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Treatment of chlorinated organic contaminants with nanoscale bimetallic particles

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Abstract

Nanoscale bimetallic particles (Pd/Fe, Pd/Zn, Pt/Fe, Ni/Fe) have been synthesized in the laboratory for treatment of chlorinated organic pollutants. Specific surface areas of the nanoscale particles are tens of times larger than those of commercially available microscale metal particles. Rapid and complete dechlorination of several chlorinated organic solvents and chlorinated aromatic compounds was achieved by using the nanoscale bimetallic particles. Evidence observed suggests that within the bimetallic complex, one metal (Fe, Zn) serves primarily as electron donor while the other as catalyst (Pd, Pt). Surface-area-normalized reactivity constants are about 100 times higher than those of microscale iron particles. Production of chlorinated byproducts, frequently reported in studies with iron particles, is notably reduced due to the presence of catalyst. The nano-particle technology offers great opportunities for both fundamental research and technological applications in environmental engineering and science. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Synthetic organic compounds account for approximately one-third of the chemical production in the US [1]. Many are intentionally or inadvertently released into the environment. Evidence has mounted that nation's ground water resource, which supplies over 50% of the drinking water in the U.S., is threatened by contamination caused by past and present industrial, agricultural and commercial activities [2]. Chlorinated solvents, such as tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl

chloride (VC), are among the most prevalent contaminants [3]. Many of these compounds are known or potential threats to public health and the environment, so there is an urgent need to understand their transport and fate in the environment and develop effective control methods.

Treatment of halogenated organic compounds (HOCs) by zero-valent metals represents one of the latest innovative technologies for environmental remediation [4,5]. Laboratory research in the past few years has demonstrated that metals can transform many HOCs such as chlorinated aliphatics, aromatics, and polychlorinated biphenyls [6–8]. Prospects for applying the zero-valent iron in field also look promising. Granular iron is usually applied in the “funnel and gate” treatment system, in which a porous wall of

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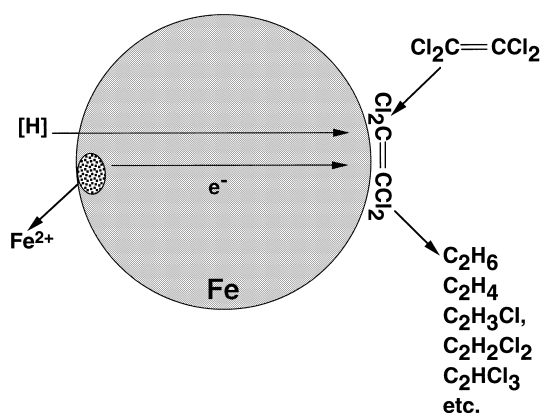
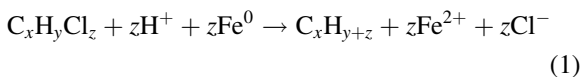


Fig. 1. Schematic of PCE dechlorination on the surface of zero-valent iron. Iron is believed to serve as an electron donor, similar to processes occurring during iron corrosion, however, with the beneficial effects of transforming chlorinated pollutants.

granular iron is constructed in the path of a contaminated ground water plume. As contaminated water passes through the reactive barrier, HOCs react with the surface of iron to produce mostly benign compounds such as hydrocarbons, chloride, and water.

In general, reactions between chlorinated organic compounds ($C_xH_yCl_z$) and iron in aqueous solutions can be expressed by the following reaction:



in which iron acts as a reductant (electron donor) for the removal of chlorine (Fig. 1). This reaction is similar to the process occurring during iron corrosion, with the beneficial effects of transforming chlorinated pollutants [5]. In laboratory studies many other metals, particularly zinc and tin, can also reduce chlorinated compounds [9,10].

