have shown that PEG and its derivatives can be grafted on different membranes by thermal, plasma or UV induced grafting (Zou *et al.* 2002; Chen *et al.* 2004) because of its hydrophilic side group. Based on our results and observations, we proposed the possible mechanism of immobilization of PEG on the PVDF membrane along with metal nanoparticles (Figure 1).

Figure 2 shows the SEM images of Ni/Fe nanoparticles immobilized on different microfiltration membranes. Well dispersed Ni/Fe nanoparticles immobilized on the membrane surface was observed. The uniform size distribution of roughly spherical Fe/Ni nanoparticles on the membranes surface indicates the low agglomeration of immobilized nanoparticles on the membrane surface. However, the particle sizes of Ni/Fe varied among membranes. The diameters of Ni/Fe nanoparticles were 30–40 nm for MCEP and Nylon 66 membranes, while the particle sizes were in the range 70–80 nm for Millex GS and PVDF membranes. In addition, slight agglomeration of Ni/Fe nanoparticles was observed on PVDF membrane. The interaction mechanisms consist of ion exchange, chelation and electrostatic interaction, and the interaction between

polyethylene glycol and metal particles may involve in preventing the particles agglomeration (Xu & Bhattacharya 2005). In addition, we also observed the change in morphology on the nylon 66 and PVDF membrane surfaces in the presence and absence of PEG grafting along with ferrous as precursor for zerovalent iron, suggesting that PEG was immobilized on the membranes through thermal graft polymerization.

Figure 3 shows the EDS analyses of the immobilized Ni/Fe nanoparticles on membranes. The contents of elemental distribution on membranes were calculated and compared. From EDX analysis, we observed that the percentage for nickel in MCEP, Millex GS, PVDF, and nylon 66 membranes were 7.4%, 7.7%, 7.5% and 26%, respectively. The high content of Ni on nylon 66 indicates a potentially high catalytic ability of nylon 66 membrane towards TCE dechlorination.

In this study, transmission electron microscopic analysis was also used to examine the morphology and particle sizes of Fe/Ni nanoparticles on membranes. Typical bright field TEM images of nanoscale Fe and Fe/Ni particles in the PEG-grafted membranes showed that the distribution of particles sizes were in the range 20–50 nm. The smaller particle size observed in TEM image was due mainly to the thinner film formed on the TEM grid, resulting in the well-dispersion of nanoparticles on Cu grids.

### TCE dechlorination by immobilized Ni/Fe nanoparticles

Figure 4 shows the dechlorination of TCE by Ni/Fe nanoparticles immobilized on different microfiltration

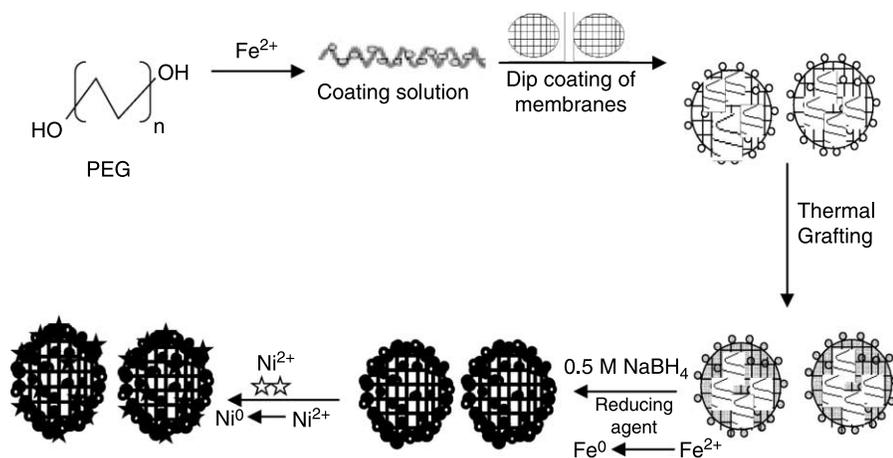
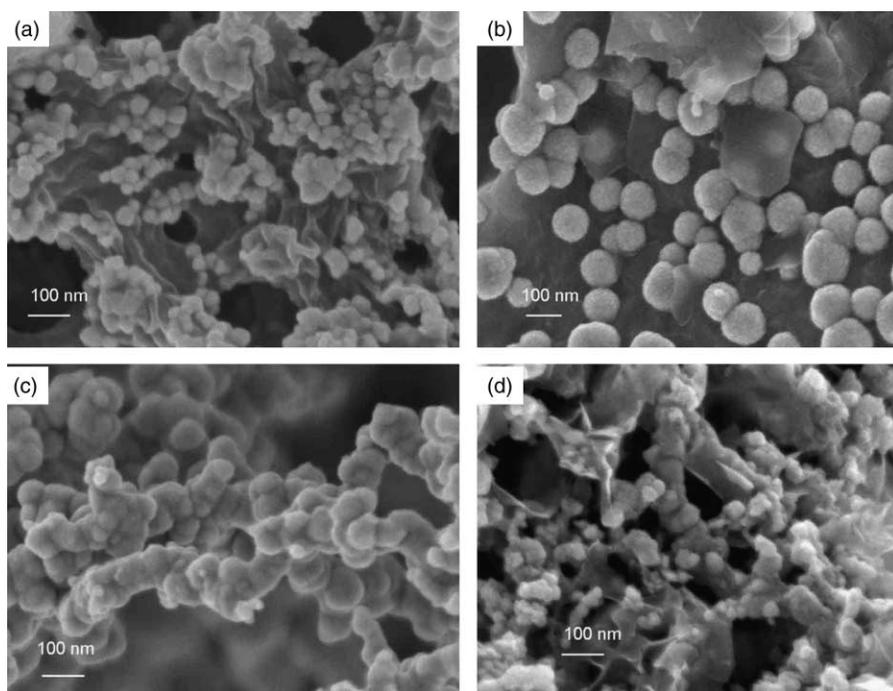


