BIMETALLIC IRON-ALUMINUM PARTICLES FOR EFFECTIVE DECHLORINATION OF CARBON TETRACHLORIDE

Wen-Shan Lee, Yu-Sheng Jhuo, ***Hsing-Lung Lien*** **(**National University of Kaohsiung, Kaohsiung, Taiwan)

ABSTRACT: Zero-valent iron (ZVI) has been successfully used for the dechlorination of organic environmental contaminants in subsurface. However, the accumulation of hydroxide precipitates onto the iron surface resulting in the loss of iron reactivity over time has emerged as a critical issue that needs to be addressed. In this paper, we present a novel material, bimetallic Fe/Al particles, for effective degradation of carbon tetrachloride. Bimetallic Fe/Al was prepared under acidic conditions where iron was readily deposited onto aluminum surface. The bimetallic Fe/Al particles are designed to take advantage of zero-valent aluminum for serving as an electron donor to prevent the formation of passive layer from iron corrosion and maintain the surface reactivity of iron. In this study, iron content ranging from 5% to 45% (by weight) was conducted. XRD analysis indicated neither iron oxide nor aluminum oxide was formed at the metal surface. A minimum full surface coverage of iron at the aluminum surface was determined when the iron to aluminum ratio was equal to 15% according to XRD measurements. Batch experiments, carried out to investigate the product distribution and reaction kinetics for the carbon tetrachloride dechlorination, indicated bimetallic Fe/Al particles at the iron to aluminum ratio of 15% exhibited optimum performance.

INTRODUCTION

The use of zero-valent metals (e.g., iron, zinc and aluminum) has been shown a great success in treatments of various contaminants including halogenated organic solvents, heavy metals, and radionuclides (e.g., Gillham and O'Hannesin, 1994; Lien and Wilkin, 2005; Gu et al., 1998). In particular, implementation of full or pilot scale *in situ* permeable reactive barriers (PRBs) using zero-valent iron (ZVI) as reactive media has been demonstrated to effectively remediate groundwater contaminated with chlorinated organic compounds. The degradation processes involve the oxidative corrosion of iron and the subsequent reduction of the chlorinated organic compounds:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$C_XH_YCl_Z + 2e^- + 2H^+ \rightarrow C_XH_{Y+1}Cl_{Z-1} + HCl \quad (2)$$

In aqueous systems, this characteristic reaction of iron corrosion inevitably results in the pH increasing and the formation of iron hydroxide precipitates:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (3)$$

The accumulation of hydroxide precipitates on the metal surface caused the loss of iron reactivity over time (Matheson and Tratnyek, 1994) and eventually shortened the longevity of PRBs.

We have reported the use of bimetallic Cu/Al for reductive degradation of chlorinated methanes (Lien and Zhang, 2002). Aluminum was selected because it is an effective electron donor (the standard reduction potential of -1.667 V) under both acidic and alkaline conditions. To prevent the formation of a passive layer on the iron surface, we developed a novel material, bimetallic Fe/Al particles. Bimetallic Fe/Al particles consist of the core metal (aluminum) and the shell metal (iron). Unlike conventional ZVI technology that iron acts as an electron donor, bimetallic Fe/Al particles are designed to use aluminum as a source of electrons that may keep the iron surface from corrosion and maintain the surface reactivity of iron.

In this paper, the objective was aimed at investigating the feasibility of using zero-valent aluminum as the source of electrons to prevent the formation of iron oxide and maintain a fresh surface of iron so that the iron-mediated dechlorination can be effectively preceded without declining the reactivity of iron.

MATERIALS AND METHODS

Materials. All chemicals are analytic grade or better. Carbon tetrachloride (99.5%) was purchased from SHOWA. Chloroform (99%) and dichloromethane (99.9%) were obtained from J. T. Baker. A commercial available aluminum powder (99.5%, ~20 μm) and iron powder (baker analyzed reagent) were obtained from Alfa and J. T. Baker, respectively.