Many challenges still exist for implementation of the zero-valent metal technology [11]:

1. Production and accumulation of chlorinated by-products due to the low reactivity of iron powders towards lightly chlorinated hydrocarbons. For example, reduction of PCE and TCE by zero-valent iron has been observed to produce *cis*-1,2-DCE and VC [12,13]. Both compounds are of considerable toxicological concern.
2. Decrease of iron reactivity over time, probably due to the formation of a surface passivation layer, or to

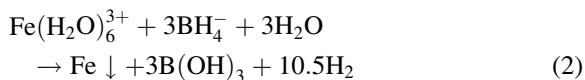
the precipitation of metal hydroxides ($Fe(OH)_2$, $Fe(OH)_3$) and metal carbonates ($FeCO_3$) on the surface of iron.

3. Engineering difficulties in constructing iron walls in deep aquifers (e.g., >30 m).

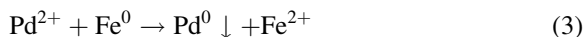
In this work, a new scheme of zero-valent metal for degradation of HOCs in the aqueous solution is developed to address the above-mentioned shortcomings. Nanoscale metal particles, with diameter in the range 1–100 nm, are synthesized in the laboratory. These particles are characterized by high surface area to volume ratio, high level of stepped surface, and high surface energy [14,15]. Furthermore, a bimetallic structure [16,17] is adopted in which a thin layer of catalyst (e.g., Pd, Pt) is doped on the surface of a reductant (e.g., Fe, Zn). The presence of catalyst reduces activation energy and increases the rate of dechlorination reactions, more importantly, curtails production of chlorinated byproducts. Methods for the preparation of nanoscale bimetallic particles, reactions with model chlorinated organic contaminants, and potential applications of the nanoscale bimetallic particles in pollution control and environmental remediation are presented.

2. Experimental methods

Nanoscale Fe particles are synthesized by adding 1.6 N $NaBH_4$ aqueous solution dropwise to a 1.0 M $FeCl_3$ aqueous solution. Fe^{3+} is reduced and precipitated according to the following reaction [18,19]:



Bimetallic complexes were then prepared by the method of reductive deposition. For example, the iron particles were coated with a thin layer of Pd by saturating the wet iron precipitates with an ethanol solution of $[Pd(C_2H_3O_2)_2]_3$, causing reduction and subsequent deposition of Pd on the Fe surfaces:



Similarly, Pd/Zn was prepared by saturating Zn powders with the ethanol solution of $[Pd(C_2H_3O_2)_2]_3$. Dry metal particles were obtained by washing the wet precipitates with acetone, and drying at 110°C for 6 h.

It was observed that the color of Fe particles changed from black to reddish-brown within a few hours, indicating significant surface oxidation. No observable color change was noticed on the dry Pd/Fe surfaces, suggesting that Pd-modified Fe is stable in the air.

BET surface areas of the nanoscale metal particles were measured using the nitrogen adsorption method at 77 K with a Gemini 2360 surface analyzer. Prior to measurement, samples were acid-washed and degassed at 250°C with a flow of N₂. The particles were observed by a Phillips EM 400T transmission electron microscopy (TEM) at 120 kV to measure the size and size distribution. Crystal structure of the particles was examined with an APD 1700 automated powder diffractometer (XRD) with nickel-filtered Cu K_α radiation ($\lambda=0.1542$ nm).