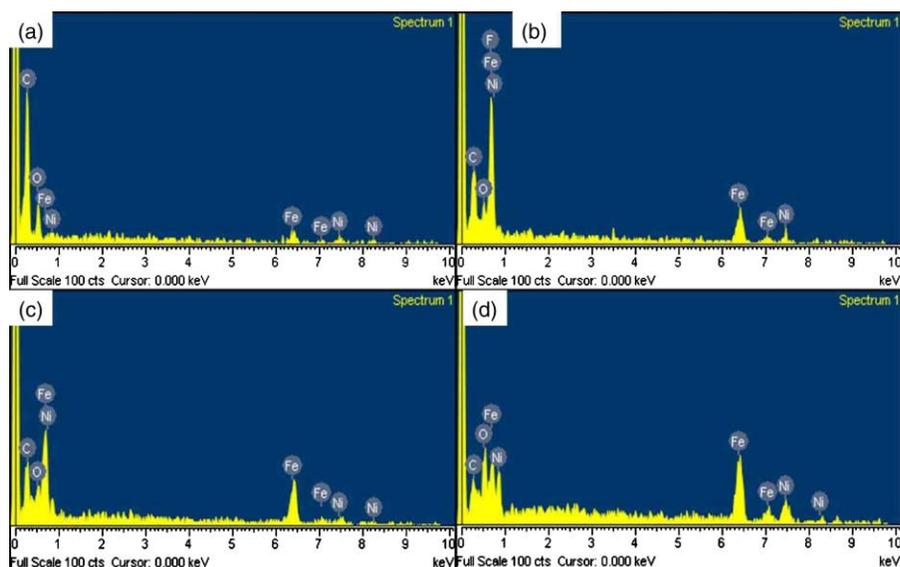
Figure 1 | Possible mechanism for immobilization of bimetallic nanoparticles on microfiltration membranes. Schematic presentation for immobilization of nanoparticles on membranes by thermal grafting.



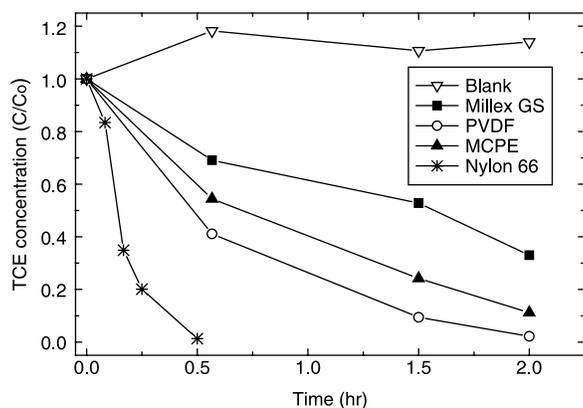
**Figure 2** | SEM images of Ni/Fe nanoparticles immobilized on (a) MCEP, (b) Millex GS, (c) PVDF, and (d) Nylon 66 membranes.

membranes under anoxic conditions. The dechlorination of TCE by immobilized Ni/Fe was rapid. However, the dechlorination efficiency of TCE by Ni/Fe varied when different membranes were used as the supports. A total of 67% TCE was dechlorinated by Ni/Fe

nanoparticles on Millex GS within 2 h, while a nearly complete dechlorination of TCE was observed when Ni/Fe nanoparticles were immobilized on Nylon 66 membranes. The efficiency and rate for TCE dechlorination by membrane-based bimetallic Ni/Fe nanoparticles



**Figure 3** | SEM-EDS spectra of nanoscale Fe/Ni particles on (a) MCEP, (b) Millex GS, (c) PVDF, and (d) Nylon 66 membranes.