Preparation of Bimetallic Fe/Al Particles. Micro-sized bimetallic Fe/Al particles were prepared using the microscale commercial available zero-valent aluminum as a precursor in a fume hood under ambient temperature and pressure. To prepare the iron to aluminum ratio of 25%, 2.4 g of aluminum powder was added into a 1000 mL glass beaker containing 2.9 g $FeCl_3 \cdot 6H_2O$ in 25 mL deionized water and the suspension was mixed with a magnetic stirrer. 10 mL of concentrated HCl was slowly added to the glass beaker. Immediate fume evolution was observed. 10 mL of distilled water was added quickly to dissipate heat for 30 seconds. Under acidic conditions, ferric ions were reduced to elemental iron and deposited onto the aluminum surface to for bimetallic Fe/Al.

$$Fe^{3+} + Al^0 \rightarrow Fe^0 \downarrow + Al^{3+} \quad (4)$$

Bimetallic particles were then washed by 2 L deionized water and harvested via vacuum filtration.

Batch Experiments. Batch experiments were conducted in 150 mL serum bottles (Wheaton). In a typical experiment, the initial concentration was approximately 31.7 mg/L. The metal loading of bimetallic Fe/Al was 3 g/100 mL. The serum bottles were then capped with Teflon Mininert valves and mixed on a rotary shaker (30 rpm) at room temperature (22±1℃).

Analytic Methods. Concentrations of carbon tetrachloride and its intermediates were measured by a headspace-gas chromatograph (GC) method. At selected time intervals, a 50-μl headspace gas aliquot was withdrawn by a gastight syringe for GC analysis. Headspace samples were analyzed by a HP4890 GC-FID equipped with a DB-624 capillary column (J&W, 30 m × 0.32 mm). Temperature conditions were programmed as follows: oven temperature at 45℃ for 5 minutes; injection port temperature at 250℃; and detector temperature at 300℃.

Solid-Phase Characterization. Characterization of bimetallic Fe/Al particles was conducted by using X-ray diffraction (XRD) and a surface area analyzer. XRD measurements were performed using a Rigaku X-ray diffractometer (Rigaku Co.) at 40 kV and 20 mA with a copper target tube radiation (Cu Kα) producing X-rays with a wavelength of 1.54056 Å . The specific surface area of the particles was measured by Brunauer-Emmett-Teller (BET) N_2 method using a COULTER SA 3100 surface area analyzer (Coulter Co.).

Kinetics Analysis. The rate of transformation for carbon tetrachloride in a batch system is described as a pseudo-first-order rate model [4]:

$$\frac{\mathrm{dC}}{\mathrm{dt}} = -k_{obs}C = -k_{SA}\rho_m a_s C \qquad (5)$$

where C is the concentration of carbon tetrachloride (mg/L); k_{obs} is the observed rate constant (h^{-1}); t is time (h); k_{SA} is the surface area normalized rate constant ($L/m^2/h$); ρ_m is the metal loading (g/L); and a_s is specific surface area of metals (m^2/g).

RESULTS AND DISCUSSION

Figure 1 illustrates the XRD patterns of zero-valent aluminum, zero-valent iron, and bimetallic Fe/Al at different iron content ranging from 5% to 45%. The characteristic peaks of aluminum appeared at 38.6°, 44.9°, 65.2°, and 78.5° where the main diffraction peak is near at the diffraction angle (2θ) of 38.6°. The peaks assigned to iron were at the positions at 44.7° and 65.0° (insignificant). It is apparent that both metals have similar XRD patterns at diffraction angle between 38° and 70°. Nevertheless, XRD analysis still provided useful insight into the structure of bimetallic Fe/Al. At the iron content of 15%, a minimum full surface coverage of iron on bimetallic Fe/Al particles was achieved. The main diffraction peak (38.6°) is nearly negligible and characteristic peaks of aluminum at 65.2° and 78.5° were not observed. This also provided clear evidence that the peak at near 44.8° is associated with the iron. Further, XRD measurements indicated when the iron to aluminum ratio was equal or more than 25%, the surface of bimetallic particles was completely dominated by iron because the main diffraction peak (38.6°) and other characteristic peaks of aluminum at 65.2° and 78.5° were not observed. Below 15% of iron content, the surface of bimetallic Fe/Al particles was consisted with both aluminum and iron. Specific surface area of bimetallic Fe/Al particles with iron content of 45%, 25%, 15% and 5% was 32.3, 19.5, 13.7, and 7.7 m^2/g, respectively.