Batch experiments were conducted to test reactivity of the laboratory synthesized nanoscale particles for the dechlorination of several chlorinated pollutants (PCE, TCE, *trans*-DCE, VC, and several chlorinated aromatic compounds). In single compound experiments, 15 ml of 20 mg/l of PCE, TCE, *trans*-DCE, or VC aqueous solutions, and 1.0 g freshly prepared bimetallic powders were charged into a 50 ml vial with a Teflon mininert valve. The serum bottles were mixed on a platform shaker at ambient temperature (22±1°C). Parallel experiments were conducted without metal particles (blank), or microscale Fe particles (>99.9%, <10 μm, Aldrich). For experiments with a 10-compound mixture of chlorinated compounds (2-chloronaphthalene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachloroethane, 1,2,4,5-tetrachlorobenzene, and 1,2,4-trichlorobenzene), a stock solution of the organic mixture was combined with 0.1 g of metal powder in a 2 ml vial and agitated on a rotary shaker (30 rpm). Organic compounds in aqueous solutions were extracted with 0.5 ml pentane and analyzed by a Hewlett-Packard Model 5890 GC equipped with an electron capture detector (ECD) and a BD-624 capillary column (J&W Scientific). Detection limits were about 5 μg/l for chlorinated ethylenes and 10 μg/l for chlorinated benzenes. Hydrocarbon products in the headspace were identified with a GC-MS (HP 5970 GC MSD). Amounts of organic compounds volatilized into the headspace were corrected applying

Henry's law. Production of chloride ion in solution was determined by ion chromatography (Dionex 120).

3. Results

Analysis of TEM micrographs showed that most of the particles were in the range of 1–100 nm. Average BET surface area of the particles was 33.5 m²/g. In comparison, a commercially available microscale Fe powder (<10 μm, Aldrich) has an average surface area to weight ratio of 0.9 m²/g as measured by the same method. XRD pattern indicates that the iron particles are crystalline.

Rapid and complete dechlorination of PCE, TCE, DCE and VC was achieved by using the nanoscale iron and palladized iron particles as shown in Fig. 2. In all experiments, initial organic concentration was 20 mg/l, and metal to solution ratio was 2 g/100 ml. The amounts of organic compounds in blank runs (without metal particles), and in the runs with microscale Fe particles (Aldrich Fe) remained relatively constant within a period of 3 h, indicating insignificant leak and adsorption to glass wall of the serum bottles and slow reaction with the Aldrich iron. The palladized nanoscale Fe particles exhibited the highest reactivity. Both PCE and TCE were completely dechlorinated by the synthesized nano-Pd/Fe bimetallic particles within less than 0.25 h (our measurement had been made at the earliest). *cis*-DCE was dechlorinated within 1 h and VC within 1.5 h, respectively. On the other hand, it took relatively longer to achieve complete dechlorination by using the nanoscale iron (between 2 and 3 h). In runs using the nanoscale metal particles, no chlorinated byproducts (<5 μg/l) were detected in the solution. Final reaction products in the headspace were identified to be only hydrocarbons, including ethene, ethane, propene, propane, butene, butane, and pentane. Simultaneous increases in chloride concentrations were also observed in the aqueous solutions.

Fig. 3 depicts experimental results designed to characterize the different roles of Pd and Fe in the bimetallic particle. Experimental conditions were similar to those described in Fig. 2. Nanoscale particles of Pd were used alone (Pd), or together with nanoscale iron particles (Pd+Fe). The results showed that little degradation of TCE was observed in the presence of Pd particles alone, likely due to the fact