**Figure 4** | TCE degradation by different Microfiltration membranes immobilized with  $\text{Fe}^0/\text{Ni}^0$ .

followed the order Nylon 66 > PVDF > MCEP > Millex GS.

The pseudo first-order kinetics with respect to the concentrations of chlorinated hydrocarbons was commonly used to calculate the pseudo first-order rate constant ( $k_{\text{obs}}$ ) (Johnson *et al.* 1996; Tratnyek *et al.* 2001; Doong *et al.* 2003)

$$\frac{dC_{\text{TCE}}}{dt} = -k_{\text{obs}}C_{\text{TCE}} \quad (1)$$

Where  $k_{\text{obs}}$  is observed pseudo first order rate constant ( $\text{h}^{-1}$ ) and  $C_{\text{TCE}}$  is aqueous phase concentration of TCE ( $\text{mg L}^{-1}$ ). Several studies (Johnson *et al.* 1996; Doong *et al.* 2003) have shown that the reduction of contaminants by ZVI appears to be a surface-mediated reaction and the reaction rate is first-order with respect to the amount of available metal surface area. Therefore, the normalized surface reaction rate constant  $k_{\text{sa}}$  ( $\text{L m}^{-2} \text{h}^{-1}$ ) can be determined by the following equation:

$$\frac{dC_{\text{TCE}}}{dt} = -k_{\text{SA}}a_{\text{S}}\rho_{\text{m}}C_{\text{TCE}} \quad (2)$$

$$k_{\text{SA}} = \frac{k_{\text{obs}}}{a_{\text{S}}\rho_{\text{m}}} \quad (3)$$

Where  $a_{\text{s}}$  is the specific surface area of the Ni/Fe ( $\text{m}^2/\text{g}$ ) obtained by BET surface area analysis,  $\rho_{\text{m}}$  the mass concentration of metal ( $\text{g/L}$ ), and  $k_{\text{SA}}$  the surface-area-normalized reaction rate constant ( $\text{L h}^{-1} \text{m}^{-2}$ ). Table 1 shows the pseudo-first-order rate constants for TCE dechlorination by Ni/Fe immobilized on different membranes. The  $k_{\text{obs}}$  for

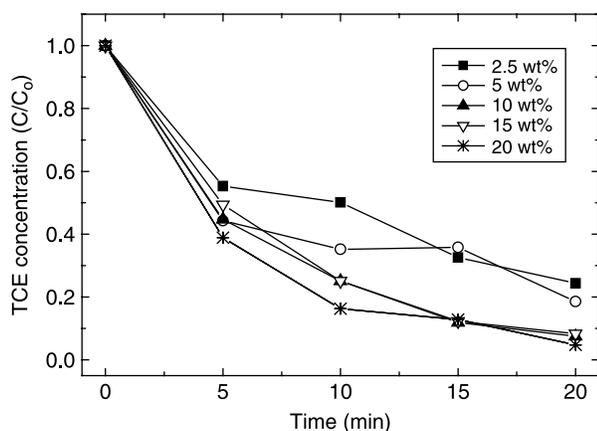
**Table 1** | The pseudo-first-order rate constants for TCE dechlorination by Ni/Fe nanoparticles immobilized on different microfiltration membranes under anaerobic conditions

Rate constants	Millex GS	MCEP	PVDF	Nylon 66
$k_{\text{obs}}$ ( $\text{h}^{-1}$ )	0.705	0.975	1.664	6.441
$k_{\text{SA}}$ ( $\text{L h}^{-1} \text{m}^{-2}$ )	0.050	0.072	0.024	0.172

TCE dechlorination by Ni/Fe was  $0.705 \text{ h}^{-1}$  for Millex GS,  $0.975 \text{ h}^{-1}$  for MCEP,  $1.664 \text{ h}^{-1}$  for PVDF, and  $6.441 \text{ h}^{-1}$  for Nylon 66. In addition, a complete degradation of TCE with the production of ethane as the major degradation product was observed within 25 min. The carbon mass balance was 93%, clearly indicates that hydrodechlorination was the major mechanisms for TCE dechlorination. The presence of second catalytic metal changes the catalytic cycle for TCE degradation (Schrack *et al.* 2002). TCE adsorbed on the Fe/Ni nanoparticles first, and then dechlorination reaction took place on the surface of bimetallic Ni/Fe nanoparticles, resulting in the formation of ethane as the final product.