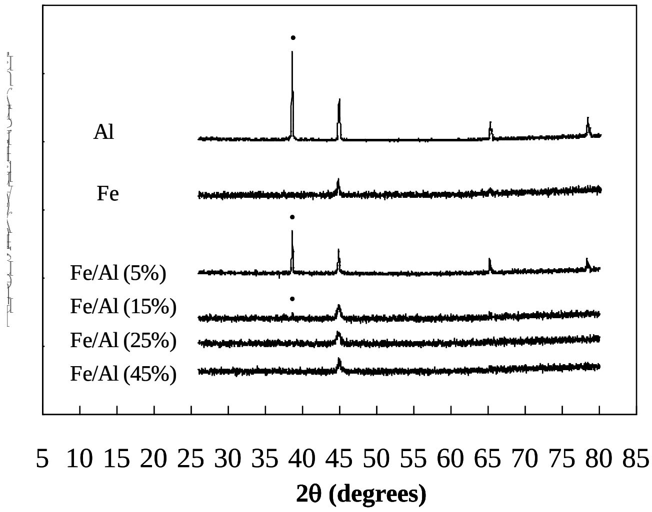

FIGURE 1. XRD patterns for iron, aluminum, and bimetallic Fe/Al at various iron content. The solid circle indicated the position of the main peak of aluminum.

Figure 2 shows the transformation of carbon tetrachloride by Fe/Al (15%) under neutral pH conditions. Carbon tetrachloride was completed dechlorinated within hours and produced reaction intermediates such as chloroform and dichloromethane, and final products including methane, ethylene and ethane. Peak amounts of dichloromethane (~17%) were observed at about 36 hours. Methane, ethylene, and ethane accounted for 28%, 7%, and 9% of the carbon tetrachloride lost, respectively. The observed rate constant of Fe/Al was estimated using Eq. 5. Results indicated the degradation of carbon tetrachloride by Fe/Al follows the behavior of first-order kinetics (R^2 = 0.995) and the observed rate constant of Fe/Al was determined to be approximately 0.12 h^{-1}.

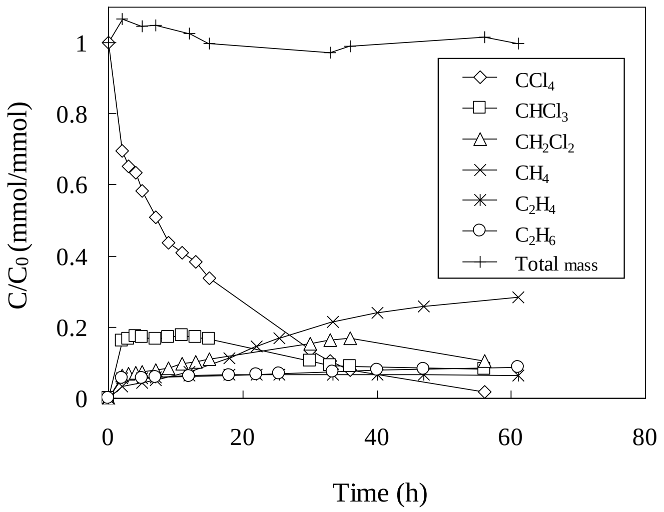

FIGURE 2. Transformation of carbon tetrachloride by bimetallic Fe/Al (35%) at neutral conditions.