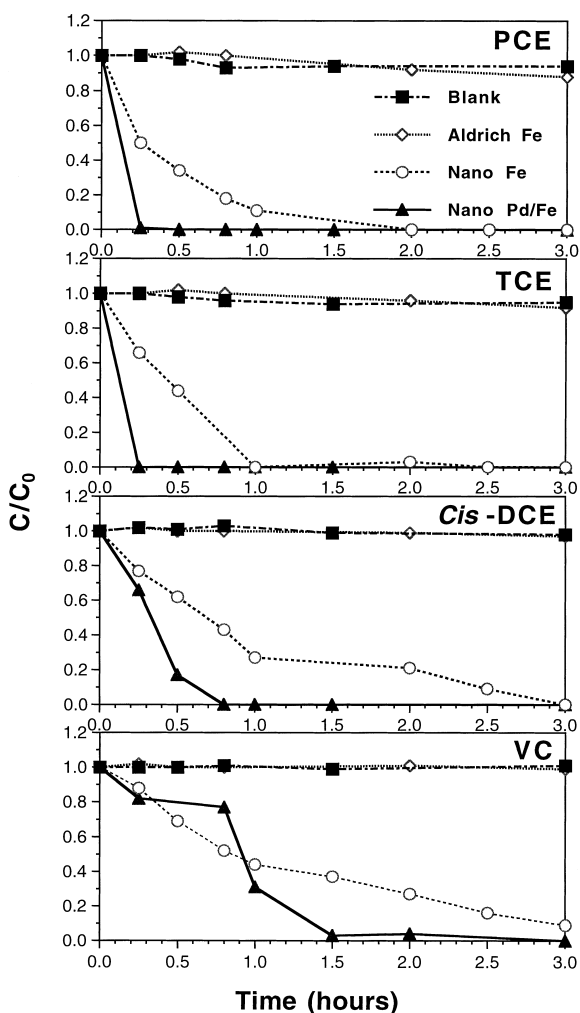


Fig. 2. Transformation of PCE, TCE, *cis*-DCE and VC by microscale Fe (Aldrich Fe), nanoscale Fe (Nano Fe), and nanoscale Pd/Fe particles (nano Pd/Fe). Initial organic concentration was 20 mg/l. Metal to solution ratio was 2 g/100 ml.

that no electron donor was present. Pd possesses very high redox potential and is a poor electron donor for TCE dechlorination. Physically mixing Pd and Fe particles together produced no better than Fe alone. Only by doping Pd on the surface of Fe to form integrated bimetallic complexes (Pd/Fe) can the system achieve the enhanced reactivity (Fig. 3).

In another experiment, Pt, instead of Pd, was used as the catalyst. Fig. 4 shows that in the presence of nanoscale iron particles, 98% TCE was degraded in

60 min. In the presence of Pt/Fe, the same amount was reduced within 50 min. In comparison, complete reduction of TCE was achieved within less than 20 min by the nanoscale Pd/Fe under similar conditions. Nickel was also observed to promote dechlorination of PCE, TCE, DCEs and VC. As shown in Fig. 5, nickelized iron (Ni/Fe) exhibited higher activity than the nanoscale iron for dechlorination of 9.7 mg/l *trans*-DCE, but lower compared with the Pd/Fe particles.

Many metals such as Zn and Al have very negative redox potentials and can substitute iron as reductants. Fig. 6 gives results of transformation of TCE by zinc and palladized zinc complex. In this experiment, a microscale zinc powder was used (<10 μm , Aldrich). In blank samples, TCE concentration decreased by about 7% at the beginning and then remained relatively constant within a period of up to 56 h. It is well known that pure zinc is very reactive in the presence of oxygen. A passivation layer of zinc oxides can quickly form on the surface which in turn inhibits its reactivity. Applying Pd on the Zn surface can prevent passivation and enhance its reactivity. As shown in Fig. 6, greater than 90% of TCE was reduced within 20 h using the Pd/Zn complex. Meanwhile, in the presence of zinc powders, little TCE was reduced for as long as 56 h. No reaction products (hydrocarbons or chloride) were detected by using zinc alone.

Experiments were also performed to test reactivity of the nanoscale metal particles for treatment of a mixture of chlorinated compounds (Fig. 7). An EPA chlorinated aromatic compound mixture solution containing 2-chloronaphthalene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachloroethane, 1,2,4,5-tetrachlorobenzene, and 1,2,4-trichlorobenzene was used. Total initial organic concentration in the solution was about 10 mg/l (Fig. 7(a)). As shown in Fig. 7(b), about 90% of the chlorinated aromatic compound was reduced within 24 h. Small amounts of chlorinated compounds (1,2,3-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, hexachlorobenzene) that remained in the solution were completely (detection limits <10 μg) reduced within 48 h. Similar results were also observed for dechlorination of PCB mixtures by using the nanoscale Pd/Fe particles [15].