The surface-normalized rate constants ( $k_{\text{SA}}$ ) for TCE dechlorination were  $0.050 \text{ L h}^{-1} \text{m}^{-2}$  for Millex GS,  $0.072 \text{ L h}^{-1} \text{m}^{-2}$  for MCEP,  $0.024 \text{ L h}^{-1} \text{m}^{-2}$  for PVDF, and  $0.172 \text{ L h}^{-1} \text{m}^{-2}$  for Nylon 66. The  $k_{\text{SA}}$  value reported for TCE degradation by Ni/Fe immobilized on nylon 66 was found to be higher than those reported values ( $(1.15-9.80) \times 10^{-2} \text{ L h}^{-1} \text{m}^{-2}$ ) (Ritchie *et al.* 2001; Kim & Carraway 2003; Tee *et al.* 2005). This means that the catalytic property of nickel and the effect of different methods used for synthesis of bimetallic system has an impact on the enhancement of the TCE degradation rate. The reason for the increase in dechlorination rate may be due primarily to the increase in the Fe/Ni clusters on the surface of immobilized nylon 66 membrane. Several studies (Johnson *et al.* 1996; Schrick *et al.* 2002) have depicted that the close contact of Fe and Ni can be considered as catalytic reactive site. Therefore, the coating of nickel on the membrane surface is considered to play a critical role in enhancing the dechlorination of TCE.

To further understand the role of Ni on the dechlorination of TCE, various amounts of Ni contents ranging from 2.5 to 20% was employed. Figure 5 shows the dechlorination of TCE by immobilized Ni/Fe nanoparticles as a function of Ni content. The efficiency and rate for TCE



**Figure 5** | Dechlorination of TCE by Ni/Fe nanoparticles immobilized on different membrane in the presence of various amounts of Ni.

dechlorination increased upon increasing Ni amounts. The dechlorination efficiency increased from 76% at 2.5 wt% Ni to 95% at 10 wt% Ni, and then reached the plateau when further increased the Ni content to 20%. In addition, the  $k_{obs}$  for TCE dechlorination also increased from  $4.38 \text{ h}^{-1}$  at 2.5 wt% Ni to  $8.1 \text{ h}^{-1}$  at 20 wt% Ni. When the Ni/Fe mass concentration increased, the reactive Fe site concentration and adsorptive Ni site concentration increased simultaneously, which leads to the increase in reaction rate. The bimetallic Fe/Ni particles have been proven to be very effective to accelerate the dechlorination reaction. Several studies have addressed the effect of additive loadings toward the dechlorination efficiency of chlorinated hydrocarbons by Fe. Tee *et al.* (2005) investigated the role of bimetallic Ni/Fe nanoparticles on the dechlorination of TCE. A higher degradation rate of TCE was observed upon increasing the Ni loading from 2 to 25 wt%, and then the  $k_{obs}$  decreased when greater Ni loading was added. Moreover, Lin *et al.* (2004) 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  $k_{obs}$  was also observed when Ru loading increased to 2.0 wt%. In this study, we found that the dechlorination efficiency and rate of TCE slightly decreased when the mass loading of Ni increased to 25%, which means that the loading of Ni at 20 wt% is the optimal dose for immobilized Ni/Fe on TCE dechlorination. The possible explanation is that the addition of metal ions may increase the numbers of Ni nanoparticles on the surface of Fe, thus enhancing the catalytic activity for hydrodechlorination. The high loading

of second dopant metal, however, leads to the aggregation of fine catalytic nanoparticles into large ones, and subsequently decreases the reaction rate of chlorinated hydrocarbons.

## CONCLUSIONS

In this study, the dechlorination of TCE by immobilized Ni/Fe on different microfiltration membranes was investigated. A complete dechlorination of TCE was achieved within 25 min by nanoscale Fe/Ni particles immobilized on nylon 66 membrane. The dechlorination rate obeyed the pseudo first order reaction, and the efficiency and rate for TCE dechlorination by Ni/Fe followed the order Nylon 66 > PVDF > MCEP > Millex GS. The surface-normalized rate constants for TCE dechlorination were found to be higher than those reported values. A carbon mass balance of 93% with ethane as the major end product was obtained, which means that the dechlorination of TCE by immobilized Ni/Fe nanoparticles is an environmentally friendly technology for the detoxification of chlorinated hydrocarbons in water.

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