Effects of iron content on the effectiveness of Fe/Al for the degradation of carbon tetrachloride under near neutral pH conditions are given in Figure 3. Because the reaction is surface-mediated, degradation rates are expressed as surface area normalized rate constants (k_{SA}) to account for the effect of surface areas. The maximum degradation rate was found at the theoretical ratio iron to aluminum ratio of 15%, which was approximately 10 times greater than the higher ratio of iron content. As discussed above, the minimum full surface coverage of iron was determined when the iron to aluminum ratio reached 15%. Taken together, these results indicated that the bimetallic Fe/Al particles with a minimum full surface coverage of iron have the best dechlorination efficiency.

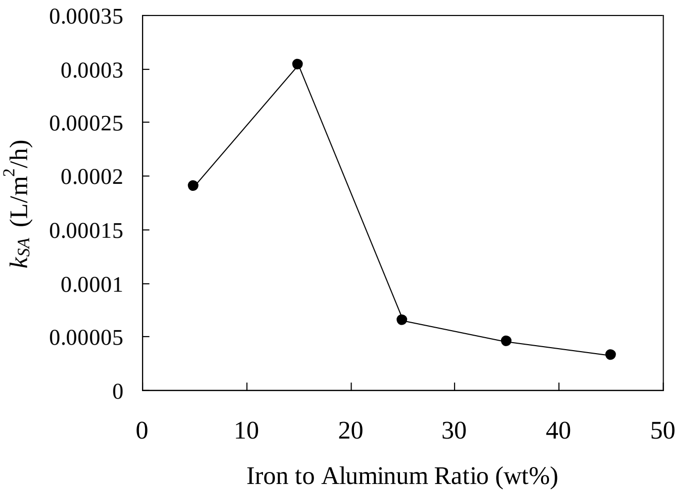

FIGURE 3. Effects of iron content on the effectiveness of Fe/Al for the dechlorination of carbon tetrachloride.

As shown in Figure 3, no significant difference between the ratio of 25% and 45% was observed in terms of the degradation rate. This indicated that the excessive amount of iron did not enhance the degradation rate and from application points of view, tended to increase costs. The degradation rates remained relatively constant at higher iron content could therefore be attributed to the formation of the minimum full coverage of iron at the aluminum surface. Because the degradation of carbon tetrachloride using bimetallic particles is a surface-mediated reaction, for a non-catalytic metal like iron, reductive dechlorination involved direct electron transfer. The reducing power of mono-metallic iron depends only on the redox couple of iron and its ionic forms ($\Delta E^o = +0.447 \sim +0.037$ V) while the reducing power of bimetallic Fe/Al particles is largely enhanced by the galvanic cells ($\Delta E^o = +1.625$ V). Electrons transferred from inner aluminum may be limited by the excessive iron. As a result, the performance of Fe/Al at higher iron content turned out to behave as iron alone. At the lower iron content (iron to aluminum ratio of 5%), the slow degradation of carbon tetrachloride by Fe/Al was also observed. Further, XRD measurement indicated the surface was partially covered by iron. Because the dechlorination reaction preferentially occurred at the Fe/Al surface as revealed in Figure 3, the outer surface of Fe/Al without the coverage of iron inevitably deteriorated the effectiveness.

CONCLUSIONS

The bimetallic Fe/Al particles have been shown to effectively dechlorinate carbon tetrachloride. The optimum performance of bimetallic Fe/Al particles was determined when the iron to aluminum ratio of 15%, where a minimum full surface coverage of iron was also observed according to XRD analysis. Insufficient and excessive amounts of surface iron were found when the iron content was less or greater than 15%. Beyond full surface coverage of iron, the excessive amounts of iron, that may limit electron transfer from inner aluminum to outer surface, caused the bimetallic Fe/Al to act as iron alone. On the other hand, insufficient amounts of iron resulted in the partial coverage of iron at the aluminum surface. The outer surface of bimetallic Fe/Al without the coverage of iron declined its effectiveness. In addition, carbon tetrachloride was transformed to chloroform (20%) and dichloromethane (<1%) by bimetallic Fe/Al.

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