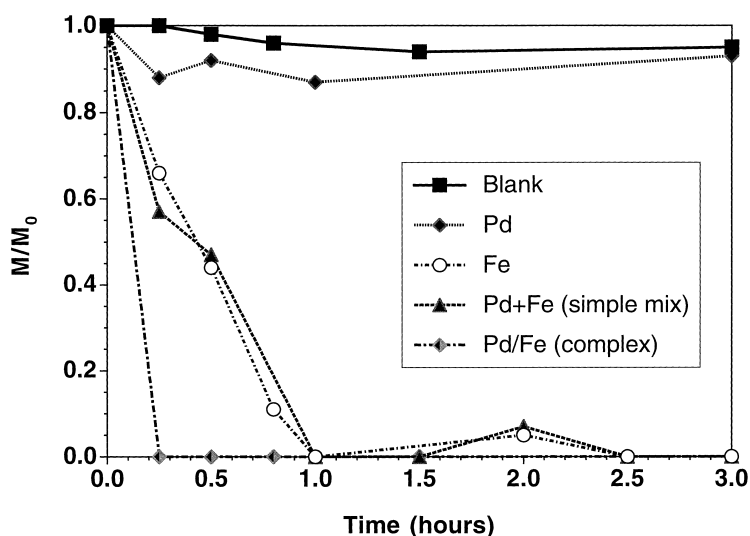


Fig. 3. Reactions of TCE with nanoscale Pd particles (Pd), nanoscale Fe (Fe), nanoscale Pd and Fe (Pd+Fe, simple mixing), and nanoscale palladized Fe particles (Pd/Fe, complex). Initial organic concentration was 20 mg/l. Metal to solution ratio was 2 g/100 ml.

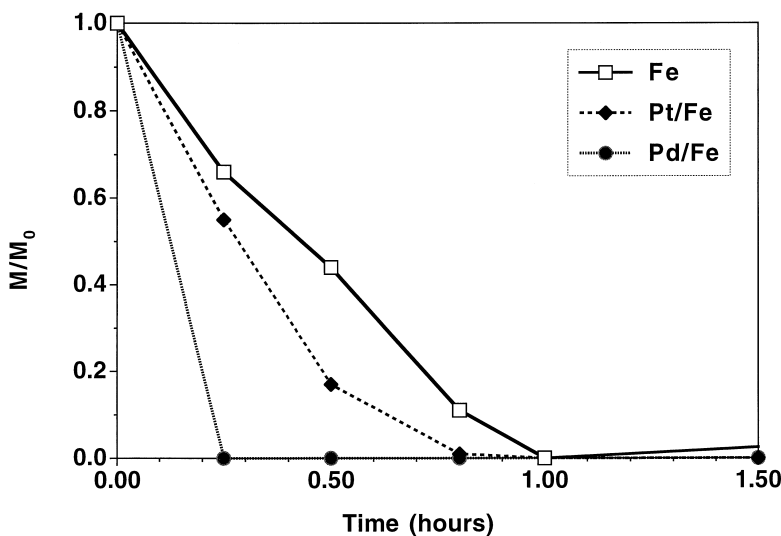


Fig. 4. Reactions of TCE with nanoscale Fe particles (Fe), Pt-modified Fe (Pt/Fe), and Pd-modified Fe (Pd/Fe). Initial organic concentration was 20 mg/l. Metal to solution ratio was 2 g/100 ml.

4. Conclusions and discussions

Results obtained under laboratory conditions have demonstrated the following:

(1) The laboratory synthesized nanoscale metal particles have specific surface areas 1–2 orders of magnitude higher than commercially available micro-scale metal particles. A comparison of the average

diameters and specific surface areas of the synthesized nano-particle and several iron particles used in published studies [20] is presented in Table 1.

(2) Both the nanoscale Fe and Pd/Fe particles can completely and quickly dechlorinate PCE, TCE, DCEs and VC to form various hydrocarbons. The reaction rates for both nanoscale Fe and Pd/Fe follow the trend PCE>TCE>*cis*-DCE>VC. This trend is con-

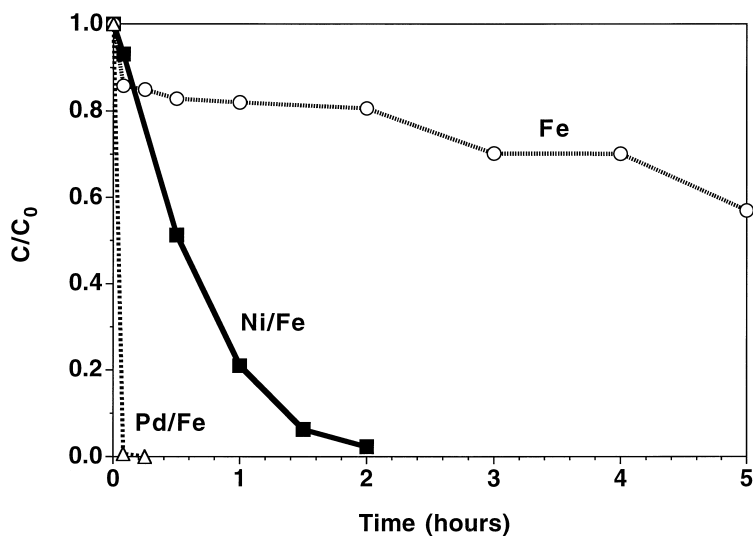


Fig. 5. Reactions of *trans*-DCE with nanoscale Fe powders (Fe), Ni-modified Fe (Ni/Fe), and Pd-modified Fe (Pd/Fe). Initial organic concentration was 9.7 mg/l. Metal to solution ratio was 10 g/100 ml.

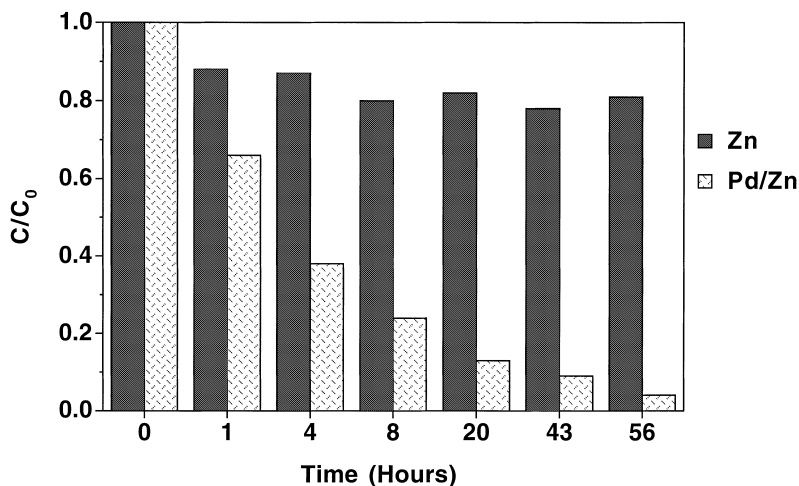


Fig. 6. Reactions of TCE with microscale Zn powders (Aldrich Zn), Pd-modified Zn powders (Pd/Zn). Initial organic concentration was 20 mg/l. Metal to solution ratio was 2 g/100 ml.

sistent with the redox potentials of these organic compounds in which PCE has the highest redox potential and VC the lowest [21,22].

(3) Nanoscale Pd/Fe particles can also completely dechlorinate chlorinated benzenes.

(4) The nanoscale Fe particles have higher surface reactivity than microscale Fe particles (based on per unit surface area). Palladized Fe works even better. To compare the reaction rates observed under different

experimental conditions, it is useful to consider the surface-area-normalized reactivity of various metal particles. The rate of degradation of a chlorinated organic compound in a batch system can be described by the following equation [20]:

$$\frac{dC}{dt} = -K_{SA} a_s \rho_m C, \quad (4)$$

where C is the concentration of organic compound in

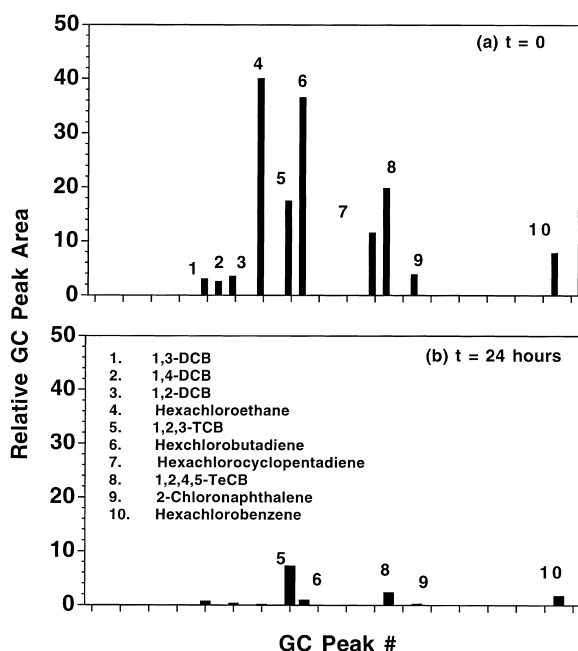


Fig. 7. Transformation of a mixture of chlorinated compounds by nanoscale Pd/Fe. (a) Relative GC peak areas at $t=0$; and (b) relative GC peak areas at $t=24$ h. Total organic concentration was 10 mg/l at $t=0$. Metal to solution ratio was 5 g/100 ml.

Table 1
Sizes and specific surface areas (a_s) of various metal particles

Source of iron	Grain size (mm)	Surface area (m^2/g)
Master builder	0.23	3.3
Fisher electrolytic	0.15	0.287
Aldrich	0.10	2.4
EM science	0.15	0.14
Fisher electrolytic	0.15	0.0567
Fisher filings	0.43	1.635
Fisher electrolytic	0.15	0.70
Fisher electrolytic	0.15	0.061
VWR		1.24
Nanoscale iron (this study)	<0.0001	33.9

Except the values for the nanoscale iron particles, all others are from [20].

the aqueous phase (mg/l), K_{SA} the surface-area-normalized rate coefficient (l/h/m^2), a_s the specific surface area of metal (m^2/g), ρ_m the mass concentration of metal (g/l), and t is the time (h).

Here K_{SA} is the specific reaction rate constant, a parameter for assessment of the overall surface reactivity. Fig. 8 offers an example of a multicycle experiment in which 0.05 mg of *trans*-DCE was spiked every 20–30 min into a 5 ml nano-Pd/Fe solution. As shown in the figure, complete reduction of *trans*-DCE in each cycle took about 20–30 min and there was no apparent slowdown or rate decrease over a period of 16 cycles. Best-fit values of K_{SA} were obtained by using Eq. (4) for each experimental cycle. Average K_{SA} for degradation of *trans*-DCE by the nanoscale Pd/Fe particles was 0.01 l/h/m^2 . In comparison, K_{SA} for microscale iron particles was about 10^{-4} , almost 100 times lower. Similar rate increases were also observed for dechlorination of PCE, TC and VC.

(5) Evidence strongly suggests that, within a bimetallic system, one metal likely serves as catalyst (Pd, Pt, Ni) while the other as electron donor (Fe, Zn) as illustrated in Fig. 9. Iron is a very effective reductant. Catalytic properties of Pd, Pt and Ni are different, likely due to their differences in surface atomic structures and their electron properties [23]. More studies are needed to address the exact catalytic nature of these bimetallic complexes.

(6) Results from this study are consistent with previous studies suggesting the dechlorination reactions are surface-mediated redox reactions [24]. Various hydrocarbons are observed, similar to the mechanisms in Fisher–Tropsch synthesis.

In summary, overall performance of a nanoscale bimetallic complex for treatment of chlorinated organic pollutants is enhanced by: (1) expanding the surface area, (2) increasing the surface reactivity, and (3) curtailing production of byproducts. We believe that the approaches outlined here offer opportunities for both fundamental research and technological applications of nanoscale particle technology in pollution control and environmental remediation. For example, instead of building iron walls in the subsurface, nanoscale metal particles could be injected directly to contaminated aquifers [25]. The nanoscale particles can be anchored onto solid supports such as activated carbon, zeolite, and silica for ex situ treatment of contaminated waters and industrial effluents. The nanoscale metal particles also provide useful tools for elucidating fundamental mechanisms of dechlorination at the metal–solution interfaces.

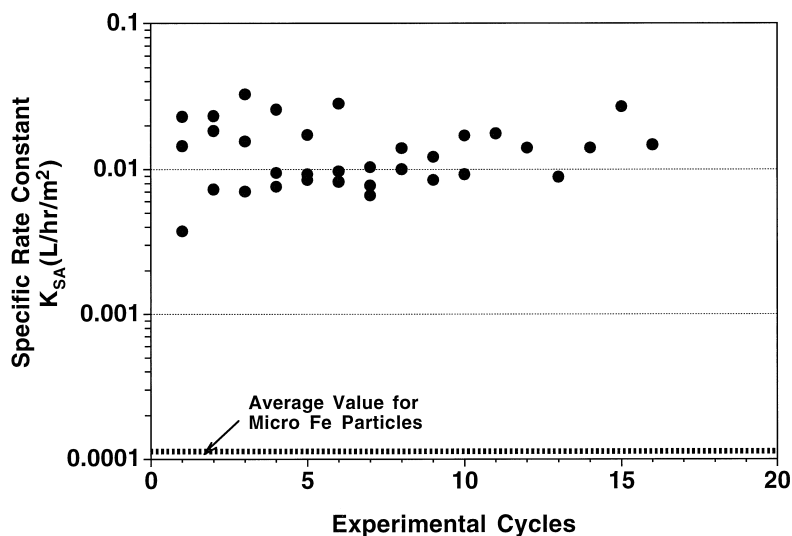


Fig. 8. Best-fit surface-area-normalized reactivity constant (K_{SA}) using experimental data obtained from multiple cycle experiments. K_{SA} for microscale iron was from [20].

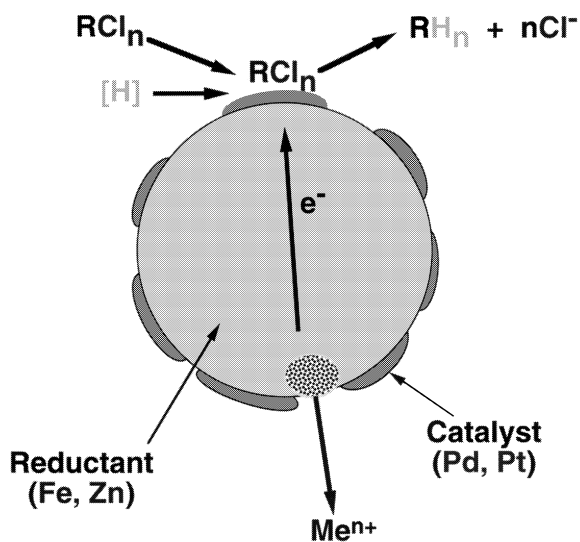


Fig. 9. Schematic of a nanoscale bimetallic particle for treatment of chlorinated solvents. The particles, with diameters in the range 1–100 nm, have high surface area to volume ratio, high level of stepped surface, and high surface energy. Within a bimetallic complex, one metal (Fe, Zn) serves primarily as electron donor while the other (Pd, Pt) as catalyst.

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